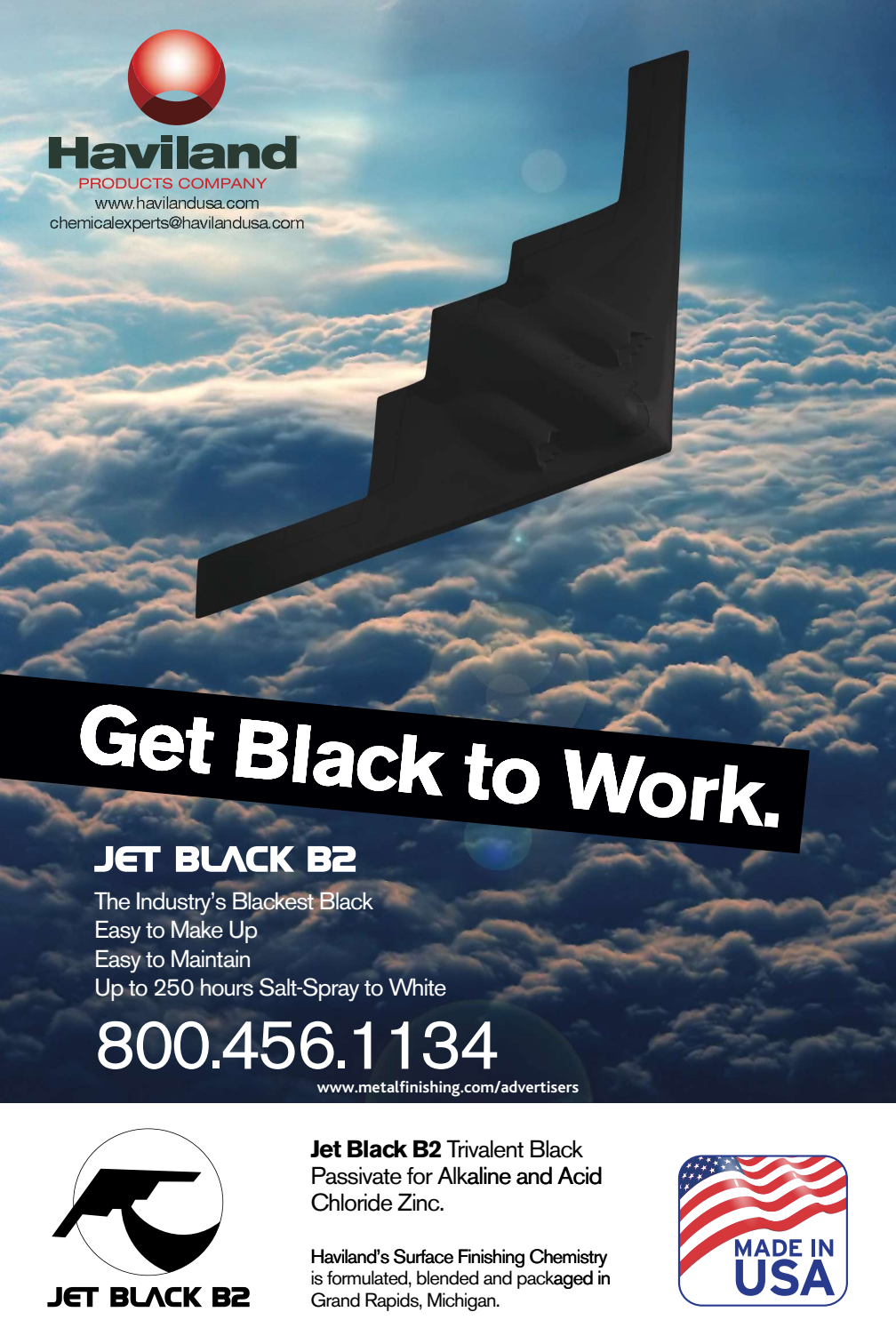

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EVERYTHING YOU NEED TO KNOW ABOUT MECHANICAL/MASS FINISHING

BY EUGEN HOLZKNECHT, RÖSLER METAL FINISHING USA, BATTLE CREEK, MICH.

Mechanical surface finishing, also known as mass finishing or vibratory finishing, is a surface finishing technology that has been around for more than six decades. At the time it was invented in the 1940s, mechanical surface finishing revolutionized whole industries with regard to their surface finishing methods. Large international companies like Volkswagen and Mercedes-Benz in Germany were literally queuing up to initially get a hold of rotary barrels and, later on, the first mass finishing vibrators. Delivery times of 24 months or more were not unusual.

Deburring previously was a purely manual operation with extremely high personnel costs, poor quality, and no consistency or repeatability of results. Then, all of a sudden, manual finishing operations could be replaced with a mechanical process that significantly reduced personnel costs but, more importantly, one that consistently produced higher-quality parts with a high degree of repeatable results.

SOPHISTICATED SUPERFINISHING OF HIGH-VALUE COMPONENTS

Over the years, mechanical surface finishing has evolved from a simple deburring method into a sophisticated technology covering a broad range of industries and applications. Here are just a few examples of "high-tech" mechanical finishing applications:

- **Grinding and polishing of medical implants, such as artificial knees, hips, ankles, etc. In the medical implant industry, special mass finishing processes have been replacing robotic grinding and buffing systems (Fig. 1).**
- **Superfinishing of automotive gears down to a surface roughness of <2 (0.05 µm) to increase the life of power trains, reduce running noise and, at times of high fuel cost, reduce the weight of these components without jeopardizing their reliability (Fig. 2).**
- **Surface finishing of aero-engine components, such as turbine blades, blisks, turbine disks, vanes, etc. In combination with shot peening, mass finishing processes reduce the "maximum exhaust gas temperature" (MEGT) and increase the time intervals between engine overhauls. Better surface finishing of turbine blades also increases the acceleration and compression of the air mass flow in turbines, resulting in lower fuel consumption—an invaluable technical benefit with today's high cost of kerosene (Fig. 3).**

Unfortunately, mechanical surface finishing is a largely empirical process and, for this reason, it is one of the least understood and appreciated manufacturing technologies.

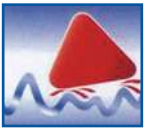
The intention of this article is to provide a better understanding of mechanical surface finishing with particular emphasis on the role of the finishing



Deburring: Burrs are removed, as if numerous little files were grinding on the part (Fig. 4).



Radiusing: Sharp edges on the parts are ground off and transformed into smooth, round contours.



Surface smoothing: "Peaks" are ground off creating a smooth surface.



Polishing: A continuation of the smoothing process—decorative and functional surfaces are polished to a high gloss finish with extremely low Ra values (Fig. 5).



Ball burnishing/ball polishing: Polishing of mainly aluminum and stainless steel parts with media made from stainless steel.



Degreasing: Oily, greasy parts (e.g., stampings) are cleaned (degreased) and at the same time finished (deburred, radiused, etc.).



Surface cleaning: Intensive cleaning of dirty parts (e.g., descaling, derusting) (Fig. 6).

media. Selection of the right media is key to the success of any surface finishing process. Hopefully, the information to follow will help provide some pointers toward the right media selection.

A VERSATILE TECHNOLOGY FOR MANY FINISHING APPLICATIONS

Mechanical surface finishing, generally referred to as "mass finishing," offers a wide range of finishing solutions. While the removal of burrs is the most commonly known application, mass finishing offers many other finishing solutions, of which the most important ones are:

INTERACTION OF VARIOUS MASS FINISHING COMPONENTS

Frequently, mass finishing is considered a "low-tech" technology that is noisy, dirty, and wet. And many users do not pay enough attention to selecting the right components required to optimize their finishing operation. The results of such negligence are usually high finishing cost and a high scrap rate usually requiring a lot of rework.

All this could be easily prevented, if the users would pay a bit more attention to the optimum interaction of the various components involved in any mass finishing process (Table 1):

Figure 7 shows an example of a vibratory mass finisher.

VIBRATORY FINISHING MEDIA: A LARGE VARIETY FROM WHICH TO CHOOSE

In the "old days," when the first mass finishing methods were developed, media consisted of crushed grinding wheels, river pebbles, and slag. Over the last few decades, mass finishing media evolved into a high-



Figure 1: Medical implants in various finishing stages.



Figure 2: Automotive gear before (left) and after (right) superfinishing.



Figure 3: Various finished air foils.

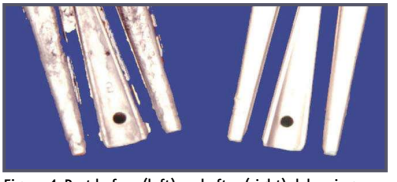


Figure 4: Part before (left) and after (right) deburring.



Figure 5: A polished part.



Figure 6: Part before (left) and after (right) cleaning (descaling shown).



Figure 7: Vibratory mass finisher *(Image courtesy of Rösler)*.



Figure 8: Mass finishing "media" from 60 years ago.

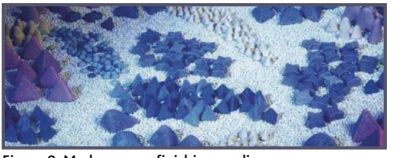


Figure 9: Modern mass finishing media.



Figure 10: Rösler test lab in Battle Creek, Mich.

Component	Function
Mass finishing machine	(1) Induces the energy to put the parts/media mass into motion and (2) Creates a "rubbing" action between parts and media
Water	(1) Serves as a coolant for the process (2) Absorbs potential dust (3) Dissolves and distributes the compound in the work bowl
Compound	(1) Dissolves dirt and grease from the parts surface (2) Cleans the media to keep its "grip" on the part surface (3) Together with the water flushes media- and metal-fines from the work bowl
Media	(1) Generates the desired surface finish—deburring, radiusing, smoothing, polishing, etc.—by constantly "rubbing" on the part surface (2) "Cushions" the parts from each other, thus avoiding impingement

Table 1: Selecting the Proper Components to Optimize Finishing Operations

ly sophisticated product line consisting of different materials, geometric shapes, and sizes (Figs. 8 and 9). Today there are a huge variety of media that a user can choose from. And if mass finishing has an "artistic" element, it lies in the selection of the right media with regard to type, shape, and size.

Only with the right media choice can the desired surface finish be achieved. Many times the media selection process requires comprehensive and time-consuming processing trials. But the payback for such efforts generally is substantial in the form of optimum and cost-effective finishing results. Figure 10 shows a partial view of a present-day test laboratory.

Main Types of Mass Finishing Media

Mass finishing media are generally classified into the following categories:

- **Ceramic (including porcelain polishing media)**
- **Plastic (mainly polyester-based, but also including urea/formaldehyde media)**
- **Steel media (in hardened carbon steel and stainless steel)**
- **Organic media (for example, granules made from corn cob and walnut shells)**
- **Other media (for example, glass beads, polyamide micro-beads, etc.), which play only a minor role in vibratory finishing and are not discussed further**

The most commonly used mass finishing media are either ceramic- or plastic-based. They account for approximately 80–90% of all media used in mass finishing applications. All other media are specialties that are used for certain applications,

Ceramic and plastic media always have one common characteristic:
They consist of a carrier that is mixed with certain types of abrasives!

such as pressure deburring, ball burnishing, drying, and dry polishing.

Whereas in the case of ceramic media the carrier is clay, in the case of plastic media the carrier is either polyester or urea resin.

The most common abrasives used in ceramic and plastic media are:

- **Silica (sand)**
- **Brown and white fused alumina (aluminum oxide)**
- **Silicon carbide**
- **Zirconium**

Depending on the application, mesh sizes can vary between 40 and 400. The different types of media, how they are made, and for what applications they are generally used, are subsequently described.



Figure 11: Ceramic media

CERAMIC MEDIA (Fig. 11)
Density: 95–110 lbs/ft3.
Production method: extruded or pressed.
Firing temperatures: 2,100–2,400°F.
Available shapes: triangle, star, ellipse, cylinder, arrowhead, tri-star, pyramid, cone, rhomboid, parabolic, ball.
Applications: Due to their relative high density, ceramic media are generally used for aggressive grinding on "tough" metals, such as steel, stainless steel, titanium, and so on. However, certain ceramic media can also be used for fine grinding—producing low Ra values on the part surface. Porcelain media, made from pure alumina, can be used for polishing, producing a high-gloss surface.
Limitations: Ceramic media can chip, and chips may lodge in bore holes and undercuts.



Figure 12: Plastic media

PLASTIC MEDIA (Fig. 12)
Density: 60–85 lbs/ft3
Production method: Abrasive/liquid resin mix is poured into molds at room temperature; mix hardens within 15–20 minutes.
Available shapes: triangle, tri-star, double wedge, cone, pyramids of different shapes, parabolic.
Applications: Due to their somewhat lower density, plastic media are generally used on softer metals, such as aluminum, zinc, and brass. Applications range from relatively aggressive deburring/radiusing to pre-plate surface finishes.



Figure 13: Steel media

STEEL MEDIA (Fig. 13)
Density: 210–250 lbs/ft3 (depending on size)
Material: hardened carbon steel, standard carbon steel, stainless steel.
Production method: Cut to length from wire/round bar and then forged.
Available shapes: Sphere (ball), satellite, oval, angle-cut cylinder, etc.

Applications: Pressure deburring of steel parts, ball burnishing (or ball polishing) of mainly stainless steel parts, occasionally also aluminum parts.

ORGANIC MEDIA
Material: Mostly corn cob or walnut shell granules.
Applications: For drying of parts after vibratory finishing. Also used for high-gloss polishing of metal parts, mainly stainless steel, aluminum, titanium, etc., in combination with a mixed-in polishing paste.

SELECTION CRITERIA: MEDIA SHAPE, SIZE, AND ABRASIVE CONTENT

Media shape, size, and abrasive content are crucial for achieving the optimum surface finish.

MEDIA SHAPE

The geometry of the parts to be finished generally determines the shape of the media to be used. A simple rule of thumb is:



Figure 14: Round and compact media.

Round and compact media (Fig. 14): Use for standard applications. There is less danger of media lodging in the part; lower danger of chipping (in the case of ceramic media); and lower wear rate. Typical shapes include: cylinder, cone, ball.



Figure 15: Media with sharp edges.

Media with sharp edges (Fig. 15): For parts with complex geometry and difficult-to-reach surfaces. Danger of chipping; higher wear rate. Typical shapes include: tri-star, triangle, arrowhead.

MEDIA SIZE

The required finish usually determines the media size (Fig. 16):



Figure 16: Small and large media.

Small media size: Produces a smoother surface by having more contact with the part surface; usually requires longer processing times and more gentle processing.
Large media size: Faster removal of burs and radiusing of sharp edges on the parts; produces a rougher surface than small media; more aggressive grinding required.

ABRASIVE TYPE

Silica: For deburring/deflashing of relatively soft metals, such as aluminum, brass, and zinc.
Silicon carbide: For aggressive grinding on difficult-to-machine metals. This abrasive produces dark surfaces.
Aluminum oxide: Characteristics are similar to silicon carbide.
Zirconium: Used in plastic media for adding weight. Mainly used for fine grinding of all kinds of metals.

HOW DO YOU SELECT THE CORRECT MEDIA? BY ASKING THE RIGHT QUESTIONS!

Selecting the right media requires much experience and possibly, as mentioned

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earlier, processing trials. However, by asking the right questions, media selection becomes easier:

What is the desired surface finish?

Aggressive deburring on steel parts requires a different media than—for example—a surface smoothing application on aluminum parts. In the first case, a relatively "fast-cutting," large-sized ceramic media may be required, whereas in the latter a "fine-grinding," small to mid-sized plastic media may be needed.

What is the desired wear rate?

All vibratory finishing media wear! Of course, you want to select the media that will do the job at the lowest possible wear rate and, thus, cost!

Can chipping of the media be an issue?
If media chipping is an issue, ceramic media usually is not an option.

What about separation of parts and media?

After the finishing process, the finished parts must be separated from the media. With ferrous steel parts, magnetic separation may be an option. Otherwise, there must be a distinct difference in size between parts and media to allow separation by vibratory screening.

And what of media lodging?

Depending on the part geometry and size, media lodging may be an issue. By selecting the right media size and shape, media lodging in the parts may be minimized or altogether prevented.

Last but not least: How about media color?

If lodging cannot be prevented, the media should at least have a bright color so that lodged media can be easily detected and removed from the part.

THE CORRECT MEDIA CHOICE MAKES ALL THE DIFFERENCE

Vibratory finishing media may not be the most exciting subject to talk about—unless you are infected by the mass finishing virus! But considering the consequences of the wrong media choice—poor surface finish, high scrap rate, and lots of rework (all of this associated with high cost) —for the user of mechanical surface finishing it is definitely worthwhile to pay a bit more attention to this subject. Hopefully, this article was able to shed some light on the various factors that need to be considered in the selection of vibratory finishing media for a specific surface finishing task.

THE SCIENCE OF SCRATCHES—POLISHING AND BUFFING MECHANICAL SURFACE PREPARATION

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POLISHING

Mechanical finishing refers to an operation that alters the surface of a substrate by physical means such as polishing and buffing.

Polishing plays a vital role in the development of a quality product. The term polishing is not to be confused with buffing. The definition of polishing is surface enhancement by means of metal removal and is generally done by an abrasive belt, grinding wheel, setup wheel, and other abrasive media. A definite coarse line pattern remains after such a polishing operation. This polishing effect removes large amounts of metal from a particular surface.

Buffing is the processing of a metal surface to give a specific or desired finish. The range is from semibright to mirror bright or high luster.

Polishing refers to an abrading operation that follows grinding and precedes buffing. The two main reasons for polishing are to remove considerable amounts of metal or nonmetallics and smooth a particular surface. This operation is usually followed by buffing to refine a metallic or nonmetallic surface.

POLISHING WHEELS

Polishing wheels can be made up of a different variety of substrates such as muslin, canvas, felt, and leather. Cotton fabric wheels as a class are the most commonly used medium for general all-round polishing due to their versatility and relatively modest cost. Polishing wheels can have a hard consistency, such as canvas disks, or a soft consistency, such as muslin, sewn together. The most popular wheels are composed of sewn sections of muslin disks held together by adhesives. The types of adhesives used include those with a base of silicate of soda and the animal-hide glue type.

Felt wheels are available in hard densities to ultrasoft densities. The outside periphery or face of the wheel must be kept true and be absolutely uniform in density over its entire surface. Felt wheels can be easily contoured to fit irregularly shaped dimensions. Felt wheels are generally restricted to use with finer abrasive grain sizes.

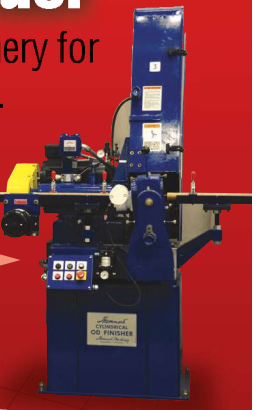
In general, the more rigid polishing wheels are indicated where there is either a need for rapid metal removal, or where there are no contours and a flat surface is to be maintained. Conversely, the softer types with flexibility do not remove metal at such a high rate.

In addition to polishing wheels, precoated abrasive belts can be obtained in any grit size ready for polishing operations. Metallic and nonmetallic articles are polished on such belts running over a cushioned contact wheel with the proper tension being put on them by means of a backstand idler. Where a wet polishing operation is desired, the use of abrasive belts in wet operations needs to have a synthetic adhesive holding the abrasive particles to the belt backing. This synthetic adhesive must have a waterproof characteristic.

When determining the belt's grit size, the condition of the surface is what will dictate the aggresiveness of a belt. Too aggresive belt can put in larger imperfections than those initially in the surface.

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BURR REMOVAL

The removal of burrs is a breaking of sharp edges. Burr removal is done by the following methods: hand filing, polishing, flexible polishing, satin finishing, brushing, and tumbling. Functional parts do not necessarily need a decorative finish and usually deburring becomes the final mechanical finish.

Burrs can be removed by hand methods such as filing, which is very labor-intensive making mechanical means preferred in most cases. Parts that contain restricted areas can be processed using set-up polishing wheels and muslin buffs coated with a greaseless compound. See the discussion on polishing wheels (above) and buffing. Processing methods will be determined by the configuration of the part. If a part contains a heavy burr yet the edges are straight, a rigid set-up wheel is needed. Where the contours are irregular and the burrs not excessive, a sewn or loose cotton buff with a greaseless compound works more efficiently. If extreme flexibility is required, a string wheel with greaseless compound or a tampico wheel with aluminum oxide, grease-based material is required.

BUFFING

Buffing is the processing of a metal surface to give a desired finish. Depending on the desired finish, buffing has four basic categories: satin finishing, cutdown buffing, cut-and-color buffing, and luster buffing. Satin finishing produces a satin or directional lined finish; other types of satin finishing are brushed or Butler finishing. Cutdown buffing produces an initial smoothness; cut-and-color buffing produces an intermediate luster; and luster buffing (color buffing) produces high reflectivity or mirror finish.

TYPES OF BUFFING COMPOUND COMPOSITIONS

Greaseless compound is used to produce a satin finish or a directional lined finish. Greaseless compound contains water, glue, and abrasive. As its name implies, it retains the abrasive on the buffing wheel in a grease-free environment, leaving the surface of the finished part clean and free of greasy residue. The principal uses of greaseless compound are for satin finishing or flexible deburring.

Generally, the abrasive contained in such compounds is silicon carbide or fused aluminum oxide. Grades are available in abrasive sizing from 80 grit to finer depending on the degree of dullness required on a particular base metal. Silicon carbide abrasives are used for the finishing of stainless steel and aluminum. Aluminum oxide grades are used for brass and other nonferrous metals, as well as for carbon steel prior to plating.

To produce a finer satin finish on nonferrous materials, fine emery and hard silica are used. For Butler finishes on silver plate and sterling, fine buffing powders of unfused aluminum oxide and soft silica are used. Greaseless compounds are applied to a revolving buff by frictional transfer. The buff speed is 4,000 to 6,000 surface feet per minute (sfm). The material then melts on the cotton buff, adheres to the peripheral surface, and dries in a short period of time. This produces a dry, abrasive-coated wheel with a flexible surface. The buffing wheels on which greaseless compounds can be applied are sewn muslin buffs, pocketed buffs, full disk loose buffs, and string wheels. The coarser the abrasive particle, the duller the satin finish; the finer the abrasive particle, the brighter will be the satin finish.

BAR COMPOUNDS

Bar compounds contain two types of ingredients; binder and abrasive. The binder can consist of one or more materials taken from animal or vegetable fats as well as petroleum and similarly derived products. Animal fats are such mate-

rials as fatty acids, tallows, and glycerides. Waxes can be from vegetable, insect, or petroleum-based products. Petroleum-based or vegetable-based oils also may be used. The animal and vegetable materials are more saponifiable and will produce a water-soluble soap when combined with alkali. Petroleum, mineral oils and waxes are unsaponifiable and, therefore, might create subsequent cleaning problems.

Each ingredient is added to the binder to transmit a specific effect to the bar compound such as lubricity, degree of hardness, or improved adherence to a buffing wheel. A binder also controls the amount of frictional heat that can be developed on a surface. This is called slip. There is a wide range of abrasives used in buffing compounds, a few of which will be described.

BUFFING ABRASIVES

Aluminum Oxide and Other Powders

Aluminum oxide powders, fused and unfused, are the abrasives most commonly used in the buffing of hard metals. Chromium oxide is used to achieve the highest reflectivity (color) on stainless steel, chromium, and nickel plate. To achieve a high reflectivity (color) on brass, gold, copper, and silver, iron oxide is generally used. Aluminum oxide is chemically represented as Al_2O_3.

The unfused aluminum oxide is white in color. This is manufactured from bauxite or hydrated aluminum oxide by heating it at elevated temperatures. This heating process, called calcination, gives the abrasive the common name calcinated alumina. The higher the calcination temperature, the more water of hydration is driven off and the harder the crystalline material becomes.

When the calcinated temperature is about 950°C, the product produced is a soft alumina having a porous structure. This type of abrasive is used for luster or color buffing. When the calcined temperature is about 1,250°C, a harder alumina is produced. This type of abrasive is used for cutting. Soft aluminas are used to produce luster or a higher reflectivity on all metals, both ferrous and nonferrous. The harder aluminas will cut and remove more metal from the surface of castings or extrusions of aluminum, brass, and other metals.

When alumina is heated to 1,850°C, fused aluminum oxide (Al_2O_3) is produced. This material is made in an electric furnace at approximately 2,000°C. Bauxite, when mixed with alumina and other oxide materials, produces a specific crystalline structure whose hardness can be varied to meet specified physical properties. This fused mass is then cooled and crushed. In the crushing process, the material is ground, screened to the appropriate size, treated magnetically, and acid washed. It is then

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Table I. Hardness of Abrasive Materials

Abrasive Type	Chemical Symbol	Mohs' Scale
Aluminum oxide (fused)	Al_2O_3	8-9+
Aluminum oxide (calcined)	Al_2O_3	8-9+
Tripoli-silica	SiO_2	7
Silicon carbide	SiC	9.6
Iron oxide (red rouge)	Fe_2O_3	6
Chrome oxide (green rouge)	Cr_2O_3	8-9

rescreened to its final classification (grit sizing).

The difference between fused aluminum oxide and calcined alumina is that the fused oxide is of a crystalline structure that is much harder than that of the calcined alumina. Fused aluminum oxide is used mainly on abrasive belts or setup wheels for polishing. As for buffing, fused aluminum oxide is used for cutting down ferrous metals. The abrasive sizing is generally from 60 grit to -325 grit for buffing compounds.

Tripoli

Tripoli is considered to be microcrystalline silica, which is made naturally. It is highly suitable for buffing of aluminum, brass, copper, and zinc die cast or other white metals. Tripoli and silica can be used as a cutting abrasive or a so-called cut-and-color abrasive for nonferrous metals. Tripoli should not be classified as an amorphous silica, but it is microcrystalline in nature. Crystalline silica may cause delayed lung injury for people when exposed to it over a long period. Users of products containing these abrasives should be aware of this possibility and should wear a mask and work in a ventilated area.

Silicon Carbide

Silicon carbide (SiC) is of a crystalline structure that is harder than fused aluminum oxide. It is formed by mixing coke and silica in an electric furnace at approximately 1,900 to 2,400°C. The material is cooled, ground, and sifted to the required grit size similar to the processing of fused aluminum oxide. The crystalline structure of SiC is a hexagonal.

Red Rouge

The chemical formula for rouge is Fe_2O_3; it is also called jeweler's rouge. Its purity is 99% ferric oxide. The crystalline structure of ferric oxide is spherical. Rouge is used mainly on precious metals to give an exceptional high luster.

Green Rouge

The chemical formula for chromium green oxide is Cr_2O_3. The hardness of chromium oxide is 9 Mohs as opposed to iron oxide, which is 6 Mohs, and is used to produce an exceptional luster or color on ferrous as well as nonferrous metals.

These abrasives mentioned represent a small percentage of material available to give a specific finish required on a particular substrate. See Table I for typical hardness values.

Although the wheel speeds for buffing with grease bars will vary greatly from job to job and operator to operator, the figures in surface feet per minute given in Tables II and III will serve as a guide for hand buffing operations. Buffing wheel speeds for automatic operation may vary with the design of the machine and the contact of the work to the wheel. It can, therefore, be more definitely fixed without depending on the physical ability of the hand buffer to main-

Table II. Wheel Speeds for Hand Buffing, sfm

	Cutting Down	Luster Buffing
Carbon and stainless steel	8,000-9,000	7,000-9,000
Brass	6,000-9,000	6,000-9,000
Nickel	6,000-9,000	6,000-8,000
Aluminum	6,000-9,000	6,000-7,000
Zinc and other soft metals	5,000-8,000	6,000-7,000
Chromium		7,000-8,000

tain the correct position and pressure against the wheel.

LIQUID SPRAY BUFFING

Liquid spray buffing compositions have largely replaced bar buffing compositions on automatic buffing machines. Unlike the bar compound previously discussed, liquid buffing compound is a water-based product. The liquid buffing compound has three main constituents: water, binder, and abrasive. Water is used as the vehicle to transport the binder and abrasive to a buffing wheel through a spray system. This water-based liquid is an oil/water emulsion. In this emulsion the abrasive particle is suspended and could be thought of as particles coated with a binder material. The emulsifying materials act as a device to hold the oil-soluble molecules onto the water molecules.

Larger abrasive particles offer less surface area (when compared with the weight of that particle) than several smaller particles. Surface area and density play an important role in the suspension of any liquid emulsion. Stability is the ability to keep the abrasive particle in suspension. When the abrasive particles tend to fall out of suspension, their weight factor is greater than the ability of the emulsified material to maintain stability. Viscosity, therefore, plays an important role in a suspension. A totally unstable emulsion will settle out under all circumstances.

The flow characteristics of a liquid buffing compound are controlled generally by the viscosity of that compound as well as its degree of slip. The viscosity stability of any emulsion is established by its thixotropic nature, which means the viscosity becomes lighter in direct proportion to the amount of shear to which the compound is subjected.

As the degree of slip is increased, the flow characteristics of the compound will also increase in direct proportion to the resultant change in slip or the resultant change in the coefficient of friction.

The gel-type property of an emulsion is broken down by the action of the pump, thus producing viscosity changes. The changes are determined by the amount of shearing action of the pump and the length of time. This breakdown is necessary to allow the transfer of the buffing compound from the pump to the spray gun, which often requires a significant distance.

The viscosity of a liquid compound is measured under a constant set of conditions. To measure viscosity, a representative sample from a batch is needed. This sample must be in a state of equilibrium for a defined period and at a constant temperature. A viscometer is used with a specific spindle. This reading multipled by a factor will give a viscosity reading in centipoise. A deviation of 25% is normal. The control of viscosity of a compound is somewhat difficult. Variations in raw materials or the method of blending are two reasons for viscosity changes. Viscosity is an arbitrary measurement.

Liquid compounds are supplied to the spray guns by means of either air pressure feed tanks or drum pumping equipment. Air pressure is varied depending on the viscosity of the liquid compound, the length and diameter of the fluid lines feed-

Table III. Production Buffing Techniques

Material to Finish	Satin Finishing	Cutdown Buffing	Color Buffing
Aluminum	Aluminum oxide greaseless compound light head of dry tripoli bar. Loose or ventilated buff or string wheel, 3,000 to 5,000 sfm	Tripoli bar or liquid compound. Loose or ventilated buff, 6,000 to 8,000 sfm	Rouge, silica, unfused aluminum oxide bar or liquid compound, loose or low-density ventilated buff, 6,000 to 8,000 sfm
Brass	Aluminum oxide greaseless compound. Loose or ventilated buff, string wheel 3,500 to 5,500 sfm	Tripoli bar or liquid compound. Ventilated loose or sewn buffs, 5,000 to 8,000 sfm	Rouge, silica or unfused aluminum oxide bar or liquid compound, loose or low-density ventilated buffs, 5,000 to 8,000 sfm
Hard chromium	Aluminum oxide greaseless compound. Loose buff, 5,000 to 6,500 sfm		Chromium green oxide or unfused aluminum oxide bar or liquid compound, loose or ventilated buff, 5,000 to 6,500 sfm
Chromium decorative plate	Lubricated silica greaseless compound, loose buff, 3,000 to 4,500 sfm	For burnt areas: Combination fine fused and unfused aluminum oxide bar, loose or ventilated buff, 6,500 to 8,000 sfm Tripoli bar or liquid compound. Loose sewn or ventilated buffs, 5,500 to 7,500 sfm	Chromium green oxide, unfused aluminum oxide bar. Loose or ventilated buff, 6,500 to 8,000 sfm
Copper	Aluminum oxide greaseless compound. Loose or ventilated buff string wheel, 4,500 to 6,000	Tripoli bar or liquid compound. Loose or ventilated buff, 5,000 to 7,500 sfm	Rouge, silica, or unfused aluminum oxide bar or liquid compound, loose or low-density ventilated buff, 5,500 to 7,500 sfm
Copper plate	Aluminum oxide greaseless compound. Loose or packed buff, string wheel, 3,000 to 5,000 sfm	Tripoli bar or liquid compound. Loose sewn or ventilated buff, 5,000 to 8,000 sfm	
Nickel and alloys	Aluminum oxide greaseless compound. Loose or ventilated buff, 5,000 to 7,500 sfm		Chromium green oxide or unfused aluminum oxide bar or liquid compound, loose or ventilated buff, 5,000 to 8,000 sfm
Nickel plate decorative	Aluminum oxide greaseless compound. Loose or ventilated buffs, 4,500 to 5,500 sfm	Aluminum oxide bar or liquid compound. Ventilated, sewn, sisal finger or tampico buffs, 8,000 to 10,000 sfm	Chromium green oxide, or unfused aluminum oxide bar or liquid compound, loose or low-density ventilated buff, 6,500 to 7,500 sfm
Steel and stainless steel	Silicon carbide or aluminum oxide greaseless compound. Loose or ventilated buff, 4,500 to 6,500 sfm	Tripoli bar or liquid compound. Loose ventilated or sewn buffs	Chromium green oxide and/or unfused aluminum oxide bar or liquid compound, loose or ventilated buffs, 8,000 to 10,000 sfm
Zinc	Aluminum oxide greaseless compound. Loose or ventilated buff, 5,500 to 6,500 sfm		Silica or unfused aluminum oxide bar or liquid compound, loose or low-density ventilated buffs, 6,000 to 8,000 sfm

ing the spray guns, and the actual number of spray guns. With one or two spray guns close to the tank, 10 to 15 psig tank pressure may be sufficient, while 6 to 8 guns could require 40 to 45 psig tank pressure.

A drum pumping system is inserted into a steel drum. The pump then transfers the compound through a fluid line or manifold that feeds the guns. Depending on the size of the system, the drum pump is operated at 10 to 40 psig air pressure.

The spray gun is usually mounted in back of the buffing wheel so it will not interfere with the operator and is at a distance from the buffing wheel face so that complete coverage of the face of the buff is obtained with proper regulation of the spray gun. An opening in the dust collecting hood allows the compound to be sprayed from this position. Where buffing machines are totally enclosed, there are no hoods to interfere with the placement of the guns. The spray guns are actuated by air, which is released, in the case of manually operated lathes, by a foot valve that allows the buffer to keep both hands on the part being buffed. With automatic machines, solenoids allow the flow of air to operate the guns. The solenoids are connected to an electric timer where an on-time and an off-time can be set depending on the frequency of the compound needed on the buff face.

A buffing head is a series of buffing wheels put together producing a buff face. This buff face can vary in length depending on contact time needed to do a certain job function. To adequately apply buffing compound to the wheel face, spray gun movers or multiple gun set-ups are usually employed. This allows the liquid compound to be applied across the entire buff wheel face. Spray guns will generally produce a fan of 10 to 12 inches per gun.

In manual operations, the main advantage of the spray composition method is to save the operator time. He or she does not have to stop buffing to apply the cake of conventional solid composition. The operator can remain buffing and apply the liquid compound by the use of a foot peddle, hence less motion is used in applying the compound thus increasing productivity.

In the case of automatic machines, the spray equipment replaces mechanical application. Shutdown time for regulation of mechanical applicators in most cases amounts to more than 25% of the theoretical maximum production time. This is almost entirely eliminated.

The advantages of liquid spray buffing for both automatic and manual buffing procedures are as follows:

1. Optimum quantity of composition is readily controlled on the buff surface, the composition being supplied regularly rather than haphazardly. With buffing bars, an excess of composition is present when the first piece is buffed and an insufficient amount is present for the last piece of work before another application of the bar. If this were not true, the operator would handle the bar of composition more often than the work. Using the spray method, the desired amount of composition is present for each piece buffed.
2. With a deficiency of composition of buffing compound present, the buffing cloth is worn excessively. Spray compositions, eliminating this deficiency of coating, also eliminate this cause of unnecessary buff wear.
3. Solid buffing dirt is packed into the crevices of the work when an excess of buffing composition is present. The serious cleaning problem presented by this dirt is well known. As there need be no excess of composition using the spray method with properly formulated compositions, cleaning after buffing is greatly simplified.
4. Significant savings can be realized in compound consumption, because

all the liquid composition brought to the lathe can be used. There are no nubbins left over.

5. Where high pressures exist between the work and the buffs, a deficiency of compositions has often resulted in such a high frictional heat that the muslin buff catches fire. The spray method eliminates this hazard by keeping the buff properly coated at all times; however, a spray composition must be selected that does not constitute a fire hazard, which would be present if a liquid composition were composed of volatile, combustible fluids.

When using bar compound on an automatic machine, wheel speeds must be maintained in the higher range to generate sufficient friction to exceed the melting point of the bar; however, much lower wheel speeds may be used when liquid compounds are used. The ability to slow down the surface feet enables more intricate parts to be buffed. The lower buffing wheel speeds with large buff faces and liquid compound allow the slowly rotating work to be

pushed up into or "mushed" into the buff wheel. Although the amount of work per unit of time might be lowered, this is compensated by increasing the buff contact time on the work by using wide-faced buffs.

Airless spray systems provide a significant breakthrough in developing a highly efficient method of applying liquid buffing compositions for automatic and semiautomatic buffing operations. Such a system uses high fluid pressures in the range of 600 to 1,800 psi. Specially designed, air-activated drum pumps generate such high fluid pressures and deliver custom-formulated, heavy viscosity liquid buffing compounds to special automatic spray guns with tungsten carbide insert nozzles. Much like the action of a watering hose, the high fluid pressures force the heavy liquid buffing compounds through the orifice of the spray gun for controlled fracturing of the compound. This high velocity spray is capable of penetrating not only the wind barrier around a rotating buff, but has enough force behind it to impregnate the cloth buff up to a 1.5-in. depth, depending upon the construction and speed of the buff. Overspray, so common to regular external atomizing spray systems, is practically eliminated.

Deep saturation of the buff with the compounds provides more consistent and uniform finishes, with reduced compound consumption up to 35%. Extended buff life also reduces changeover downtime. Operating costs are further reduced with lower compressed air consumption because airless spray guns do not require atomizing air to apply the compounds.

Airless spray buffing systems presently in operation limit applications to custom-formulated, heavy viscosity liquid buffing compounds containing tripolis and unfused aluminum oxides. Properly designed drum pumping systems must be used. High pressure fluid hose and fittings are also necessary. The high fluid pressures generated in airless spray buffing systems make it necessary to exercise certain precautions. When adjusting the spray guns, operators must be careful not to allow the force of the spray to come in contact with exposed skin, since the force of compound is strong enough to break the skin.

Liquid abrasive compounds offer so many recognized advantages that their use is now accepted by the finishing industry as standard procedure for high production buffing.

POLISHING AND BUFFING OF PLASTICS

Due to the dies used to mold plastic, little buffing or polishing is required. Some do require removal of flash, parting lines, sprue, projections, gates, and

imperfections from areas that may need further surface finishing. Plastics cut and machined generally need abrasive finishing to bring back their original luster using belt polishing and buffing. Plastic compounds are formulated to remove large amounts of stock without generating too much frictional heat between the part and the wheel (preventing crazing of the plastic). Some buffing compounds contain built-in antistatic materials so that the buffed surface resists the adhesion of airborne lint. When buffing plastic, the material becomes statically charged.

On surfaces of plastic laminates, where fibrous fillers are completely covered with either a thermoplastic or thermosetting plastic, polishing and buffing recommendations are the same as those given for the particular plastic binder involved.

Heavy flash removal, sprues, flat surfacing, and beveling on thermosetting and thermoplastic articles are usually done with wet belt sanding. Special waterproof abrasive belts are most generally used. The abrasive grit size is determined by the amount of flash that must be removed.

For flexible polishing of thermosetting plastic articles, greaseless compound provides a dry and resilient abrading face for removal of light or residual flash, imperfections in the surface, and cutting tool marks, or for smoothing out irregularities on the contours left by the belting operation. Thermoplastic articles readily distort with frictional overheating. To avoid this problem minimum work pressure against the coated buff wheel and low peripheral speeds are needed. To assure low frictional heat development, grease sticks also can be applied to the coated buffing wheel. This gives added lubrication and lowers the amount of drag, which produces the heat buildup.

BUFFING OF PLASTIC

Buffing is usually divided into cutdown and luster or color buffing. Cutdown buffing produces a semigloss finish from the dull, sanded surface resulting from belt sanding or greaseless compound operations. This semigloss finish is adequate as a final finish in some cases. Where a higher luster is required, this cutdown buffing is the intermediate operation prior to the final high luster buffing.

The most popular buffs used are full disk sewn 80/92 count cloth for cutdown and full disk loose, bias type, or ventilated 64/68 count for luster. Buffing pressure should be at a minimum and the buff speed slow to prevent "burning" the plastic. Keeping the buff well lubricated with buffing compound in the cutdown operation helps minimize the burning.

MILL AND ARCHITECTURAL FINISHES (STAINLESS STEEL)

The main concern of most fabricators of stainless steel is to remove welds and machining marks, and blend and simulate the final finish with the original mill finish or the sheet or coil stock. To refine the area of welds and machining marks, standard rough polishing procedures used are as those previously discussed. Note that the final surface finish must closely approximate the original mill finish. There are eight basic stainless steel mill finishes used in the industry by product designers and architects. Mill finish Nos. 3, 4, 6, 7, and 8 are produced mechanically using some type of abrasive media and buffing wheels. Finish Nos. 3 and 4 have proven to be the most popular among fabricators of dairy, kitchen, cafeteria, chemical equipment, and architectural and decorative structures. The simplest way to produce these blended finishes is with string wheels coated with greaseless abrasive compositions containing 80, 120, or 180 grit abrasive, operating at relatively low speeds.

Narrow, flat, or curved areas can easily be blended with a portable power tool and a string wheel up to 8 inches in face width. Medium or very wide areas are finished

with a string wheel log held with two hands or by two operators. Such a polishing log is made up of string wheel sections on a desired width shaft of a sufficiently powered portable tool. The greaseless compound is applied to the rotating string wheel log and allowed to dry a few minutes. String wheel blending is then quickly accomplished in the direction of the lines of the original mill finish.

Mill finishes Nos. 6, 7, and 8 are most generally used on consumer products, although on some architectural sections they are produced for contrasting patterns.

BASIC STAINLESS STEEL SHEET FINISH DESIGNATION

The following list of stainless steel sheet finish designations includes a brief description of how each finish is obtained.

Unpolished Finish No. 1: A dull finish produced by hot rolling to specified thickness, followed by annealing and descaling.

Unpolished Finish No. 2D: A dull finish produced by cold rolling to specified thickness, followed by annealing and descaling. May also be accomplished by a final, light roll pass on dull rolls.

Unpolished Finish No. 2B: A bright finish commonly produced in the same way as No. 2D, except that the annealed and descaled sheet receives a final, light cold-roll pass on polished rolls. This is a general purpose, cold-rolled finish, and is more readily polished than the No. 1 or No. 2D finishes.

Polished Finish No. 3: An intermediate polished finish generally used where a semipolished surface is required for subsequent finishing operations following fabrication, or as a final finish with a 50- or 80-grit abrasive compound.

Polished Finish No. 4: A general purpose bright polished finish obtained with a 100 to 180 mesh abrasive, following initial grinding with coarser abrasives.

Buffed Finish No. 6: A soft satin finish having lower reflectivity than No. 4 finish. It is produced with a greaseless compound, #200 grit, top dressed with white rouge or chromium green rouge.

Buffed Finish No. 7: A highly reflective finish produced by buffing a surface that has first been refined to approximate a No. 6 finish, then buffed lightly with a white rouge without removing satin finish lines.

Buffed Finish No. 8: The most reflective finish commonly produced. It is obtained by flexible polishing with successively finer abrasive compounds, then buffing extensively with a very fine chromium green rouge bar compound.

FINISHES FOR ARCHITECTURAL ALUMINUM

Due to the different aluminum alloys, variations in final surface finish may occur. Variations may also occur by the type of buffing equipment used, type and size of the buff wheels, peripheral speed of the buff, the type of abrasive composition used and operator's technique. When using automatic equipment, the operator technique is replaced by a mechanical system controlling such variables as pressure, time cycle, conveyor speed, and contact time against the buffing wheel, resulting in a more consistent finish.

Aluminum and its alloys are soft metals with a high frictional coefficient. As previously discussed, tripoli or silica is used for a cutdown or cut-and-shine operation on aluminum. Calcined alumina compounds are used for shine on the aluminum surface.

DESCRIPTION OF ARCHITECTURAL FINISH DESIGNATIONS

Series (a) As fabricated. No buffing or polishing required.

Series (b) Medium bright soft textured satin finish.

Series (c) Bright buffed finish over soft texture satin.

Series (d) Bright buffed finish on original surface.
Series (e) Coarse directional satin finish.
Series (f) Medium directional satin finish.
Series (g) Fine directional satin finish.
Series (h) Hand-rubbed satin-type finish (small areas only).
Series (i) Brushed finish.
Series (j) Nondirectional satin finish.

GENERAL RECOMMENDATIONS

The following recommendations are step-by-step instructions for obtaining the designated architectural finishes.

Series (b) Finishes: Polish with a wheel coated with an abrasive and cement paste with 80 to 150 grit on sewn or ventilated buffs, lightly lubricated with special bar or liquid lubricants. Buff speed 6,000 sfm. Final polish with a wheel coated with an abrasive and cement paste with 320 grit using the same buff and same speed.

Series (c) Finishes: Polish with an abrasive and cement paste coated wheel, 320 grit on sewn or ventilated buff. Light lubrication with special bar or liquid lubricant. Bright buff with clean working tripoli bar compound or liquid tripoli buffing compound on ventilated, sewn, or loose buff. Buff speed 7,000 sfm.

Series (d) Finishes: Bright buff only over original surface as for series (c) finishes. No prior polishing required.

Series (e) Finishes: Coarse satin finish with greaseless compound of 80 grit over glue base buff sizing on a ventilated or sewn buff, or with liquid abrasive 80 grit on the same type buff. Lubricate the dried compound head with a special bar or liquid lubricant. Buff speed 6,000 sfm.

Series (f) Finishes: Medium satin finish with greaseless compound, 120 grit, over a blue base buff sizing on ventilated or sewn buffs, or with liquid abrasive 120 grit on the same type buff. Lubricate dried compound head with a special bar or liquid lubricant.

Series (g) Finishes: Fine satin finish with greaseless compound, 150 grit, on a ventilated, sewn or loose buff, or with liquid abrasive 150 grit on the same type of buff. Lubricate dried compound head with a special bar or liquid lubricant. Buff speed 6,000 sfm.

Series (h) Finishes: Hand rubbed finish, using coarse steel wool lubricated with a special liquid lubricant. Final rubbing with No. 0 steel wool.

Series (i) Finishes: Brush type finish produced with string wheels coated with greaseless compound, 80 grit. String wheel speed 6,000 sfm. Buff head may require some light lubrication with a special bar lubricant, depending on alloy of aluminum. Nylon impregnated wheels are also used for this finish.

Series (j) Finishes: Brush type finish produced with a string wheel coated with greaseless compound, 80 grit, but operated at a slow speed of 2,000 to 3,000 sfm. May also require some light lubrication with a special bar lubricant. Again, nylon impregnated wheels may also be used.

When high production satin finishing is required for series (e), (f), (g), and (i), use a liquid greaseless abrasive. Such compositions may be applied automatically with properly designed spray equipment. Light lubrication of the satin finished head, when required, is done with nonmisting, low atomizing spray equipment.

SAFETY REQUIREMENTS OF POLISHING AND BUFFING

Due to increased concern for industrial and environmental safety, state and federal authorities have drawn up guidelines for controlling industrial hazards. These guidelines protect the user as well as the environment.

Buffing processes propel dust particles, cotton lint, abrasive dust, and metallic dust into the air. Microcrystalline silica, or tripoli, which is used in buffing compounds, is a good example of such dust. According to OSHA permissible exposure limits, exposure to airborne crystalline silica shall not exceed an 8-hour time-weighted average limit as stated in 29 CFR Part 1910 1000 Table Z-3 for Mineral Dusts, specifically "Silica: Crystalline: Quartz (respirable)." The threshold limit value and biological exposure indices for the 1987-1988 American Conference of Governmental Industrial Hygienists is 0.1 mg/m3 (respirable dust).

Excessive inhalation of dust may result in respiratory disease including silicosis, pneumoconiosis, and pulmonary fibrosis.

The International Agency for Research on Cancer (IARC) has evaluated *Monographs on the Evaluation of the Carcinogenicity Risk of Chemicals to Humans, Silica and Some Silicates* (1987, Volume 42), that there is "sufficient evidence for carcinogenicity of crystalline silica to experimental animals" and "limited evidence" with respect to humans.

A conventional particulate respiratory protector is required based on considerations of airborne concentrations and duration of exposure. Refer to the most recent standards of the American National Standard Institute (ANSI Z.88.2), the Occupational Safety and Health Administration (OSHA) (29 CFR Part 1910 134), and the Mine Safety and Health Administration (MSHA) (30 CFR Part 56). The use of adequate ventilation and dust collection is also required.

Grinding, polishing, or buffing operations that generate airborne contaminants in excess of exposure limits into the breathing zones of employees should be hooded and exhausted as necessary to maintain legal exposure limits. A hood used for the control of contaminants from a grinding, polishing, or buffing operation should be connected to an exhaust system that draws air through the hood to capture air contaminated by the operation and to convey the contaminated air through the exhaust system.

Where large quantities of exhaust air cause negative pressures that reduce the effectiveness of process exhaust systems or cause a carbon monoxide hazard due to back-drafting of flues of heating devices, provisions shall be made to supply clean make-up air to replace the exhausted air. The make-up air supply, where necessary, should be adequate to provide for the combined exhaust flows of all exhaust ventilation systems, process systems, and combustion processes in the workplace without restricting the performance of any hood, system, or flue.

Dust collection equipment is available in numerous designs utilizing a number of principles and featuring wide variation in effectiveness, first cost, operating and maintenance costs, space, arrangement, and materials of construction. Consultation with the equipment manufacturer is the recommended procedure in selecting a collector for any problem where extensive previous plant experience on the specific dust problem is not available. Factors influencing equipment selection include:

1. Concentration and particle size of contaminant
2. Degree of collection required
3. Characteristics of air or gas stream
4. Characteristics of contaminant
5. Method of disposal under Federal, State, and Local Regulations.

There are many other aspects of buffing and polishing than these briefly discussed here. Though this very important contributor to the metal-finishing industry is more of an art than a science, basic engineering principles can be applied to this operation. With the proper melding of buff and compound, applied in a controlled fashion, optimum finish and maximum economy can be achieved.

For questions or comments, contact the author at a.dickman@sbcglobal.net.

BUFFING WHEELS AND EQUIPMENT

BY DAVID J. SAX
STAN SAX CORP., DETROIT; WWW.STANSAXCORP.COM

Three elements to a successful buffing operation are the buff wheel, the buffing compound, and the buffing machine. It is necessary to understand all of these elements and how they interact to achieve desired quality, productivity, cleanability, corrosion resistance, reject elimination, and overall cost-effectiveness.

WHAT IS BUFFING?

Buffing is a mechanical technique used to bring a workpiece to final finish. It also can be used to prepare the surface of a machined, extruded, or die-cast part for plating, painting, or other surface treatment. The objective is to generate a smooth surface, free of lines and other surface defects.

Buffing is not a process for removing a lot of metal. Deep lines and other more severe surface defects should be removed before buffing by polishing with a polishing wheel or abrasive belt.

Buffing usually involves one, two, or three steps: cut buffing, intermediate cut, and color buffing. These operations normally are performed by what is referred to as either "area" buffing or "mush" buffing.

Cut Buffing

A harder buff wheel and, generally, a more abrasive buffing compound, are used to start the buffing process. In cut buffing, the buff wheel and workpiece are usually rotated in opposite directions to remove polishing lines, forming marks, scratches, and other flaws.

Color Buffing

When a mirror finish is specified, a color buff step may be required. Color buffing may be performed with a softer buff wheel and less aggressive abrasive compounds. In color buffing, the buff wheel and workpiece are usually rotated in the same direction. This enhances the cut buff surface and brings out the maximum luster of the product.

Area Buffing

For localized finishing, narrow buffing wheels, positioned tangentially to the workpiece, are used. This is often is referred to as "area buffing."

Mush Buffing

To finish larger parts or parts having several surface elevations, mush buffing may be used. This involves the use of one or more wide buff wheels. In mush buffing, a part is rotated or cammed through the buffing wheel. This technique is also used to finish multiple products simultaneously.

BUFFING COMPOUNDS

Buffing compounds are the abrasive agents that remove minor surface defects during the buffing phase of the finishing cycle. Buffing compounds are available in paste or solid form. There are thousands of products from which to choose. The prime consideration in selecting a buffing compound is the substrate being buffed and the surface to be provided.

Nonferrous products made of copper, nickel, chromium, zinc, brass, aluminum, etc., frequently are buffed with compounds containing silica (generally amorphous, often "tripoli"). "Tripoli" is found in a small area of Oklahoma and is shipped all over the world. Steel products are normally buffed with compounds of fused aluminum oxide, which is available in DCF collector fines and as graded aluminum oxide in a range of grit designations.

Special abrasives are available for other purposes. For example, chromium oxide is widely used to give stainless steel, chromium- and nickel-plated products high reflectivity. Iron oxides are used to color buff gold, silver, copper, and brass. Lime-based buffing compounds are used to generate mirror finishes on nickel products.

Skilled buffing engineers can help manufacturers select the optimum equipment, buffing compounds, wheels, and buffing techniques. Cleaners and cleaning processes must be matched to the soil to be removed.

BUFFING WHEELS

Fabrics used in buffing are designated by thread count and fabric weight. Count is measured by threads per inch; weight by the number of linear yards per pound of 40-inch-wide fabric. Heavier materials have fewer yards per pound. Lower thread count and lighter weight materials are used for softer metals, plastics, and final luster. More closely woven, heavier, and stiffer materials are used on harder metals for greater cut and surface defect removal. Stiffness is a result of heavier weight, higher thread count fabrics, more material, specialized treatments, sewing, and overall buff design.

Buff wheel construction determines the action of the buff by making it harder or softer, usually by varying convolutions of the face of the wheel. This influences aggressiveness. Part configuration dictates buff design, construction, thread count, etc.

Conventional buffs employ a circular disk of cloth cut from sheeting and sewn into a number of plies. For example, some materials require from 18 to 20 plies to make a -in.-thick section. Multiple sections are assembled on a spindle to build the required face width. The density of these types of buffs is also controlled by spacers that separate the plies of fabric or adjacent faces from one another.

Industry standards for the inside diameter of airway-type buff wheels are 3, 5, 7, and 9 in. As a rule, productivity and buff wheel life increase as outside diameter increases and thread count and material content increases. Larger buffs and higher shaft rotation speeds also increase productivity and buff life.

The choice of buff center size depends on how far the buff material can be worn before the surface speed reduces to a point of inefficiency, or flexibility declines to a point where contours cannot be followed. Airway buff flexibility decreases with use as wear progresses closer to the steel center. Most airway buffs are designed with as much material at the inside diameter as the outside diameter.

Flanges

Buffing wheels require flanges for safe operation. Flanges must be sized for the specific inside diameter of each buffing wheel. It is important for all buffs that the flange be designed with sufficient strength to withstand the tremendous forces and pressures exerted in buffing. If buffs are not well designed and fabricated, centrifugal forces at higher speeds and the shock from operations can cause failure of clinching teeth, breakage of rings, and breakdown of buff sections.

MUSLIN BUFFS

The most commonly used fabrics for buffs are cotton muslins. As previously not-

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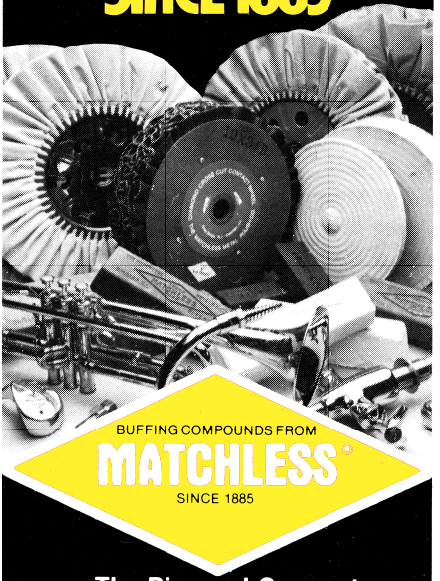
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Table I. Commonly Used Buff Fabrics

Warp (Lengthwise)	Filler (Crosswise)	Cloth Weight (Linear yd/lb of 40-in.-wide material)
60	60	3.15
80	80	3.15
86	80	2.50 (soft)
86	80	2.50 (firm)
86	80	2.50 (yellow treated at mill)

ed, fabrics are designated by thread count (e.g., 60/60, 80/80, 86/80). These designations refer to the threads per inch in the warp and fill, respectively. Fabric weights typically run from 2.5 to 3.5 yd/lb. (Table I).

OTHER BUFF MATERIALS

Flannels

Domet flannel (with nap on both sides) and Canton flannel (nap on one side and twill on the other side) in various weights are used where other fabrics fail to produce a high enough luster. Coloring of jewelry products is a typical application for such buff materials.

Sisal

Sisal is a natural hemp fiber used for fast-cut buffing of steel and stainless steel. It is a coarse fiber twisted into strand groups and frequently woven into a fabric. It has a much lower thread count than cotton muslin, sometimes five by seven per inch, and offers the advantages of greater surface defect removal. Combination sisal/cloth buffs are effective designs (Fig. 1). The sisal plies frequently are cloth covered to omit the tendency of the sisal to cut the cotton threads of adjacent cloth plies. Alternating cloth and sisal improves compound retention, reduces unravelling, and moderates cut. Kraft paper alternated with sisal also has applications.

Other Natural Materials

Occasionally, other materials are used to form buffs. For example, woven wool buffs are used on plastics, soft metals, and sterling silver. Sheepskin buffs are used to avoid surface drag or smear when buffing metals that contain lead. Russet (bark-tanned) sheepskin is used for cut. White alum (alum-tanned) sheepskin is used for color buffing.

Pieced Buffs

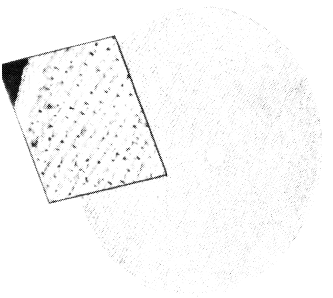
Pieced buffs are less expensive because they are made of lower-cost materials. The buffs are made of colored segments, unbleached segments and occasionally bleached material.

Combination Buffs

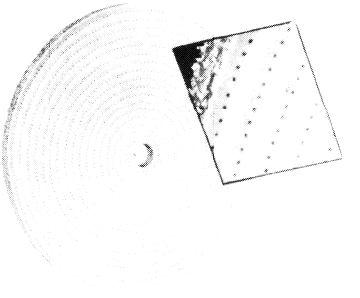
Often different materials are combined, especially sisal with cloth, and occasionally paper as well as cloths of different specifications.

Synthetic Fibers

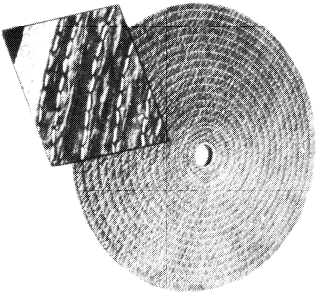
Unwoven nylon and other synthetics fibers, because of their water resistance, may be used wet or dry or with wax or grease lubricants. Buffs made of synthetics are usually operated at slow speeds, typically 2,500 sfpm, to prevent melting and streaking surfaces.



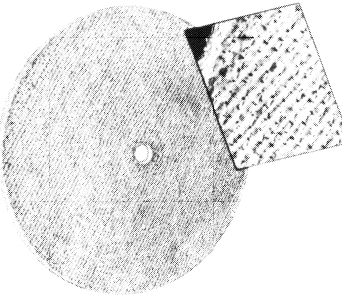
ALL SISAL



SISAL WITH CLOTH



SISAL WITH PAPER



TREATED SISAL

Fig. 1. Sisal buffs.

BUFF TREATMENTS

Treatments may be applied to fabrics (mill treatment) or to the buff after assembly (dip treatment). Buff fabrics are frequently hardened and stiffened to promote faster cutting, softened for additional flexibility to conform to contours, strengthened for longer buff life, or lubricated to prevent burning. Buff fabrics may also be treated to provide improved adhesion of buffing compound, to abrade for heavier cut, or to flameproof and make fire resistant. Treatments must be applied evenly and uniformly to avoid creating hard spots that cause uneven buffing. The treatment must not deteriorate with buff age. Unsuccessful treatments weaken the cloth and decrease buff life.

CONVENTIONAL, FULL-DISK BUFF DESIGNS

Unsewn Buffs

Conventional, full-disk buffs are made with die-cut cloth disks. Unsewn, conventional full-disk buffs may be used for luster (Fig. 2). Loose disks are turned to allow the threads of the material to lie in different directions. This results in more even wear, avoiding a square shape after being put into use. One disadvantage of this conventional design is that the fabric can fray or ravel. When held against a wheel

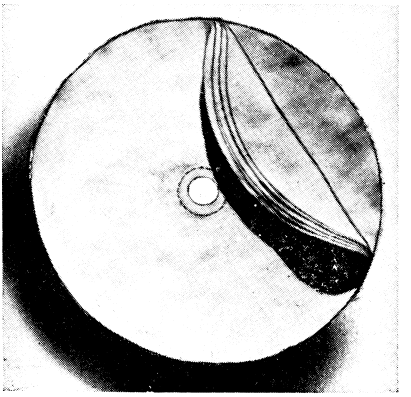


Fig. 2. Full disk buff.

rake, a cloud of threads may fly off. This shortens buff life, increases compound consumption, and adversely affects finish. Also available are solid bias sisal buffs, with every other layer being cloth, and rebuilt buffs made from reclaimed material.

CONVENTIONAL SEWN BUFFS

Conventional, full-disk buffs for heavier buffing (cut) are sewn in various ways (Fig. 3). Closer sewing is specified for cutting harder metals and for removing deep imperfections.

Concentric sewing causes a buff section to become harder as it wears closer to the sewing and softer after wear causes the sewing to break through. Spiral sewing results in more uniform density. Square sewing produces pockets that help the buff wheel to retain more buffing compound. Radial sewing, sometimes called sunray sewing, and radial arc sewing provide other variations. Tangent, parallel, ripple, zigzag, cantilever, and petal sewing are used for similar reasons. Special sewing, other than spiral, which is done on automatic machines, involves more labor in the buff manufacturing process, thus increasing the price per buff.

Folded or Pleated Buffs

Folded buffs consist of circles of cloth folded twice to form a quarter circle, resulting in a "regular-pocket" buff (18 ply), or, for more cut, three times, to form eighths of a circle to constitute a denser "superpocket" (34 ply). The segments are laid down to form a circle, with each segment overlapping the previous segment. They are sewn around the arbor hole and partway to the periphery. The folds form pockets that hold compound and flex sufficiently for contour-following capacity. Folded buffs share three design deficiencies: lack of center ventilation, a tendency to fray, and waste of material in the unused center.

Pleated Buff

Airway buff cloth may be accordion pleated to present more angles of material to the surface of the product to be finished. Pleating results in more cloth angles to reduce streaking and improve coloring characteristics. Better cutting is also achieved in some applications.

Packed Buffs

Buffs may be packed with spacers consisting of cloth or paper inserted between the larger diameter plies. The same spacer principle is used between buff sections. Both measures result in a softer wheel face. The packed buff construction is effective in contour buffing applications.

A version of the packed buff, for threaded, tapered spindles (2-12-in. diameter), is used in the jewelry industry. The center is hardened, usually with shellac. The sides of the buff may be reinforced by leather disks.

Pieced Buffs

Pieced buffs may be used in place of sewn full-disk buffs. They are made from remnants of cloth left over in the manufacture of other textile products. Such buffs

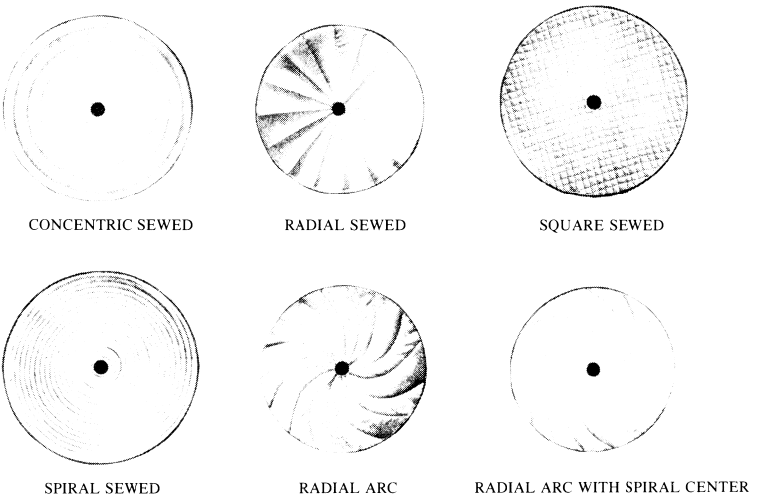


Fig. 3. Sewn buffs.

require one of the types of sewing used for full disks in order to stay together in use. The chief virtue of pieced buffs is their higher value owing to the lower cost of materials. They usually are sold by the pound (see Table II).

BIAS-TYPE BUFF WHEELS

Bias buffs are more frequently used than conventional forms. They combine flexibility and cutting power. Bias buffs are cool running and resist burning. They are naturally ventilated. Side openings in flanges, center plates, and tabs, resulting in spacing between sections, enhance their cool-running characteristics. By using material cut on the bias, the threads form an "X" at the periphery of the buff. Threads are held at a 45° angle by cross-threads. This minimizes fraying and raveling (Fig. 4).

Strips of bias-cut fabric are sewn into continuous rolls. After the rolls are cut to proper length, they are wrapped around a hub or core. They are then pulled to the desired inside diameter within the channel, usually by means of steel blades in an "Iris" machine. Straight-wound material wrapped around an oversized wheel results in a convoluted or "puckered" face; thus, the term "puckered" buff.

The "puckered" face design of bias buffs tends to break up lines left in the surface of a product from previous operations. Increasing the size of the drums varies the amount of pucker in the face. The bias buff can be adapted to various contoured parts and degrees of cutting and coloring. An advantage of the "Iris"-made buff is the elimination of material beyond the inside diameter to the arbor hole. Thus, more of the cloth is available for use.

Ventilated Bias Buffs

Although the puckered characteristic of bias buffs results in cooler running, some operating conditions require additional cooling. Steel centers with holes and ridges are designed to collect and divert more air. The air cools the buff and the work-

Table II. Approximate Weight Table for Spiral Sewed Pieced Buffs

	REGULAR Approx. 3/4 in. Thick		*HEAVY Approx. 5/16 in. Thick*		*EXTRA HEAVY Approx. 3/8 in. Thick*	
Diameter (in.)	*Lbs. Per 100 Sections*	*Sections Per 100 Lbs.*	*Lbs. Per 100 Sections*	*Sections Per 100 Lbs.*	*Lbs. Per 100 Sections*	*Sections Per 100 Lbs.*
4	*7.4*	*1351*	*8.2*	*1220*	*11.1*	*900*
5	*11.5*	*870*	*12.8*	*781*	*17.3*	*578*
6	*16.6*	*602*	*18.4*	*543*	*24.9*	*401*
7	*22.1*	*452*	*25.0*	*400*	*33.0*	*303*
8	*29.4*	*340*	*32.7*	*306*	*44.1*	*227*
9	*36.5*	*274*	*41.3*	*242*	*54.8*	*182*
10	*46.0*	*217*	*51.0*	*196*	*69.0*	*145*
11	*55.6*	*180*	*61.7*	*162*	*83.4*	*119*
12	*66.3*	*151*	*73.5*	*136*	*99.5*	*100*
13	*77.7*	*129*	*86.2*	*116*	*116.6*	*86*
14	*90.2*	*111*	*100.0*	*100*	*135.3*	*74*
15	*103.5*	*97*	*114.8*	*87*	*155.3*	*64*
16	*117.7*	*85*	*130.6*	*77*	*176.6*	*57*
17	*132.9*	*76*	*147.4*	*68*	*199.4*	*50*
18	*149.0*	*67*	*165.3*	*60*	*223.5*	*45*
19	*166.1*	*60*	*184.2*	*51*	*249.0*	*40*
20	*184.0*	*54*	*204.1*	*49*	*276.0*	*36*
21	*202.9*	*49*	*225.0*	*44*	*304.4*	*33*
22	*222.6*	*45*	*246.9*	*40*	*333.9*	*29*
23	*243.4*	*41*	*269.9*	*37*	*365.1*	*27*
24	*265.2*	*38*	*294.1*	*34*	*397.8*	*25*

piece surface. Clinch rings permit use of reusable metal inserts for substantial savings (Fig. 5).

PUCKERED BUFFS

Puckered buffs are rated by numbers. Higher numbers indicate greater cloth content, buff density, and face convolutions (Fig. 6). Higher densities and closer convolutions increase cutting and reduce streaking.

Open-Face Cloth Buffs

The open-face buff prevents loading, packing, clogging, and ridging during finishing operations. The plies are configured differently from the closed-face design. Buff material is wound singly or in groups of two, three, four, or more plies. Open-face buffs may be "straight wound" or "spiral wound" for a corkscrew or cross-cutting action that further minimizes streaking. Buff density varies with the number of plies, the amount of cloth, thread count, fabric weight, and treatment of the cloth. Buff pressure, speed, angle to the part, cloth strength, compound absorption ability, ventilation, and cloth flexibility are varied with buff design.

Bias Sisal Buffs

"Iris" equipment used to gather cloth buffs is adapted to sisal and other materials (Figs. 7-10). Some bias sisal buffs are tapered (wider at the outside than the inside diameter). This reduces gaps between hard sections that could cause

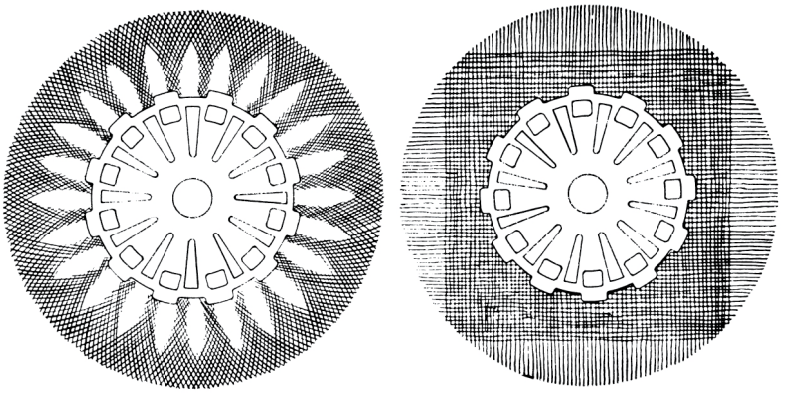
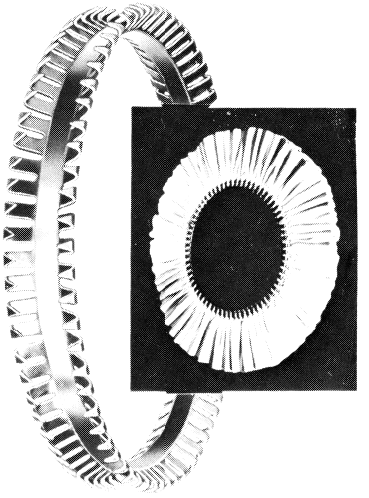


Fig. 4. Bias buff (left) versus conventional buff (right). Thread configurations of bias buffs alternate warp and filler threads. Biasing provides design efficiency by exposing all thread ends to the surface being buffed, reducing fraying of the fabric.

streaking. The tapered bias sisal buff is a long-life, cool-running buff for steel and stainless steel. Hard bias sisal buffs also are used in place of some belting operations, as well as in deburring and brushing.

Open-Cloth Bias Sisal Buff

The open cloth bias sisal (OCBS) buff is used on contoured steel and stainless steel parts (Fig. 9). It consists of woven sisal and cloth, four plies of each (eight plies total), bound together by concentric sewing before Iris gathering. The buff is manufactured in endless strips, cut to length, rolled around split drums, and gathered into clinch rings by the "Iris" machine. A variation of the open-cloth bias sisal buff is the open double-cloth bias sisal (ODCBS) buff. This design consists of two layers of cloth sewn together with one layer of sisal to make a 12-ply buff of eight plies of cloth and four plies of sisal.



Spoke Unit, or Finger Buff

Spoke unit or finger-type buffs combine great cutting power with the capacity to flex and accommodate contours and allow better workpiece coverage with fewer buffing heads. Spokeunit or finger-type buffs are made from materials that include soft cloth, stiff cloth, sisal, and coated abrasives. The material is manufactured into units, or fingers, sewn into endless belts, cut to length, wrapped around split drums, and gathered by an "Iris" machine into steel teeth. The spoke unit or finger

Fig. 5. Steel clinch ring (left) and steel clinch ring buff with open center (right). Buffs that are constructed by the clinch ring or "Iris" machine method have superior ventilation and cloth biasing, and optimal material utilization.

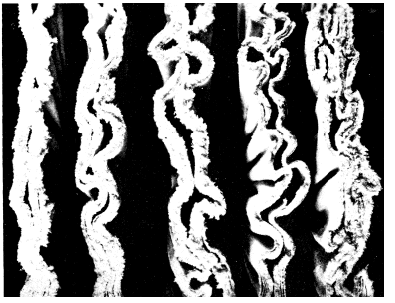


Fig. 6. Cloth bias buffs in order of increased density from closed face (left to right: 0, 2, 4, 6) to open face (far right) design.

sisal buff is usually made with woven sisal interlaced with 86/80 cloth. Acid or rope sisal is sometimes used. The cloth may be mill or dip treated (Fig. 10).

The spoke or unit bias buff runs cooler than standard bias buffs and has a knee-action flexibility that gives superior contour-following ability. The width and number of the individual units is varied within limits. The range of buff density, or hardness, is varied by choice of materials, treatments, (buff center size) plies, and type of radial stitching. Some complex products are best finished with this type of buff.

FLAP BUFFS

The flap buff (Fig. 11) utilizes separate flap units placed at right angles to the direction of rotation of the wheel. Each flap supports the other to produce a smooth running wheel. Flap wheels were originally designed for bumper polishing and buffing operations. Flaps are made of coated abrasives, sisal, cloth and combinations thereof.

POLISHING WHEELS

Polishing wheels are usually made of conventional cloth buff sections glued or cemented together. Canvas disks are cemented to the sides to protect the sewing. Glue or cement is applied to the face. Faces are struck with a pipe at angles and cross-angles to form a uniform crisscross of cracks on the polishing surface and provide sufficient resiliency to allow the wheel to make better contact with a workpiece.

Buff sections used to make polishing wheels are generally spiral sewn and made of various types of cloth, sisal, canvas, or sheepskin. Solid, one-piece wool felt, and bull neck and walrus hide are occasionally used.

Conventional straight buff sections that are glued together may cause streaking during polishing. An alternative involves inserting pie-shaped segments or other spacers between the buff sections to result in a "nonridge" polishing wheel that eliminates streaking. Various abrasive and adhesive combinations are used to grind, polish, and satin finish. These include liquid, graded aluminum oxide abrasives, greaseless compounds and burring bar compositions.

BUFFING EQUIPMENT

Significant improvements have been made in buff wheels and buffing compounds to provide consistent and predictable performance. This has helped manufacturers of automated buffing machines to develop automated equipment for low- as well as high-volume requirements and to minimize labor and overhead in the finishing operation.

MACHINE DESIGN

Mechanical buffing systems have a motor-driven shaft to which the buff wheel is applied. In addition, most machines will have a positioning mechanism, a finishing lathe, and workpiece-specific fixtures.

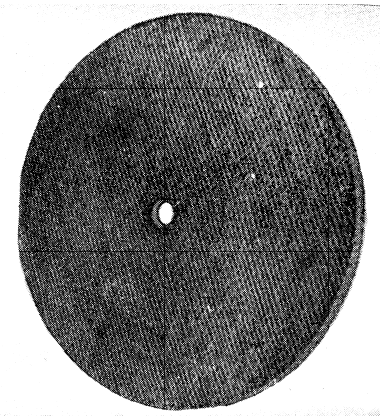


Fig. 7. Conventional sisal buff.

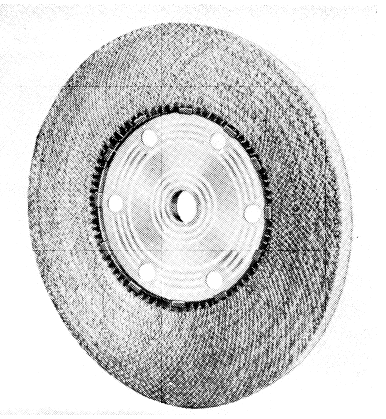


Fig. 8. Bias sisal buff.

Positioning Mechanism

Automated buffing machines orient parts against the media by mechanical methods to duplicate or replace human motions. They rotate, oscillate, tilt, and index the wheel and/or the workpiece.

Finishing Lathe

The finishing lathe is a device located in relation to the positioning mechanism. It allows a buff wheel to contact one of more surfaces of the workpiece at predetermined locations.

Fixturing

The workpiece fixture or tooling is used to position a part during the buffing cycle. Buffing machines can incorporate single or multiple fixtures. Fixtures can also be designed to automatically reorient a workpiece during the buffing cycle.

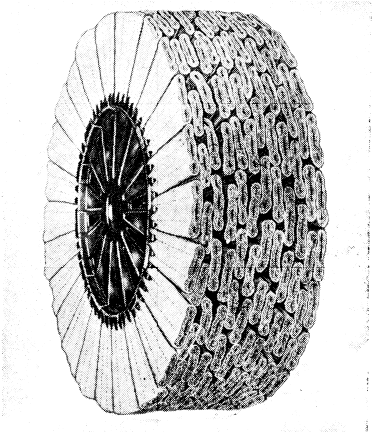


Fig. 9. Open cloth sisal buff.

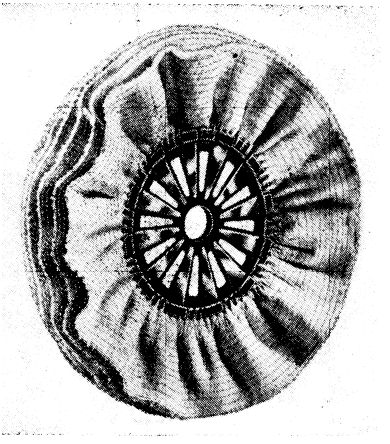


Fig. 10. Spoke unit or finger sisal buff.

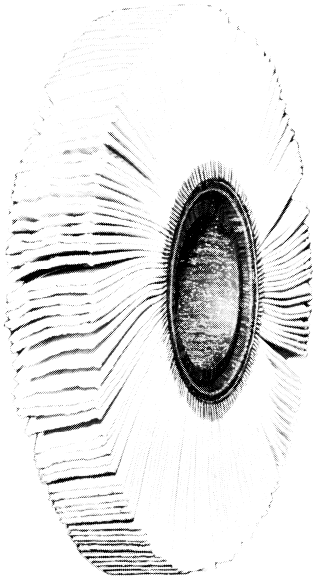


Fig. 11. Flap buff.

Buffing fixtures are unique to each part being processed, although some may be adapted to an assortment of similarly shaped parts. The design of fixtures is extremely important. Unless a part can be fixtured properly at a reasonable cost, the economical utilization of finishing equipment cannot be justified.

TYPES OF BUFFING MACHINES

Buffing machines fall within three broad categories: manual, semiautomatic, and fully automated.

Manual Machines

Manual buffing machines are used in low-volume applications and applications involving the buffing of extremely complex workpieces. Manual machines, when used in conjunction with the proper buff wheel and buffing compound, can be manipulated.

Semiautomatic Machines

Semiautomatic buffing machines are used in lower volume applications where a single finishing operation is performed on a variety of parts. Initial investment and fixturing and operating costs are low.

Semiautomatic finishing machines can be used with a single- or double-end lathe. One operator can be employed to load, unload, and operate equipment. Semiautomatic machines hold the workpiece and present it to the buff wheel. A timed cycle controls dwell and retraction. Only one fixture is required for each machine for each type of part finished. Because the machine supports the part, operator fatigue is minimized. Various types of rotation also can be performed, depending on the type of semiautomatic machine selected.

Production of semiautomatic buffing machines depends on part configuration and the degree of finishing required. By using a double-end jack with two semiautomatics, an operator can load one machine while the other is finishing a part. This can double production without increasing labor costs.

Fully Automatic Machines

Fully automatic machines are used in high-volume applications and where multiple surfaces of a workpiece must be finished. The two most common types of automatic buffing machines are rotary automatic and straight-line machines.

Rotary Automatic Machines

Rotary machines have round tables with finishing heads located around the periphery of the table. This type of machine is typically used to finish simple, round parts requiring high production. The number of finishing heads and production determine the size of the rotary.

The table of the rotary machine can move continuously or index to start, stop, dwell, and then start again, with the length of the dwell controlled by a timer. The configuration and area of the product to be finished determine which is best. Production is higher on a continuous rotary machine because the table does not

stop rotating. On an indexing rotary machine, because of the stop, dwell, and start cycle, production is lower. Parts that have surfaces that are difficult to reach and require more dwell time in certain areas may be finished on an indexing rotary machine to obtain the dwell time necessary. On each table there are rotating spindles on which the parts are fixtured for the finishing sequence. Rotary tables may have a greater number of fixtures than indexing tables, since the production and simple configuration make it more appropriate to be run on a continuous machine due to the ease of reaching all surfaces.

Straight Line Machines

There are various types of straight-line automatic finishing machines. Normally, linear workpieces are finished on straight-line machines. Straight-line machines also can be used to finish round parts if extremely high production is required. There is less limitation on workpiece size as with rotary equipment.

With straight-line automatic machines, finishing heads can be placed on both sides of the machine. In addition, various heads can be incorporated into the system for buffing and polishing. With rotary equipment, the outside periphery of a rotary table is used.

Various types of straight line machines include:

Horizontal return straight line
Narrow universal straight line
Over and under universal straight line
Reciprocating straight line
Open-center universal

The size or length of these straight-line machines can be designed and built to accommodate the desired end result; floor space is the only major limitation. Each machine normally requires only one operator for load/unload. All operations of these machines are controlled from a push-button panel located near the operator for starting, stopping, and controlling various functions.

COMPUTER NUMERICAL CONTROL BUFFING MACHINES

Buffing machine manufacturers can build equipment offering the same levels of control and flexibility available from computer numerical control (CNC) metal-cutting machines. Separate CNC workcells can be designed to combine buffing with deburring operations within a given and limited series of process steps. It also is possible to integrate a complete sequence of manufacturing operations through a universal, plant-wide parts handling system to combine fabricating, machining, deburring, polishing, buffing, painting, plating, and packaging. Such systems have a significant impact on material handling costs, daily in-process inventory levels, direct labor costs, plant floor space requirements, safety, and overall productivity.

CNC buffing systems offer a number of significant advantages. Equipment is programmed on the shop floor for reduced setup time. Buffing cycles can be reprogrammed to accommodate changing production requirements. Production data are automatically collected to support statistical process control requirements. Most important, quality is improved because part-to-part tolerances are consistent and repeatable.

WORKPIECE HANDLING

Significant advancements have been made in materials handling technology as it relates to buffing. A broad range of application-specific options is offered. These include pick-and-place workpiece load/unload systems, "blue steel" roller conveyor systems, lift-and-carry and shuttle-type in-line part transfer systems, trunnion-

type transfer tables, power-and-free conveyor systems, robotic worktables, and automated guided vehicles for transferring parts between machines.

SUPPORTING TECHNOLOGY

Buffing systems are increasingly becoming turnkey, integrated installations. In addition to the basic machine, equipment builders can offer a variety of supporting systems to ensure increased performance and improved quality.

Electronic options, beyond programmable controllers and computer numerical control systems, include the use of load torque controls, sensors, proximity switches, encoders, digital read-out devices, laser gauging, and LED programmable counters. Other supporting systems include quick-change and modular wheel assemblies, automatic tool compensation, automatic buffing compound application systems, dust collection systems, and automatic workpiece shuttle and load/unload systems.

SUMMARY

Effective buffing is accomplished through the proper selection of buffing compound, the buff wheel, and the buffing machine. In most instances, it is recommended that prototype or test parts be processed under production conditions to establish process parameters and prove production rates and quality.

IMPACT BLASTING WITH GLASS BEADS

BY ROBERT C. MULHALL AND NICHOLAS D. NEDAS
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Glass beads were originally used for decorative applications. Their use as a medium in impact blasting came about largely as a result of the aerospace buildup of the 1950s. At that time, a need developed for multipurpose media that combined the advantages of coarse, organic, metallic, and fine angular abrasives. Table I shows a comparison of glass beads with other impact abrasives for cleaning, finishing, peening, and deburring applications.

Impact blasting with glass beads is well placed to satisfy demands of the 1990s for an energy-efficient and environmentally acceptable method of metal finishing. When properly controlled, the system is safe for workers and spent media presents no disposal problems.

PROCESS BENEFITS

Glass beads are virtually chemically inert. This factor, combined with their spherical shape, provides several key benefits. Media consumption is minimized; Table II compares consumption data of impacting media on different metal surfaces of varying hardnesses. On both metals tested, glass beads offer the lowest consumption per cycle. In addition, close tolerances are maintained and glass beads remove a minimal (if any) amount of surface metal.

Impacted surfaces are free of smears, contaminants, and media embedments; high points are blended and pores sealed. A wide range of finishes from matte to bright satin are achievable. The peening action of the media further acts to impart a layer of compressive stresses on the surface of the part. This increases fatigue life, decreases susceptibility of the part to stress corrosion, and enhances surface strength.

PROCESS ENGINEERING

Proper design of impact blasting equipment is essential for each application to achieve the full benefits of high productivity and low costs. Most important, the system should be easily controllable to produce consistent results.

Key to this control is determination and maintenance of the "arc height peening intensity" of the operation. To measure the peening intensity in a particular application, special steel strips are bombarded on one side only by the blasting media. The compressive stress induced by the peening action causes the strip to bow in the direction of the blast. A series of values of arc height versus blasting time are obtained, and when plotted on a graph, yield a saturation curve. From this curve, the arc height peening intensity can be obtained.

Environmental factors, operator skill, OSHA standards, and equipment capabilities are the process parameters involved in all glass bead blasting operations—whether they are cleaning, finishing, peening, or deburring. Once all the variables are optimized and the arc height peening intensity determined, process

Table I. Impact Media Comparison Chart

	Glass Beads	Coarse Abrasives (e.g., sand)	Metallic Abrasives (e.g., steel and iron shot/grit)	Fine Angular Abrasives (e.g., aluminum oxide)	Organic Abrasives (e.g., walnut shells)
Applications:	Cleaning, finishing peening—light-medium and deburring	General cleaning where metal removal and surface contamination are not considered	Rough general cleaning and high intensity peening	Cleaning where smooth finish and surface contamination are not important	Light deburring and cleaning of fragile items
Physical Properties:					
Shape	Spherical	Granular	Spherical/irregular	Angular	Irregular
Color	Clear	Tan	Gray	Brown/white	Brown/tan
Specific gravity	2.45-2.50	2.4-2.7	7.6-7.8	2.4-4.0	1.3-1.4
Free silica content, %	None	100	None	<1	None
Free iron content, %	<1	<1	95-100	<1	None
Hardness (Moh)	5.5	7.5	7.5	9.0	1.0
Media Comparisons:					
Toxicity	None	High	None	Low	Low/none
Metal removal	Low/none	High	High/medium	High	None
Cleaning rate	High	Fast	Medium/high	Fast	Slow
Peening ability	High	None	High	None	None
Finish achieved	Range (various matte)	Rough anchor	Peened (shot): rough anchor (grit)	Various matte	Smooth
Surface contamination	None	High	High/medium	High	Medium/high
Suitability for wet blasting	High	Low	Low	Low	Low
Suitability for dry blasting	High	High	High	High	High
Size ranges available	20-325 U.S. mesh	8-200 U.S. mesh	6-200 U.S. mesh	80-325 U.S. mesh	60-325 U.S. mesh
Consumption rate	Low	High	Low	High	High
Cost comparison	Medium	Low	High	High/medium	Medium/low

Table II. Consumption Studies of Various Impacting Media Direct Pressure Dry Blasting System

Blasting Material	Target Material	Hardness, Rockwell	Average Consumption per Cycle (%)
Glass beads (106-153 µm)	Al 2024	75 B	2.1
	Al 2024	75 B	
	CRS	30 C	3.5
	CRS	30 C	
Aluminum oxide (180 grit)	Al 2024	75 B	6.0
	Al 2024	75 B	
	CRS	30 C	6.7
	CRS	30 C	
Soda-lime silicate ground glass (125 µm and finer)	Al 2024	75 B	10.6
	Al 2024	75 B	
	CRS	30 C	12.9
	CRS	30 C	
Borosilicate ground glass (125 µm and finer)	Al 2024	75 B	11.4
	Al 2024	75 B	
	CRS	30 C	13.9
	CRS	30 C	

CRS = cold-rolled steel
$^{3}/16$-in. I.D. nozzle; $^{1}/8$>-in. I.D. grit stem; 90° target angle; 6-in. target distance; 0.006 Npeening intensity; and 25 psi blasting pressure.

control is achieved by maintaining that arc height peening intensity. Any change indicates some modification in the system operation, away from optimum performance.

System control via arc height peening intensity is applicable to all cleaning, finishing, peening, and deburring operations. In cleaning, the arc height technique can be used to maintain process speed. In finishing, profilometer measurements of root mean square (rms) microinch finish can be correlated to peening intensity, thereby eliminating any subjective evaluation of performance. In peening, the degree of compressive stress induced is directly related to the arc height peening intensity. By such control, significant benefits are achieved in terms of labor productivity, reduced supervision requirements, and decline in the number of rejected parts.

As indicated in Table I, both steel shot and glass beads are available for peening applications. Steel shot with its heavier density offers a

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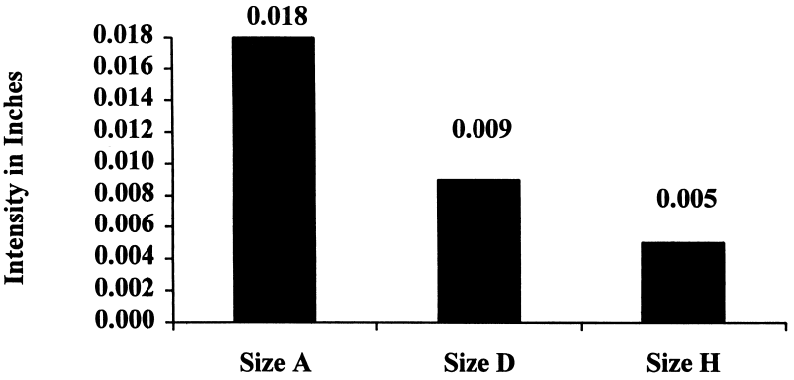


Fig. 1. Typical peening intensities achieved with solid glass beads using suction-type equipment with 1/2-in. diameter nozzle at 90o for A and H, and 85o for D.

deeper depth of compression, but requires more energy to propel while leaving dissimilar metallic smears (i.e., various forms of contamination) on the part's surface. Glass beads are often used as a secondary peening medium, removing contamination while improving surface texture and finish (lower rms) of the part.

Glass beads are also used extensively as a peening medium, achieving a wide range of arc height peening intensities in a variety of applications and industries (see Fig. 1).

Typical glass bead peening applications take place before plating and after grinding and welding on aerospace, automotive, and machine tool components.

KEY FACTORS IN USE OF GLASS BEADS

There are a few key considerations that will help the user to enjoy the benefits of glass bead impact media to the fullest.

Whether for cleaning, finishing, peening, or deburring, the work actually done depends upon the amount or weight of abrasive thrown against the target surface in a given time. It also depends upon the speed with which the material is thrown against the target. The formula:

$$I = MV^2/2$$

indicates that impact energy (I) equals one half the mass or weight (M) times the square of the velocity (V) at a 90° nozzle angle. Correction factors should be used for other angles.

As a general rule, the smallest particle that will provide the desired effect on the surface is the most efficient one to use, as this gives the greatest number of impacts per pound of glass spheres.

When the nozzle is at a 90° angle to the surface being treated, the bounceback of beads has a "blinding" effect. This interferes with the effectiveness of the blast stream and tends to increase the rate of bead consumption through breakage. Generally, an angle between 45 and 60° will give the most effective performance. In some cleaning applications, still lower angles may help speed the

work.

The work energy of the flying particles is also affected by the distance from the nozzle to the work surface. It is usually best to keep this between 4 and 8 in. to avoid loss of velocity, and to gain maximum acceleration and proper diffusion of particles into the most desirable pattern.

BEAD CONSUMPTION

Because beads can become broken after repeated impacts on the work surface, controlling bead consumption is of critical importance. It is affected by five key factors:

1. Bead size—the larger the bead, the more durable and resistant to breakage it is at a given impact intensity. This preference for larger beads must be balanced against the greater efficiency of smaller size beads, which are capable of the work required.
2. Uniformity of size—proper sizing also affects efficiency of operations. The wider the range of bead sizes in a particular "charge," the higher the rate of consumption at given conditions.
3. Roundness or sphericity of beads—the more spherical the individual beads, and the freer the "charge" from nonspherical particles, the lower the rate of bead consumption.
4. Surface hardness of material being treated—the harder the surface being treated, the higher the rate of bead consumption.
5. Angle of impingement—the closer to 90o the stream of beads is to the work surface at a given arc height peening intensity, the greater the rate of bead consumption.

APPLICATION NOTES

Cleaning

Because of the wide variety of different materials that must be removed in cleaning operations—including mill scale, rust, carbon buildup, and the like—it is often best to experiment with different nozzle angles to find which works most efficiently. Where there are internal recesses and other difficult areas, the use of the smaller bead sizes may be particularly helpful. Because a high cleaning speed usually minimizes labor cost, bead size and nozzle angle are the key considerations. Normally, a velocity that optimizes cleaning speed with a given size of bead will optimize consumption, to give the lowest total cost.

Finishing

Where appearance is of prime importance, bead size is normally the key consideration. Velocity, nozzle angle, and other factors should be adjusted, first to give maximum finishing speed, and second, to minimize consumption. This will provide the lowest total labor and material cost per unit of production. As a general rule, large beads at high intensities provide a deep matte; at low intensities large beads give a smooth, bright surface; small beads at high intensity give a dull matte, and at low intensities a bright satin. Selective masking of surfaces, the use of multiple nozzles, and a "painting" motion may be employed for highly spe-

cialized decorative effects. Automated machines are generally used for finishing.

Peening

Peening to increase fatigue resistance or to increase stress corrosion resistance is essentially a uniform "hammering" operation. Uniformity of bead size and control of the number of nonround and angular particles included is critical to process performance. The key consideration is impact intensity, which must be specified as minimum and maximum. Nozzle angles should be as close to a right angle as possible without excess bead consumption. In general, the larger bead sizes, because of their resistance to breakdown, will prove most cost effective. In peening fillet areas, it is a standard rule that beads no larger than one half the radius should be used.

Deburring

The key considerations in deburring are usually a combination of programming surface finish, while achieving sufficient impact intensity to remove or depress the burr. Bead size, which governs finish, must be adjusted to an adequate peening intensity with velocity. Proper nozzle angle will optimize consumption.

METAL CLEANING

BY ROBERT FARRELL AND EDMUND HORNER
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Simply stated, the function performed in metal cleaning is removal of material, collected in the previous operations, from the metal's surface to prepare it for subsequent operations.

Cleaning metals involves not only the selection of the type(s) of cleaners, but also the proper cleaning cycle and process equipment necessary to generate acceptable parts at a given rate (parts/hour).

An equation for such a cleaning operation may be illustrated as follows:

Process Equipment + Process Cycle + Cleaner(s) = Acceptable Parts/Hour

Each of the terms in the equation shares the burden in providing acceptable parts at a given rate for an economical operation. The equation also notes that in certain operations more than one cleaner may be required, as per a line for electroplating.

Process equipment is the equipment selected—rack line, barrel line, spiral washer, ultrasonic, etc.

SOILS

Soils are the materials left on the metal's surface from the previous operation(s) or the surface condition of incoming metal stock. Examples of the variety of soils that are encountered in metal cleaning are listed below. There may be instances where more than one soil is present on the part.

Rust	Scale (weld or heat)
Tarnish	Oxides that inhibit subsequent finishing
Smuts	Carbonaceous soils
Drawing compounds	Machining oils
Stamping oils	Spinning lubricants
Fingerprints	Buffing compounds
Polishing compounds	Metallic compounds
Glove prints	Corrosion-preventive compounds
Fluxes from brazing operations	Phosphate coatings impregnated with forming lubes
Corrosion products	Stenciling inks
Burnishing-compound residues	Brightener residues left on the surface from previous plating steps

General shop soils that accumulate during storage

These soils may generally be divided into three categories:

Organic soils are typically the lubricants used in metal forming, rolling, and machining operations. The lubricants may be based upon petroleum or synthetics (water-soluble) formulations. Soaps, lard oils, and wax bases are also encountered.

Inorganic soils include rust, heat and weld scale, smuts, and oxides (tarnish).

Miscellaneous soils include shop dirts, glove prints from handling the parts, fluxes from brazing operations, and burned-on soils from quenching operations.

As a rule soil removal is not a simple reaction, e.g., lard oil reacts with caustic soda to form a soap. The reactions can be somewhat more complex.

An important concern, which adds to the cleaning problem, is the age of the

soil. Soils that are allowed to age on the metal surface for an extended time become increasingly difficult to remove. A classic example is aged buffing compounds on zinc die castings. It is important, therefore, to clean parts soon after they arrive from their last operation.

PROPRIETARY CLEANERS

To begin with the concept of one cleaner for all soils and all metals does not exist, although chlorinated solvents have come close to achieving that honor.

Proprietary cleaners fall into the following groups: alkaline (mild to strong); neutral (pH 7.0); acidic (mild to strong); emulsion; and solvent. The physical forms of cleaners on the market may be powder, liquid, or gel.

In the development of a cleaner not only are the soils a consideration but also the base metal to be cleaned. As a rule the cleaner's function is to remove the soil and not have any detrimental effect on the metal's surface. For example, a product containing caustic soda would be satisfactory for cleaning ferrous metals but not for cleaning aluminum alloys, zinc die castings, galvanized stock, or yellow brass. Such a product would attack these nonferrous surfaces. The proper selection of a cleaner for the metal substrate to be cleaned is thus paramount.

The bulk of the proprietary cleaners used in industry fall into the alkaline group. Many solvent cleaners are being phased out because of environmental considerations and other hazards. Acid cleaners generally are used for cleaning stainless steel alloys, wrought aluminum alloys, copper, and brass alloys.

Proprietary alkaline soak and spray cleaners are generally formulated to clean a variety of metal-forming lubricants from a metal's surface, and may also find application for cleaning a variety of metals, i.e., ferrous metals, aluminum alloys, brass, and magnesium alloys.

Within the last three years the development of a new cleaner formulation has become further complicated by environmental restrictions imposed by federal and local regulations and by corporations themselves. For example, a specific requirement given for a spray cleaner was that the product must be safe on most metals within the specific allowed cleaning time, but must also be free of phosphates, silicates, chelators, and nitrites; have a low COD/BOD; and have an operating pH between 8 and 9.

If, for example, some of the restrictions encountered when formulating a cleaner were applied, it would have to have the following characteristics:

Chromate free	Noncyanide
Phosphate free	Noncaustic
Silicate free	Solvent free
Fluoride free	No foam products
Chelator free	High flash point solvents
Nitrite free	Powders or liquids
Amine free	Low BOD
Low COD	Emulsifier free
Borate free	pH of 7.0-9.0

Some of the reasons for these restrictions are self-evident such as cyanide free, solvent free, chelator free, and phosphate free.

From the collection of restrictions given one may readily note that the products of the future must be not only safe to the environment, but also relatively safe to use in the work area, and provide a cleaner that will allow the separation of the

soil from the cleaning solution.

PROCESS ALTERNATIVES

The method or combination of methods selected to clean parts is critical and will depend upon the type of final finish (plated, painted, anodized, etc.) and whether it is an in-process cleaning operation, or just a final cleaning. And, of course, the other paramount factor to be considered is the volume of work processed per hour.

The cleaning methods given may be used independently or in conjunction with one another, as in a preplate cleaning cycle, where three to four modes of cleaning are used.

Immersion (Rack or Barrel)

Rack immersion may utilize air agitation or work agitation to improve or shorten the cleaning time. In barrel lines the movement of the barrel will provide the necessary agitation to flush cleaner solution through the parts.

Power, Spray Cleaning

Spray washers (spiral spray, belt washer, spray strip line, cabinet, and monorail-type washer) provide reduced cleaning time by utilizing impingement to clean parts that may not respond to conventional soak cleaning. Spray pressures may range from 14 to 200 psi, depending upon the type of machine used. Some continuous strip spray washers may also utilize rotating brushes along with the spray cleaning solution.

Ultrasonic Cleaning

Ultrasonic energy is utilized in conjunction with aqueous cleaners or hydrocar-



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Table I. Current Density Ranges for Electrocleaning

Substrate	Current Density (A/ft2)
Ferrous metals	40-150
Copper metal and plate	25-50
Brass alloys	15-40
Zinc die castings	10-30
Nickel plate	20-30
Lead, lead alloys, and pewter	10-30

bon chlorinated solvents to clean parts. Areas of application are small precision parts, parts with complex configurations, removal of tightly adhering or embedded particles from parts, or cleaning parts for hermetically sealed units. One of the key factors in a successful ultrasonic cleaning operation, besides selecting the proper cleaner, is proper racking.

Alkaline Electrocleaning

Alkaline electrocleaners should not be used as the initial cleaner to remove the bulk of soils such as drawing compounds, stamping oils, buffing compounds, machining oils, heavy rust, and weld scales. This function should be reserved for an alkaline soak cleaner, emulsion cleaner, spray cleaner, acids or combinations thereof, which precede the electrocleaner. The electrocleaner is the last alkaline cleaning process performed on the metal surface prior to electroplating. At the point entering the electrocleaner the only soils present should consist of smuts (carbon or iron oxides), light flash rust, light oxides, and residues of soils and cleaners left on the metal surface from the prior cleaning operations.

Alkaline electrocleaning, prior to electroplating, is one of the most reliable cleaning methods available. The cleaning action not only depends upon the cleaner formulation but also utilizes the liberation of oxygen or hydrogen (depending on polarity) formed during electrolysis to scrub residues from the surface.

Of the three electrocleaning methods anodic cleaning is most frequently used, especially for steels and brass and zinc die castings.

Periodic reverse cleaning is usually confined to cleaning ferrous metals, which have as their soils heat scales (weld scale), rust, and smuts.

Cathodic cleaning must be used when electrocleaning nickel, nickel alloys, pewter, lead and lead alloys, and stainless steels.

Maintaining the proper current density, besides operating concentrations and temperature, is a paramount factor that must be maintained in order to obtain the desired results. Each metal is electrocleaned using a different current density range. The ranges for the particular metals are given in Table I.

Cathodic Pickling

Cathodic electrolytic pickling in an electroplating line is usually confined to the pickling of ferrous metals and activation of nickel-plated surfaces. Electrolytic pickling is another form of electrocleaning, but on the acid side.

The principal functions of an acid solution in an electroplating cycle are removal of rust, scale, tarnish, light oxides, metal slivers, and in some cases, smut. Electrolytic pickling is usually restricted to difficult tasks where the soils are quite heavy or where the allotted pickling time is short. The pickling action, in an electrolytic process, is assisted by the evolution of hydrogen or oxygen on

the work. These gases aid in prying off scale during pickling. Electrolytic pickling's advantages over chemical pickling can be stated as follows:

1. Pickling time is reduced.
2. The rate of pickling is affected to a lesser extent by changes in the acid concentration and by the iron salt accumulation in the solution.
3. Ferrous metals, including alloy steels, can be pickled much more readily than by a conventional acid pickle.

The acids used as an electrolytic pickle could be sulfuric acid, with or without fluoride additions, or proprietary acids (dry acid salts or liquid).

In cathodic pickling the work is made the cathode, and during pickling hydrogen is evolved on the work surface. Cathodic pickling would be selected when any of the following conditions are present:

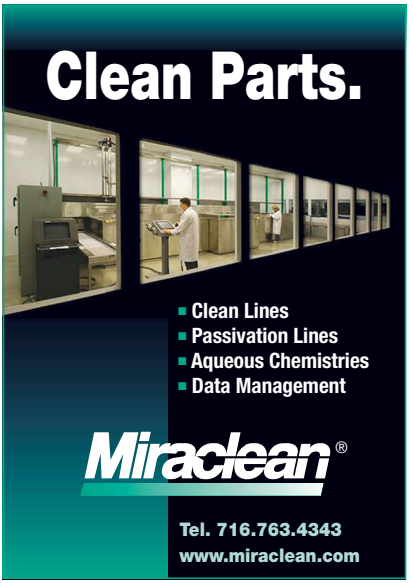
1. Dimensionally accurate fabrication or machine parts.
2. Highly finished steel (#3 finish).
3. Fabrications having deep recesses.
4. Soils consisting of light oxides or smut.
5. Activating metals.

In any pickling operation there is always the problem of hydrogen embrittlement, and in cathodic pickling this danger is increased because of the evolution of hydrogen on the work surface. Usually the pickling time is rather short—30 sec to 1 min—thus the embrittlement factor is minimized.

Anodic Pickling

In anodic pickling oxygen is evolved on the metal surface. The oxygen formed on the work surface merely performs a scrubbing action in that it aids in loosening and removing the scale, rust, and smut. Consequently, all of the pickling action is accomplished by the acid solution. The advantage of anodic pickling over cathodic is that removal of heavy layers of scale and rust may be accomplished.

Anodic pickling does a better job in removing scales, rust, and embedded soils by attacking the base metal. In this type of pickling one must expect some metal loss and, in some cases, pitting of the surface. This loss of metal may be reduced or stopped with the use of 70% by volume sulfuric acid. The problem associated with using 70% by volume sulfuric acid is the danger of smut formation. This would be prevalent in high carbon steels.



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MECHANISMS OF CLEANING

The removal of objectionable contaminants from metallic surfaces can be accomplished by mechanical processes, chemical processes, or a combination of both.

Mechanical Processes

1. The physical removal of surface layers by means of aggressive mechanical action.

   Shot blasting with glass, aluminum oxide, sand, or dry ice (CO_2) pellets.
   Mass finishing via vibratory mill or part-on-part burnishing.
   Grinding.
   Abrasive pad buffing.

2. The physical removal of surface contaminants with minimal base metal removal.

   Gas scrubbing by electrocleaning, cathodically, anodically, or periodic reverse.
   Impingement by high- or low-pressure spray.
   Turbulence, such as that supplied by slosh washers or turbo washers, in which cleaning solution is turbulently flowed over the surfaces to be cleaned.
   Cavitation supplied by ultrasonics.
   Abrasive brushing in solution.
   Abrasive slurry.
   Chemical Processes

Solubilization is the cleaning method in which surface contaminants become soluble in the cleaning solution. Examples are the dissolution of iron oxide in acids or acrylic coatings in alkaline aqueous solutions.

Emulsification is the process by which a normally insoluble soil becomes uniformly dispersed in an incompatible solvent. The most common emulsion encountered by people is milk, in which insoluble fats and proteins are dispersed in water. Emulsification is accomplished by a combination of proper surfactants, cosolvents, and coupling agents.

Saponification is the reaction of oils containing reactive fatty acids with alkali to yield soluble soaps. An example of this mechanism would be the cleaning of a lard oil lubricant from stamped steel by the use of an aqueous cleaning solution containing significant amounts of sodium or potassium hydroxide.

Wetting is the method by which a soil is displaced from the substrate surface by the use of wetting agents that have a greater affinity for the substrate surface than for the soils present. The wetting agent can work by having the same action on the soil particles present. In both cases the attraction between soil and substrate surface is eliminated and soils are removed.

Complexing is accomplished by the use of chelators, sequesterants, or complexors. The soils—typically metal soaps or lubricants—form soluble complexes with those agents and are thereby removed from the substrate. Complexors also function to prevent redeposition of insoluble or suspended soils on the substrate surface, particularly in hard water locations. Examples of complexors are organic acids and their salts, polyphosphates, and zeolites.

Defloculation is the process by which soils are broken down into finely divided particles that become suspended in the cleaning solution. Defloculation is normally accomplished in combination with mechanical action.

Other Processes

The surface cleaning of metallic substrates can be accomplished by use of heat and

high vacuum to volatilize soils and oxides.

TESTS FOR CLEANLINESS

The degree of cleaning required for the surface of a part is a function of, and dictated by, operations to follow cleaning. The cleanliness of a part can be described as a function of the removal of a specific surface contaminant such as oil and grease, oxides, or particulate matter.

Test methods used to determine the cleanliness of a surface range from crude to highly sophisticated. A summary of several tests follows.

Water Break Test

The water break test involves examination of a surface for the presence of a continuous water film that has "no water breaks." If a water-break-free film of water is present it is indicative of the absence of hydrophobic surface contaminants. Oils, greases, and water-insoluble organic compounds would be examples of hydrophobic contaminants. The water break test does not confirm the presence or absence of hydrophilic particulate contaminants or oxides.

White Glove Test

The white glove test is used to show the presence of particulate and, to a certain extent, organic contaminants on a surface after cleaning. The part may be tested while still wet from rinsing or after drying. The surface of the part to be tested is wiped with a white glove, cotton swab, or lens tissue. The material used to wipe the surface is then examined for the presence of black, gray, or off-white residue or oil staining. If contaminants are found to be present, microscopic examination or advanced chemical or surface analysis can be performed on the part surface or the item used to wipe the surface to determine the nature of the contaminants.

Other Methods

Sophisticated physical and chemical analytical methods can be applied to test for residual contaminants on surfaces that have been cleaned. Samples of parts that have been cleaned and dried can be immersed in a turbulent solution of a solvent. The solvent can then be analyzed for organic contaminants and insoluble particulate matter. The amount of contaminant found in the solvent is indicative of the degree of ceaning.

Surfaces of parts that have been cleaned can be subjected to special analysis to determine the presence of oxides, organics, and particulate contaminants. Specifications can be written for the allowable presence and concentrations of contaminants in critical cleaning operations.

Analytical techniques such as infrared microprofiling (developed by Sandia National Laboratories), X-ray photoelectron spectroscopy (Oak Ridge National Laboratory), and light reflective technology (Dow Chemical Inc.) have been used to analyze for residual contaminants in critical cleaning operations.

If soils are doped with compounds that exhibit fluorescence exposure of cleaned parts to ultraviolet light will confirm the presence or absence of residual soils.

Tests based on surface tension have been used to determine the cleanliness of surfaces. Care must be taken to ensure the use of test solutions specific to the substrate surface.

SAFETY

Unfortunately, one of the most overlooked aspects of industrial cleaning is safety.

The use of chemicals for industrial cleaning exposes the user to potential injury if proper safeguards are not employed. The potential problems are well documented in Material Safety Data Sheets, books, and articles that have been written over the years. The warnings are of little value unless they are read, understood, and acted upon by those handling, using, or working in areas in which the chemicals are used.

A summary of the safety aspects of chemical cleaning are as follows.

Acids

The use of acidic cleaners containing appreciable amounts of sulfuric acid can expose the worker to potential splashing due to exothermic reactions that can result in localized boiling. Additions should be made in a slow, controlled manner to prevent splashing and localized boiling. Acids should be added to water. Water should not be added to concentrated acids.

Addition of acid cleaner concentrates to replenish working solutions should always be made to cool solutions (<100oF). Without exception, acid-resistant goggles, face shield, boots, apron, and gloves should be worn by workers to minimize the potential for body contact with the acidic solutions.

Acid cleaners containing fluoride compounds can result in severe tissue damage. Precautions should be taken to avoid any contact with fluoride-containing solutions. If fluoride compounds are used, personnel should be trained in the treatment of fluoride burns.

The use of acid cleaning compounds can result in the evolution of flammable and explosive hydrogen gas. Care should be taken to avoid uncontrolled release of pressure when parts are cleaned in sealed cleaning chambers. Sources of spark or flame that can ignite accumulated hydrogen should be identified and removed from the area in which acid cleaning is conducted.

The use of acidic cleaners for cleaning sulfurized steel or parts that have sulfurized oil present can result in the generation of poisonous and flammable hydrogen sulfide gas. The same precautions employed for dealing with hydrogen evolution should also be employed for the potential evolution of hydrogen sulfide.

Acid cleaner tanks and equipment should be properly vented to keep worker exposure to mists and vapors below OSHA limits. The reactivity of substrate material should be evaluated prior to acid cleaning to prevent violent reaction due to incompatibility and/or part damage.

Alkaline Cleaners

The use of alkaline cleaners containing strong alkaline compounds, such as sodium hydroxide and potassium hydroxide, can result in strong exothermic reactions when working solutions are made or replenished. Additions should be made to water or working solutions in a cautious, controlled fashion to prevent splashing and localized boiling. Additions should only be made to cool solutions (<100oF). Water should not be added to alkaline powders.

The use of alkaline cleaners for etching or cleaning reactive metals, such as aluminum, zinc, or magnesium, will result in the evolution of flammable hydrogen gas that can accumulate in foam blankets or in enclosed cleaning equipment. Equipment should be ventilated and ignition sources should be removed from areas in which reactive metals are cleaned.

The use of alkaline electrocleaners will result in the evolution of hydrogen and oxygen. Tanks should be well vented to remove these gases. Foam blankets on electrocleaners should be sufficient to prevent misting without excessive accumulation of hydrogen and oxygen. Disconnect current prior to removing work from electrocleaning tanks to prevent hydrogen explosions. Personnel using, handling, or working in areas where exposure to alkaline cleaners is possible must wear alkaline-resistant personal protection consisting of safety goggles, face shield, gloves, apron, and boots. Respiratory protection should be worn when dust or mist is a problem.

Neutral Cleaners

Although the destructive effect of neutral cleaners on body tissues may be minimal, in many cases these cleaners are used hot and the possibility of thermal burns from splashing may exist. Additions to working solutions should be made slowly and cautiously in a controlled manner to prevent splashing. Additions should only be made to cool solutions (<100oF).

Equipment

A preventive maintenance schedule should be implemented for the inspection and repair of defective cleaning equipment. Hoist systems, exhaust systems, heating systems, and tank systems should be inspected on a routine basis for proper function and equipment integrity. Worn, corroded, or damaged equipment should be repaired or replaced upon discovery.

General

1. Never work alone when working with chemicals.
2. Read and understand Material Safety Data Sheets, technical bulletins, and drum labels for the materials you handle and work with.
3. Always wear the personal protective equipment specified in the Material Safety Data Sheets, technical bulletins, or drum labels.
4. If you are injured notify the appropriate personnel and get medical attention as soon as possible.
5. If a spill occurs notify the individuals in your facility who are properly trained to respond to chemical spills.

ELECTROCLEANING

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Electrocleaning is a cleaning process used in metal surface preparation, usually in preplate cycles. It is essentially characterized by the use of DC current and a specially formulated electrolyte. The work being processed may be used as anodes or cathodes, or both, depending on the application and basis material being processed. Although electrocleaning is a different and distinct method of surface cleaning, it should be considered in the context of the complete surface preparation or preplate cycle. A general cycle might include: (1) soak clean, (2) rinse, (3) electroclean, (4) rinse, (5) acid activate, (6) rinse, (7) repeat steps 3 to 6 (optional), and (8) plate.

Electrocleaners as described herein are alkaline and will generally follow alkaline soak cleaners and precede acid activation in the preplate cycle. The basic function of electrocleaners is to remove soils from the surface that could not be removed by simple immersion soak or degreasing steps. Examples of such soils are as follows:

- Adherent residues not removed in the preceding soak cleaner. Such residues include oil, fingerprints, drawing compounds, and soils driven into surface porosity or applied under pressure. These soils are generally not removed by conventional emulsification, wetting, and displacement soak cleaners.
- Finely divided particles, such as polishing compound abrasives, metallic fines from grinding or metalworking operations, carbon, and other alloying elements, may also be found on the surface. Often this fine particulate matter, generally referred to as smut, may be held to the surface by simple mechanical forces, electrostatically, or in a thin oil or grease matrix.
- Metal oxidation products, the result of exposure to the atmosphere, or a thermal process such as heat treatment, forging, welding, etc.

As explained earlier, electrocleaning must be viewed as part of the overall surface preparation process. Although an electrocleaner step may not totally remove a particular type of soil, it conditions or modifies that soil for easier removal in the subsequent steps in the cycle. For instance, an adherent oil residue may be loosened enough to be lifted in the following rinse tank. Surface oxides may be reduced or oxidized to a more soluble form to be easily dissolved in the subsequent acid tank.

ELECTROLYSIS OF ELECTROCLEANERS

As current is applied to an electrocleaner, the following electrochemical reactions take place, essentially electrolyzing the water component of the electrolyte. The alkalies serve as the conductive medium.

At the anode:

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$$

At the cathode:

$$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$$

During electrolysis, twice as much hydrogen is liberated at the cathode than is oxygen at the anode.

TYPES OF ELECTROCLEANERS

Electrocleaners are classified on the basis of two main criteria: (1) polarity of the work in the tank; and (2) the type of substrate being treated.

There are three types of electrocleaning modes as defined by polarity of the work in process and the applicability of each to a given substrate.

Anodic Electrocleaning

The work is connected to the anode side of the rectifier and is positively charged. The process is also known as reverse electrocleaning, since the polarity is opposite that of plating. As described under electrolysis, oxygen is liberated at the surface of the work (the anode) when current is applied. As the gas rises to the top, it creates a mechanical scrubbing action that loosens and lifts the soils.

Two other phenomena also take place. As oxygen bubbles are formed on the surface, they coalesce and grow before they rise in continuous layers. It is believed that the static charge holding fine particles to the surface is released through the layer of bubbles, facilitating their removal through the scrubbing action.

Chemical effects, oxidation, and drop in pH also take place at the anode surface. If excessive, the effect of oxidation can be seen, for instance, on brass, zinc, and silver as they discolor, stain, or etch. Special inhibited anodic electrocleaners are available for brass and zinc.

When nickel is anodically electrocleaned it will quickly become passive and prevent further plating unless reactivated. A similar effect is experienced with stainless steels. Regular steels are not adversely affected by the process, whereas high-carbon steels are more sensitive and require moderation in electrocleaning. Alloys of lead, nickel–silver, and silver plate are attacked or tarnished by anodic electrocleaning.

As oxygen is liberated at the anode, the net pH value tends to decrease at the interface. This effect can be noticed on steel if an electrocleaner's alkalinity is too low by design or for lack of bath maintenance. The steel is more rapidly oxidized, and precipitated iron hydroxide forms on the surface. Parts exiting the tank will have a rusty or etched appearance, especially in high current density areas. The situation can be readily rectified by increasing the alkalinity of the bath or by reducing the current density below normal operating levels until the bath chemistry is adjusted.

Cathodic Electrocleaning

The work is connected to the cathode side of the rectifier and is negatively charged. This is also known as direct electrocleaning. In this case, hydrogen is liberated at the cathode. As seen from the net amount of electrolysis, twice as much hydrogen than oxygen is generated at the cathode. Consequently, more scrubbing action and cleaning ability are expected. The use of cathodic electrocleaning, however, has not found a widespread use in the industry as the main electrocleaning mode for two reasons: (1) the concern with hydrogen embrittlement as a result of copious hydrogen release at the surface, and (2) the risk of plate out of charged impurities from the solutions on the cathodic surface. The latter may not be noticeable to the casual observer as the parts exit the tank, but it leads to poor

Table I. Recommended Electrocleaning Current Densities—Rack Applications[a]

	A/dm²	*Polarity*
Steel, low carbon	5–10	A, C
Steel, high strength	3–5	A
Stainless steel	5–8	C
Copper	5–8	A, C
Brass	2–4	A, C (anodic inhibited)
Zinc diecast	2–4	A, C (anodic inhibited)
Nickel and alloys	2–3	C
Lead and alloys	5–8	C
Silver and alloys	2–3	C

[a]In barrel applications, a fraction of the above current density values should be expected.

adhesion on plating. Contaminants leading to such adhesion failures are metallic fines, certain types of surfactants, colloids, metallic soaps, and hexavalent chromium dragged into the cleaner.

Cathodic cleaners, when kept clean and well maintained, are used for processing buffed brass, zinc, and white metal without tarnishing, and for electrocleaning nickel and high nickel steels without risking passivation. When cathodic electrocleaners are used on steel and copper to take advantage of their superior scrub-clean action, a secondary anodic electrocleaner should follow even for a few seconds. This step will deplate any impurities that may have plated on the work by cathodic action.

Periodic Reverse Electrocleaning

This method of electrocleaning of ferrous metals uses a combination of both anodic and cathodic cleaning modes. A periodic reverse (PR) unit is installed on the rectifier's output. The PR unit has a switching mechanism that reverses the polarity at controlled and timed intervals. The work in the tank assumes alternating anodic and cathodic polarities for the specified cleaning time.

Typical settings include reciprocating 10-second cathodic then 10-second anodic for the duration of the cleaning time. By alternating polarity, more cathodic or anodic may be used to effect maximum cleaning. The unit can be programmed so that the last leg of the cycle is anodic before the timer shuts off the rectifier. This ensures deplating of any charged particles that may have plated on the work during cathodic cleaning.

The continuous oxidation and reduction at the surface converts the oxides and scales on parts to more soluble forms that are picked up by complexers or chelating agents built into the cleaner formulation. PR cleaners eventually become saturated with dissolved iron oxides and must be replaced. Where practical, they can be regenerated by plating out the iron cathodically. PR cleaning is very efficient in descaling and derusting high-strength and spring steels without the use of acids in the cycle, thereby eliminating or minimizing hydrogen embrittlement.

OPERATING PARAMETERS AND PROCESS CONSIDERATIONS

Electrolysis is the main driving process in electrocleaners. The amount of gassing responsible for the scrubbing action at the electrodes is a function of the amount of current passing through the cell. Therefore, parameters controlling current should be considered.

Table II. Typical Operating Conditions for Electrocleaning

	Steel and Copper	*Brass*	*Zinc*	*Nickel and Chromium Alloys*
Alkalinity (as NaOH), g/L	50–100	15–20	15–20	30–60
Temperature, °C	60–90	50–70	50–70	50–80
Time, min	1–5	1–3	1–3	1–5

Solution Conductivity. This in turn is a function of cleaner concentration and temperature at a given voltage. The higher the concentration and temperature (up to a practical level), the higher the conductivity and the amount of gassing.
Voltage Applied. Current increases with voltage, although the latter is kept to maximum values of 10 to 12 V. Higher values are known to cause "burning" or roughness on parts.
Surface Area Being Cleaned. This parameter controls current density and, for a given rectifier setting, will directly affect the cleaning efficiency.

Adequate recommended current density ranges for different base metals are summarized in Table I. Values below these produce light to marginal electrocleaning. Higher values generally lead to etching and roughness of the surface.

Anode to cathode area ratios of 1:1 are adequate for most applications. The ratio is not critical as long as the specified current density values are maintained.

PROCESS CONSIDERATIONS

There are general considerations in the selection and proper use of electrocleaners.

Electrocleaner Formulation

Several proprietary formulations are available covering a wide range of applications. These formulations should provide the following properties:

- A suitable degree of alkalinity for the metal processed, e.g., high alkalinity for steel, lower for zinc and brass.
- A proper ratio of hydroxide to silicate to prevent insoluble silicate films from adhering to the work and affecting plate adhesion. Silicates are often used to prevent burning of steel at high current density. Nonsilicated cleaners, using different types of inhibitors, are also available. Water softeners and conditioners should be considered in hard water areas.
- An adequate amount of wetting agent and emulsifiers. Although high levels serve as cleaning agent for excess oil and grease, they inhibit the gassing action at the electrode surface and reduce desmutting characteristics. Efficient desmutting electrocleaners will have just enough surfactants to reduce solution surface tension and promote a thin foam blanket to hold down gas misting during electrolysis. Bulk oil removal should be a reserved function of the preceding soak cleaner.

Typical operating conditions of electrocleaners are given in Table II. Suppliers of proprietary electrocleaners usually tailor the parameters to specific applications, which may vary from the values shown in Table II. Alkalinity figures expressed as NaOH may represent 20–80% of the total product formulation.

Table III. Common Electrocleaning Problems

Problems	*Probable Causes*
Etching, tarnishing	Too high a current density Cleaner noninhibited for nonferrous metals Wrong polarity Temperature too high for nonferrous metals Excessive oil in solution
Roughness	Cleaner too weak causing "burns" on steel Excessive current density in anodic cleaning, pulling alloying elements to the surface. In cathodic cleaning, depositing charged particles and smut on surface Incomplete rinsing of electrocleaner
Haze under plate	Cleaner temperature too high causing dry-on film Cleaner too weak Incomplete rinsing after cleaner Inefficient soak or precleaning prior to electrocleaning Hexavalent chromium contamination
Poor adhesion, blisters, pitting of plate	Cleaner too weak Current density too low or too high Cleaning time too low or too high Reverse of intended polarity Hexavalent chromium contamination Insufficient rinsing after cleaning Excessive oil/grease in cleaner

Process Control

Control of electrocleaners is usually done by titration of the alkali contents. Maintenance additions will replenish alkalies, as well as surfactants and other components included in the formulation.

Although the essential components can be maintained, contaminants build up and eventually interfere with the proper performance of the bath. Oils and grease, if not adequately removed in the preceding soak cleaner, may result in water breaks out of the electrocleaner tank. Grease etch is a result of such a buildup. It shows as jagged etch spots after plating. It is due to uneven current distribution around non-wetted spots on the surface being electrocleaned. Hexavalent chromium trapped in cracked rack coatings and dragged into the electrocleaner is another source of contamination. This leads to drastically reduced cleaning and haze under nickel plate.

Stripping chromium-plated parts for rework in the process electrocleaner has a similar effect. Hexavalent chromium contamination can be readily detected as the cleaner turns yellow–orange and foaming seems to subside. Compatible chromium reducers are used to counter this effect. They reduce the chromium to trivalent if the cleaner is not heavily chelated and allow most of it to precipitate as the hydroxide. The solution color changes to light green, indicating the reduction process has taken place.

Equipment Maintenance and Operation

Corrugated or mesh steel can be used as anodes or cathodes to provide optimum surface area and solution circulation. Periodic cleaning of the anode/cathode is necessary to remove plated-on smut, oxides, and other charged particles. Using the tank as the anode or cathode is not recommended, as it leads to uneven current distribution and a source for stray current. Many electrocleaning problems, such as under- and over-cleaning, have been traced back to such a practice. A summary of common problems is given in Table III.

Polypropylene or lined tanks are recommended for alkaline electrocleaners fitted with steel, stainless steel, or Teflon heaters. Recirculating pumps are recommended to prevent stratification and ensure overall homogeneity. It should be noted that solution inlet and outlet must be located at two opposite diagonal top and bottom corners of the tank for efficient solution movement.

Cleaner filtration is gaining in popularity with the aim of prolonging the bath life between discarding and bath replacement intervals. Several filtration techniques have been proposed, ranging from simple bag filtration to complete systems of oil skimmers, coalescers, and ultrafiltration. Since the cost of such systems varies appreciably, a feasibility study must be undertaken before adopting a particular system. In general, however, it has been reported that any type of filtration does increase the bath life at least by 20% and up to five times or more.

LIQUID CLEANERS

The use of liquid cleaners to replace powder versions has gained momentum and wide acceptance in the industry. These new cleaners are formulated to economically provide all the performance criteria of the powders. The advantages of liquid cleaners include the capability of automatic feeding tied to conductivity controllers. The automated system continually monitors the solution strength and makes additions on demand. Consequently, better bath control is achieved, eliminating wide swings in concentrations. Automatic recording capabilities of concentration and temperature can be achieved for statistical process control.

Tank additions of liquid concentrate eliminate the hazards associated with additions of alkaline powders to hot cleaner solutions. As a result of better controls, these liquid systems have substantially increased bath life in many installations.

Another advantage confirmed by users of liquid cleaners is sludge reduction on waste treatment by 70–80%, which adds to the economical advantage of these systems.

ELECTROCLEANING OF STRIP AND WIRE COILS

Strip and wire are continuously fed through the line. There is no direct contact with anodes or cathodes in the electrocleaner tank. A bipolar electrical effect is used to provide the polarity as follows. Two separate steel grids are positioned several feet apart in the direction of work flow. The first grid is anodically connected, the second, cathodically. The strip travels between two closely spaced jaws of each grid without touching them. As a result of the bipolar effect, the strip assumes the opposite charge of the grid. It becomes cathodic through the first grid, then anodic through the second, achieving the desired electrocleaning effect.

ULTRASONICS—A PRACTICAL APPROACH

BY KENNETH R. ALLEN
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Ultrasonic cleaning is the introduction of high-frequency sound waves into a liquid, usually between 20 and 80 kHz. The resulting action is called "cavitation." Cavitation is created by high- and low-pressure areas produced in the solution as the sound waves pass through it. In low-pressure areas microscopic vapor bubbles form. The pressure rises rapidly as the next sound wave passes through the area, violently imploding the minute bubbles, releasing the energy that does the cleaning.

The Transducer

This device converts high-frequency electrical energy into mechanical motion. The transducer physically oscillates at its resonant frequency. There are two basic types, magnetostrictive and piezoelectric. Magnetostrictive transducers are metallic, usually made of laminated nickel and are typically silver brazed to a plate. Piezoelectric transducers are composed of man-made crystals and are mounted in various ways, the most common being epoxy bonding.

The Generator

The generator converts low-frequency line power at 50 to 60 cycles per second to high-frequency power (20-80 kHz) that matches the resonant frequency of the transducer. Generators designed to drive piezoelectric transducers often have automatic tuning or frequency controls to compensate for fluctuations in the resonant frequency of the crystal transducer. Typically, magnetostrictive generators do not have automatic tuning because the resonant frequency of the magnetostrictive transducer is more stable.

THE APPLICATION OF ULTRASONICS FOR CLEANING

In general ultrasonics is used in precision-cleaning applications of more complex parts. It has the ability to clean in narrow crevices and small holes that would not be easily accessible by a spray washer or other methods of cleaning. Difficult soils, such as buffing compounds and baked-on carbon, are also good candidates for ultrasonics. In other words the more complex the part configuration and more stubborn the contaminant, the more likely ultrasonics will be of benefit to the cleaning process.

There are also many other factors that contribute to the cleaning process equation such as the type of soil, chemical limitations, temperature, cycle time, piece part volume, etc. I attempt to illustrate how these parameters interrelate to ultrasonic cleaning.

There are three types of energy available in any given cleaning application: (1) thermal energy, (2) chemical energy, and (3) mechanical energy.

The success of a cleaning application depends on the balance and relationship of these three types of energy. The fourth parameter is time, which increases the effectiveness of all three energies.

Ultrasonics is only one type of mechanical energy. It is only one part of the equa-

tion for a successful cleaning process. Other forms of mechanical energy used in cleaning would be simple immersion, spray, turbulation, agitation, and rotation of the part. The selection of the type of mechanical energy depends to a great extent on the relationship of the heat applied to the process and the type of chemistry used. Many times companies only consider the chemical aspects when converting a vapor degreaser, trading the solvent for another chemical. A more successful approach considers all of these parameters, which maximizes the investment.

Ultrasonics is not a magic force, nor is it right for every application. It is just another form of mechanical energy to enhance a chemical process.

Thermal Energy: (1) Acts as a catalyst to enhance chemical energy. (2) Raises the energy level in any type of process. (3) Can condition a contaminant to be acted upon by chemical and mechanical energies, especially ultrasonic applications.

Chemical Energy: (1) Provides a method to break molecular bonds. (2) Acts primarily on organic contamination. (3) Provides many properties to do many jobs, i.e., degreasing, pickling, phosphating, etc. (4) Can be polar (water soluble) or nonpolar (water insoluble).

Mechanical Energy: (1) Provides energy to physically remove contamination from the part surface. (2) Is used to enhance chemical and thermal energy. (3) Is available in many forms, including spray, agitation, turbulation, and ultrasonics.

Using a combination of these energies, and finding the balance for your application, can be a challenging project. The relationship of the chemistry, the temperature of the bath, and the degree of mechanical motion the part can withstand are all critical factors in choosing your cleaning method.

Examples

If your part is not complex, made of steel, is not susceptible to mechanical damage, and only contaminated with cutting oil, you probably will not need ultrasonic cleaning. A typical process might look like this:

Temperature, 160°F
Chemistry, pH neutral
Agitation bath with oil
separation
Cycle time, 5 min.

Take the same part and add blind holes 2 in. deep by in. in diameter. The process might look like this:

Temperature, 160°F
Chemistry, pH neutral
Turbulation, parts fixtured with a rotating basket and oil separation
Cycle time, 5 min.

If this same part has been sitting around in storage and has corroded, the process might look like this:

Temperature, 180°F
Chemistry, pH 12.5
Turbulation with rotation, no oil separation
Cycle time, 10 min.

At this point one might need to introduce ultrasonics as the mechanical catalyst in the equation. The cycle is getting long and the temperature is getting high. By introducing a high degree of mechanical action it may be possible to reduce both:

Temperature, 140°F
Chemistry, pH 12.5
Ultrasonic with rotation
Cycle time, 5 min.

REAL LIFE

A manufacturer of aviation hardware was using a vapor degreaser to remove oil and 50% nitric acid at 170°F to deoxidize aluminum parts prior to brazing. By using ultrasonics it was possible to combine both processes in one clean line.

1. Ultrasonic degrease in an aqueous-based solution pH neutral at 140°F.
2. Hot water rinse.
3. 5% citric acid at 140°F with ultrasonics.
4. Deionized rinse at 160°F.
5. Deionized rinse at 160°F.
6. Hot air dry.

The capital equipment cost to the manufacturer was $160,000; however, because of savings in operating costs by eliminating the degreaser and eliminating waste disposal of the nitric acid, the R.O.I. was less than eighteen months. Moreover, this process is much safer and gave the user a dramatic increase in quality.

The main factor in this application is that the ultrasonics allowed this manufacturer to use a much less hazardous acid by adding a high degree of mechanical energy to the process, thereby enhancing a neutral pH bath for thorough degreasing instead of 1,1,1-trichloroethane.

Another example of the successful application of ultrasonics is in plating; especially in reel-to-reel plating of strip. Most plating lines use strong alkalines at approximately 170°F and electrocleaning for soil removal at the beginning of the plating line. In many cases the strip or parts have gone through a vapor degreaser. The problems with this type of cleaning are that it limits line speed, and high pH chemistries are usually not free-rinsing. This causes contamination of the plating baths with carryover and high rinsewater usage. The parts also must be degreased prior to plating because high pH tends to emulsify oil and deplete the chemistry. By using high-intensity ultrasonics most of these problems are eliminated. Ultrasonics is being used in reel-to-reel plating with a pH neutral detergent at 140°F in place of the electrocleaner. Because of the neutral detergent any oil will float and can be separated with a coalescer. This often leads to the elimination of the vapor degreaser prior to plating as well. It is free-rinsing and, in most cases, the line speed can be doubled. The advantages are many: the plating baths do not get contaminated, water usage is cut in half, product quality is more consistent, chemical and waste treatment costs are lower, and output of the line is doubled.

These examples are only two of hundreds like them that illustrate the benefits of applying the proper type of mechanical energy to a process. Table I provides a list of parts typically cleaned in ultrasonic processes.

When trying to determine if ultrasonic cleaning can help you keep these few things in mind:

1. Is the part a complex shape?

Table I. Typical Applications for Ultrasonic Cleaning

Diesel fuel nozzles
Turbine engine blade and vanes
Bearings, races, and rings
Aircraft fuel nozzles
Flatware (buffing compound)
Stamped parts (pieces or strips)
Pistons
Piston rings
Valve lifters
Battery cans
Die castings (buffing compound)
Textile spinnerettes
Rachet handles (buffing)
Valve plates, refrigeration
Continuous strips, up to 200 fpm
Golf club heads (buffing)
Computer disk drive hubs
ABS valve bodies

2. Does the part have small crevices, blind holes, or deep recesses?
3. Is the part delicate? Will strong agitation damage it?
4. Will strong chemistry damage the part? (Example—you cannot use high pH on aluminum).
5. Will high temperature affect the part?
6. Is the cleaning cycle time limited because of part volume?

If the answer to most of the questions is "yes" then you are a candidate for ultrasonic cleaning. Future trends are dictating cleaner parts, better quality, and a safer environment. Ultrasonics can be a tool to help you.

SIZING THE SYSTEM

Once you have determined that ultrasonics is right for your application the next question is "How do I choose the right power level, tank, configuration, etc.?"

It takes a certain amount of energy to achieve the "threshold of cavitation," i.e., the level of energy required to achieve cavitation. The problem is that when you put a load in the tank, you attenuate or absorb energy. If you do not have a good Watt density (power level) you can fall below the threshold, and cavitation ceases. In other words the heavier your load, the more power or Watt density you will need. Some ultrasonic manufacturers calculate in terms of Watt density per area of radiating face such as 5 to 7 W/in^2. Others recommend power levels in terms of volume, typically in 40 to 75 W/gal. Because the displacement of the ultrasonic transducer is a mass relationship a volumetric determination seems more realistic. It is desirable to have the transducer/diaphragm moving mass exceed the mass of the cleaning load. This usually assures sufficient driving energy to compensate for load attenuation.

In most general degreasing applications 40 to 60 W/gal seems adequate; however, in applications such as removing burned-on carbon in turbines or removing a diamond lapping compound, Watt densities of 100 to 150 W/gal are common.

Often the number of transducers seems to be used as a yardstick to measure how much power is in a tank. This is not an accurate method and should not be used to compare manufacturers. Most types of crystal transducers can range

from 20 to 50 Watts per transducer. Magnetostrictive transducers can range from 50 to 1,000 Watts per transducer. You would need twice as many of one type to get the same energy in a given volume as another. This is why the W/gal approach is a more reliable method of determining if the power available will be adequate.

Piezoelectric and magnetostrictive devices vary in their construction, power output per transducer, and methods of attachment, i.e., epoxy bonded or silver brazed. The efficiencies in general—considering all parameters—are similar. Typically, you find piezoelectric in lower power applications and magnetostrictive in higher power ranges. It is safe to say that the more power, the more expensive; therefore, if you are cleaning lightly soiled parts or printed circuit boards a low Watt density is adequate. But, if you are decarbonizing jet engines or large textile spinnerettes, a high Watt density tank is a much better choice.

Trying to determine the size of the tank can be difficult. Trying to scale up any type of manufacturing process can be challenging. If it is possible you should test clean production lots in the laboratory or in equipment to closely approximate the manufacturing environment. Choose a tank size that will adequately accept your part or basket with enough clearance to allow for easy placement and extraction. The other consideration is liquid displacement. As a general rule your part volume should not displace more than 25% of the total tank volume. The reason for this is to maintain enough liquid level to cover the part. You do not want to displace solution out of the overflow weir every time you put a basket of parts in the tank. You will have to constantly add water to maintain a consistent level.

There are two things that are usually overlooked that will greatly enhance any equipment selection. Make sure that the ultrasonic tank has adequate filtration and a sparge/overflow system with oil separation when oil is being removed from the parts. This keeps the floating oil from redepositing on the parts and keeps the particulate level down in the tank. It also has the additional benefit of enhancing the cavitation because high amounts of suspended solids also attenuate (reduce) the ultrasonic activity. The money spent on filtration will be recouped by way of reduced chemical consumption, cleaner parts, more consistent quality, and reduced cycle times. Removing as much oil as possible will give similar benefits. The preferred type of oil separation is usually a coalescing system. Oil wheels work but do not remove oil fast enough in a production situation.

The next thing to consider is an adequate rinse system. "You cannot get clean dishes out of dirty dishwater." The same applies to clean parts. Your part will only be as clean as your final rinse. As a minimum a two-tank cascading system should be considered.

WHEN SHOULD I CONSIDER AN ULTRASONIC RINSE?

Ultrasonic rinsing typically is not considered because of cost considerations. It adds 30 to 40% increased cost to most clean lines; however, if the holes in your part retain water due to capillary action, then an ultrasonic rinse will be required. This is because a heated static rinse will not remove trapped chemicals and debris from tiny capillary holes. Small blind holes are rinsed by diffusion rather than by flushing. Ultrasonics will add the impingement energy necessary to flush these difficult areas. Typical parts that require an ultrasonic rinse are textile spinnerettes, ultra-high-pressure diesel-fuel nozzles, hypoder-

mic needles, and parts that nest or stick together. In a cascading system the ultrasonic rinse should be the final rinse. Again, the best way to make your final process determination is by doing careful laboratory analysis.

Be sure to work with an equipment supplier who can help you develop a process and choose the chemistry and equipment. Most major ultrasonic and cleaning equipment suppliers have laboratory facilities and will do sample parts cleaning for you at no charge. Take advantage of the resources available to you.

AQUEOUS WASHING SYSTEMS

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As we enter the new millennium aqueous washing systems have become the dominant method of cleaning in the industrial marketplace as manufacturers strive to become environmentally compliant.

To claim that aqueous systems have come into their own market niche is an understatement. Aqueous systems clean better, meet higher cleanliness tolerances, and perform at higher production rates than traditional solvent cleaning systems. Aqueous cleaned parts are film and residue free.

For an aqueous system to be successful proper equipment and process selection or configuration is necessary. This is best achieved by interaction between the end user and the chemical and equipment suppliers.

DEFINITIONS

It is important that the end user establish some ground rules or definitions that the equipment is to be designed around. The end user must define the following:

Parts

The end user should define the part or parts, their maximum size, and geometry. It also should be determined whether, during the cleaning cycle, parts can come in contact with one another, or whether parts must be maintained in a proper geometry, or even fixtured.

Productivity

The end user must determine the productivity level, in terms of parts per hour, that the system is to generate. If multiple parts are to be processed, depending upon the equipment utilized, the equipment should also be sized and designed to ensure that product flow through the machine does not cause any part mixing.

Material Handling

The end user should discuss how the parts are to come to the aqueous system. The manner of delivery of components, whether they are in baskets, totes, on blue steel, egg crated, or in large hoppers, may determine equipment configuration, as well as the degree and need for automation. Parts can feed into systems directly in bulk, in baskets, or in line.

Acceptable Cleanliness Standard

The end user needs to establish or supply a cleanliness specification. Various types of aqueous systems are geared for large particulate and oil removal only, while other systems are capable of achieving high precision and low mil-pore or low total molecular weight cleaning criteria. By specifying the cleaning requirement this will also help determine the type and the configuration of the aqueous system to be utilized.

Once the end user has defined part geometry, productivity, product delivery, and cleanliness specifications the type of aqueous system to be utilized can be defined.

Mechanical Interaction

The above end-user defined parameters are important to determine the type of mechanical interaction that the aqueous system is to develop. Mechanical interaction is the most important part of system design and can determine the success or failure of the system. Various forms of mechanical interaction can be employed simultaneously. The standard types of mechanical interaction can be defined as follows:

1. Soak
2. Spray
3. Soak and spray
2. Soak with turbulation
3. Soak with ultrasonics
4. Vertical agitation
5. Vertical agitation with ultrasonics
6. Vertical agitation and rotation
7. Vertical agitation and rotation with ultrasonics

The lowest level of mechanical interaction is soaking alone, the highest degree of mechanical interaction is vertical agitation and rotation with ultrasonics. By determining the type of mechanical interaction to be employed, the end user can determine the degree of cleanliness or the cleaning specifications that the machine will be capable of achieving. Other factors to be defined by the end user and the system supplier include the following:

Chemistry

Establish what chemistry is to be employed, its pH and concentration level or ratio, and the ability of the chemistry to interact and remove the soils and oils on the parts. Most chemistries are alkaline and the percentage of chemistry to maintain a uniform process must be controlled.

Temperature

The temperature of the chemistry should be selected so as to ensure that the chemistry is working at its maximum capability. The heat source to maintain temperature and components for spray or pumping loss is to be specified (i.e., electric, steam, or gas). Enough heat is necessary to bring cold parts to temperature for chemical interaction, and for drying.

Time

The time should be selected so that the components are involved with mechanical interaction and chemistry to achieve an acceptable production level and an acceptable cleanliness specification.

Drying

The drying specification determines how dry components have to be or whether they have to be dried spot free.

Summary of Cleaning Parameters

In summary, part geometry, productivity, part delivery, and cleanliness specifications are normally defined by the end user. The type of mechanical interaction, the chemistry, its concentration and pH, temperature, time, and drying are nor-

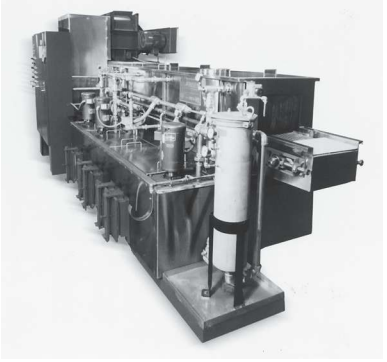


Fig. 1. Belt spray system with wash/rinse/rust inhibit/recirculating hot air dryer, oil coalescor, and wash filtration.

mally derived through product testing and interaction between suppliers and end users. It should be understood that satisfying all of these requirements is necessary for the success of an aqueous system. Parts should be tested in large volumes to insure repeatable results.

MECHANICAL ACTION

Since the most important part of the aqueous cleaning cycle is mechanical interaction, the following are some definitions for the standard types of mechanical interaction available.

Soak

Soaking of parts in chemistry relies solely on the mechanical interaction of chemistry to attack, dissolve, and/or emulsify soils. For soak to be successful it is imperative that chemistries be aggressive and that adequate time be utilized to ensure that the chemistry has the ability to interact effectively with soils. Even in soaking, some form of part movement normally takes place as parts are either introduced to a soak tank or withdrawn. It is likely that this small amount of mechanical interaction or part movement will, in effect, do more work than the soak cycle itself.

Spray

Spray is a widely used form of mechanical interaction in aqueous systems. Spray is used on belt systems, monorail systems (see Figs. 1 and 2), cellular and centralized washers, and with cabinet systems that used low-, medium-, or high-pressure delivery of solution.

Spray systems are designed to direct solution so that it impinges the parts from above, from the sides, and from below. The solution is normally directed by spray headers utilizing nozzles to generate overlapping spray patterns. Parts are typically drawn through spray zones by some form of conveyance, such as belts, monorail, rotating turntable, or rotating baskets. The spray solution is designed to impinge the part surfaces at pressure and high volume. Spray impingement loosens and removes soils. It is necessary to understand that high volume is as important as high pressure, as it is the volume of solution that causes dirts and soils that are removed by the spray impingement to float away or be removed from the parts. The combination of pressure and volume, in conjunction with heated chemistry, is effective in removing soils, oils, dirt, chips, and other by-products associated with manufacturing.

In most cases spray can only be delivered from four axes, while most parts have a minimum of six geometric axes. Likewise, spray can be easily deflected. Spray is not well suited for cleaning blind holes or complex geometries. If parts are processed in baskets, parts positioned on the outside may mask effective cleaning of other components in the middle of the basket, as parts on the surface of the basket will be the ones effectively engaged by spray while parts in the middle of the basket must rely on solution volume and drippage for effective cleaning.



Fig. 2. Access covers from Fig. 1 removed to view spray headers.

For this reason parts in baskets in cabinet cellular washers are rarely filled more than 60%. This allows parts in the middle of the basket to eventually migrate to the exterior of the basket, if the basket is rotated.

Spray systems can also be used as in-line manufacturing cleaning systems. The same belt that it used to transport the parts through the washer can transport parts from one location to another location, thus acting as a material handling unit.

Spray systems should also be designed to ensure that the various spray chambers are shrouded with baffles, both before and after spray zones, to minimize overspray and solution drag-over. A belt can act as a natural pump and adequate drain area is necessary on belt systems to minimize carryover of wash solution to rinse zones, or as the belt returns, from rinse to wash zone. In all instances where spray systems are employed, sufficient drain area or drain cycles are required to allow the parts, belt, and baskets to adequately drain to minimize contamination of subsequent spray zones or to maintain rinse tank clarity.

Soak and Spray

Belt or monorail systems can be equipped with soak zones, these being areas where the part is drawn through a soak stage prior to being sprayed. The soak area will ensure that all areas of the component are exposed to chemistry and can initially loosen and emulsify some soils and oils as parts are drawn through the soak zone, prior to spray impingement. This greatly assists the ability of the spray to flush and remove soils. Rotary drum systems also typically employ soak and spray.

Rotary drums are designed to move parts through various operations in a horizontal cylinder, the interior of the cylinder equipped with a helix (see Figs. 3 and 4). This automatically advances parts forward as the drum rotates and allows a large quantity of parts to be effectively engaged by the mechanical interaction generated by the machine; this a combination of soak and spray impingement, as well as high volume of solution delivery. The parts are soak cleaned and spray cleaned simultaneously. Spray headers are positioned so that the spray engages the parts as they are lifted out of the soak solution. After the soak section, the parts continue to be engaged by spray. The spray typically uses a combination of spray impingement and high-volume solution delivery. The soak section loosens contaminants. The high-pressure spray impingement is generated by directed stainless steel spray nozzles and is designed to dislodge contaminants from the parts. In short the combination of soak and spray impingement dislodges soils; the high-volume delivery flushes the soils, oils, and other contaminants away.

In a rotary drum system the mass of parts is gently tumbled in the aqueous cleaning and rinsing solutions. This gentle tumbling action provides an effective method of completely exposing all edges and surfaces of components to the action of the soak, impingement spray, high-volume solution delivery, rinsing solutions, and to the drying action. The rotation of the drum causes parts to rotate and move. The movement within the drum causes all surfaces and edges to be exposed to the cleaning action; therefore, all areas of parts are engaged by the



Fig. 3. Rotary drum system, wash, rinse, dry with soak, and spray zone.

cleaning capability of the system. It is the combination of part movement, immersion, high-pressure spray, and high-volume solution delivery that is more effective than spray alone in dislodging contaminants and soils from all areas of the parts.

Parts do contact one another in a rotary drum system. If no part contact is permitted this would not be a system of choice.

Soak with Turbulation

Turbulation is, in essence, exciting the cleaning bath; that is, causing fluid movement within the bath. This is accomplished by using either aerators or impellers to cause the cleaning solution to become a fluidized bed of continuous movement. When parts are introduced to a turbulated bath, the solution moves around areas of the components. This rapid movement of solution has the ability to emulsify oils and dislodge soils.

In turbulated systems care should be taken to ensure that parts do not mask one another. Turbulation moves tremendous volumes of solution but lacks any driving force to penetrate a basket or a layer of parts. This masking is sometimes offset by ensuring that there is part movement in the turbulated bath. Part exposure to turbulation is accomplished by either rotating or articulating the part. Small components placed in baskets require this rotation movement. The basket itself and the parts in a basket will act as a mask for the turbulation solution. By rotating the basket, parts in the interior of the basket may eventually be drawn or positioned at the exterior of the basket where they may be somewhat engaged by the turbulated solution; therefore, full baskets or even baskets three quarters full of parts cannot be effectively cleaned with turbulation due to no or minimal part movement. Similar to a rotary drum system there is some part-to-part contact due to partially full baskets that are typically rotating.

Turbulated systems like spray are not effective for cleaning ID or blind hole areas.

Vertical Agitation and Rotation

Vertical agitation develops the highest degree of mechanical interaction between parts and chemistry. The vertical agitation movement produces a natural hydraulic cleaning action, generating cavitation in the tank, which forces the cleaning solution between parts and in/out of recesses and cavities. This vertical agitation movement of parts in an aqueous solution generates a flushing action that scrubs all parts surfaces, crevasses, holes, and recesses clean. The agitation movement forces solution between components and



Fig. 4. Rotary drum system with top drum enclosure cover totally removed. Solid drum section is used for soak and spray. Perforated sections for spray and drain.

in/out of holes.

Parts in many instances are cleaned in baskets (see Figs. 5 and 6). But unlike spray or turbulation systems, parts in baskets do not mask themselves, allowing full baskets of components to be effectively cleaned due to the agitation movement. The mechanical action of agitation removes oils and greases, while loosening and removing metallic fines and chips. One hundred percent immersion of baskets in and out of solution is much more effective than partial immersion.

Adding rotation to the agitation further enhances this capability by allowing all holes, recesses, and cavities to fill and drain effectively with the aqueous chemistries.

With the vertical agitation concept, the amount of agitation can be adjusted for each tank in a process. With the advent of programmable controllers, systems can be programmed to agitate and rotate baskets under solution while occasionally raising the baskets out of solution to drain, then totally immersing the baskets in solution again. Baskets can effectively rotate out of solution for complete draining prior to transfer to subsequent tanks. This drain cycle greatly reduces chemistry drag over and prolongs rinse tank clarity. Vertical agitation systems are also very effective for chip removal, as turbulation can also be added to vertical agitation systems. The turbulation in vertical agitation systems serves a second purpose. The turbulation keeps chips and fines in suspension in the solution until they can be evacuated by high-volume pumps and filters.

The vertical agitation movement also makes this concept readily adaptable for use with ultrasonics. The agitation can be programmed to move slowly up and down while moving through a focused ultrasonic field. This slow up-and-down movement exposes the entire workload to the full power of the ultrasonic scrubbing action, allowing full cavitation, generated both by ultrasonics and agitation, to effectively engage components. In agitation systems, ultrasonics are sidewall, bulkhead mounted. This will guarantee that the parts will pass through the high-concentration ultrasonic field. Slow rotation through the ultrasonic field also ensures 100% exposure, allowing blind holes to be effectively filled with solution and engaged with the ultrasonic energy.

Drying

Good dryer design employs louvers that will direct the air flow directly against the components and baskets, if they are employed. The dryer design should contain an internal duct system that directs the air flow from multiple directions against the parts or baskets. This design will ensure uniform exposure of all surfaces, edges, and recesses of components to this air flow.

As with interaction of chemistry with components, time is a variable in the drying process and end users should be aware that shortening dryer time to save space can be detrimental and compromise the effectiveness of dryer design.

On belt- or monorail-type systems, air knives can be used prior to drying to remove puddled water from recesses and cavities. Air knives are important when parts cannot rotate, either prior to or in the drying process.

Air knives on belt or monorail systems can also be used between wash and rinse stages to minimize cross-tank contamination. This will effectively remove chemistry residues from the belt as well as parts. Newer style air knives can employ either low pressure and volume shop or self-generated air-style delivery systems.



Fig. 5. Five-tank vertical agitation and rotation system with material handling and closed-loop wastewater treatment system. System utilizes a wash,ultrasonic wash, three counterflow rinses, and rotation of baskets in a recirculation hot-air dryer.

THE AQUEOUS PROCESS

Most aqueous processes require, as a minimum, a wash, a rinse, and a dry. There may be multiple wash and rinse stages, depending upon the desired cleanliness level.

Typically, wash requires a mild alkaline cleaner that is heated. Care should be taken in the selection of the cleaner to ensure that it is compatible with alloys being cleaned and has the ability to emulsify or split oils and remove other contaminants.

The purpose of rinses is to remove residual chemistry remaining on parts. If only one rinse is employed, a flow of clean water into the rinse tank on a continual basis to an overflow dam is necessary to maintain rinse clarity. A system employing two rinses should consume half the water that a single-rinse system will require. Likewise, three rinses will utilize half the water that a two-rinse system will use to maintain final rinse tank clarity. Depending upon cleanliness specification and whether spot-free drying is necessary, RO or DI waters may be necessary for final rinses.

If RO or DI water is employed consideration should be made to prevent flash rusting on ferrous components. It may be necessary to add rust inhibitors or wetting agents to rinse tanks to prevent flash rusting while rinsing ferrous components.

WATER QUALITY

If incoming municipal waters contain a high level of chlorine, sulfur, salts, or other contaminants it may be necessary to treat this water prior to use. Water hardness and poor quality of water can affect the ability of the aqueous chemistries to work. Likewise, poor water quality can affect drying and cause water spotting.

SYSTEM CONSTRUCTION

All aqueous cleaning systems should be constructed with stainless steel for tanks and wetted surfaces. Whereas mild steel construction was acceptable in the past the greatest cost factor in manufacturing an aqueous system is labor. Stainless steel, although three times the cost of mild steel, should have a cost impact of less than 20% on the overall system. Mild steel construction will always oxidize in time and cause degradation of baths, compromise the ability to clean, and cause rinsewater to always contain ferrous oxides. Stainless steel construction overcomes these shortcomings and should give an aqueous system a minimal 20-year life.



Fig. 6. Vertical agitation and rotation system with access doors open. System agitates baskets 24 in. X 24 in. X 12 in. through a prewash, wash, and two counterflow rinses prior to dry.

FILTRATION

Filtration will greatly prolong bath life and allow for a more uniform cleaning process. Aqueous chemistries are designed to remove soils. Most chemistries are designed to emulsify or suspend soils in the wash bath. In time these soils will build up in the wash bath.

For spray-type systems filtration should be inline between pump and spray headers. Filters should be constructed of stainless steel and sized to be, as a minimum, 20% above pump volumetric flow rate.

For bath-type systems filtration should be designed to exchange the total volume of the bath every three to five minutes. A tank bath of 200 gal should have, as a minimum, a 40 gpm pump and 50 gpm filter system. Filtration is designed to remove suspended finds, particulate, soils, dirt, etc. Good filtration will prevent redeposit of the soils on the parts.

OIL REMOVAL

Most chemistries are designed to split petroleum and tramp oil and cause the oil to float to the tank surface. Many types of oil removal systems are available and vary in price, complexity, and efficiency. Disk, belt, and decant systems are marginally effective. Coalescing and ultrafiltration are the most effective. Coalescing systems with surface skimmers or spargers are required for bath or agitating systems to ensure that the top surface of the water is free of oil prior to the removal of parts.

Oil coalescers are normally freestanding units constructed of stainless steel. A coalescer is designed with perforated partitions, making it multiple tanks. The first area is a still tank. The second area is normally filled with polypropylene tubes. The polypropylene tubes are efficient in their ability to collect oil. The tubes attract oil globules to as small as 20 micron. When the oil globule builds and reaches a dimensional size of between 100 and 200 microns it breaks free from the polypropylene tube and floats to the surface of the tank where it is skimmed; therefore, the coalescer is effective in removing oil as small as 20 micron. The coalescor collects only oil and not water and chemistry.

The coalescer then pumps clean water to a sparger pipe positioned to skim the top surface of the tank to an overflow weir. The overflow weir is connected to the coalescer and the system operates as a closed loop.

Emulsified oils must be handled differently. Membrane or evaporation technologies must be incorporated to deal with the emulsified oils in a solution bath.

WASTE TREATMENT

Alkaline chemistries and rinsewaters, by themselves, are normally not an environmental issue. Chemistries are designed to remove soils and oil from parts. If the soils are heavy-metal laden they will have to be treated accordingly. If petroleum-based oils are used, coalescing and other oil-extraction systems can readily remove these oils from baths prior to discharge.

If emulsified oils are present in the bath these will have to be dealt with as regulated by local EPA authorities. Either evaporation or membrane technologies, such as ultrafiltration, should be employed to remove emulsified oils prior to solution discharge to drain.

Normally rinsewaters are sufficiently free of heavy metals and emulsified oils and may be readily dischargable.

In summary local sewer authorities may dictate the type of treatment required for alkaline baths and how these baths are to be disposed. In all instances cost of disposal is normally far less costly than dealing with or disposing of solvents.

EQUIPMENT SELECTION

As stated previously end users have to define part geometry, productivity, material handling, and cleanliness specification. Once these are known tests can be conducted to determine which type of system and the type of mechanical interaction that is best suited to meet end users' needs. Although cost is always a consideration to determine the proper selection of the type of aqueous cleaning system to be used, capability should be the driving force in proper equipment selection. It is important that the system achieve cleanliness specifications at the production levels desired.

Good interaction must be achieved between end user and the equipment supplier to ensure that any proposed system is equipped with adequate mechanical interaction to achieve the desired level of cleanliness, that there is adequate rinsing to ensure removal of residual chemistries with a minimal level of acceptable water usage, and that dryer design will achieve the level and quality of dryness desired.

The equipment costs for aqueous systems normally are higher than solvent systems, but the operating costs are normally less. The purchase costs for aqueous chemistry and chemistry disposal is a small fraction of the purchase and disposal cost of solvent-based chemistries.

In summary aqueous cleaning systems have come of age. They can more effectively clean to a higher cleanliness level than is achievable with solvent systems. Aqueous systems leave no residue on parts.

Aqueous systems are environmentally friendly, end-user friendly, and can consistently achieve desired results.

Aqueous systems offer a cleaning solution and are considered environmentally compliant. With new EPA guidelines and restrictions you can be assured that aqueous systems will become even more dominant in the 21st century.

PICKLING AND ACID DIPPING

BY STEPHEN F. RUDY
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Acid treatment identifies a process whereby the base metal is subjected to mild, moderate, or aggressive etching. It's reasonable to assume the solution pH is below 2.0. What happens chemically can be illustrated by the reaction between metal, oxide, and acid:

Metal Oxide+Acid=Metal Salt+Water
Metal+Acid=Metal Salt+Hydrogen (proton)
Hydrogen (proton)+Hydrogen (proton)=Hydrogen (gas)

The metal, as is, contains an oxide surface layer before immersion in the acid bath. This condition was probably accentuated by a previous reverse electrocleaning step. The oxide layer hurts the prospective finish two ways: adhesion of electrodeposits to the base metal will be poor, and the metal surface in an oxide condition is a poor conductor. The oxide must be totally and cleanly removed. Depending on the degree of surface acid treatment, this can be done in a single immersion, double immersion, or cathodically in an electrified acid. Acid formulations, available in liquid or powder, are available in three common forms:

Single constituent, mineral, inorganic type.
Combination of two or more acids. May consist of inorganic and organic acids.
Single or multiacid combinations, which also contain surfactants, dispersants, and inhibitors.

The acids dissolve oxides and smuts. They also remove scales and rusts. Sulfuric acid is perhaps the cheapest of the acids used and it's much less fuming. Hydrochloric acid provides a much better rate of pickling action at lower temperatures but does generate more fumes. Hydrochloric acid is also widely used for stripping chrome- and zinc-plated deposits off parts and rack tips.

Phosphoric acid must be heated to achieve acceptable pickling activity, and formation of light iron phosphate films on the surface may be detrimental if electroplating is part of the cycle. Surfactants and wetting agents lower the solution surface tension, permitting the bath's active agents to more readily penetrate into and attack undesirable surface coatings and films. Other functions of wetting agents and surfactants include emulsification of residual oils and grease (not removed in previous alkaline cleaning or carryover) and formation of a thin surface foam blanket to help retard the corrosive effects of fumes and mists. Dispersants prevent redeposition of removed soils. Inhibitors provide two-fold effects: controlled pickling, which prevents excessive surface action, and prevention of immersion deposits in aged, contaminated baths.

A review of the acid dips available and their respective activities should help to clarify the solution selection process.

This issue of the *Metal Finishing Guidebook* contains additional discussions, references, and suggestions for activation and pickling, as well as more detailed information regarding rinsing, analysis, testing, and related subjects. The chapter "Surface Preparation of Various Metal Alloys Before Plating and Other Finishing

Table I. Operating Parameters and Applications for Acid Dips

Acid Type	Concentration Range	Temperature	Time	Agitation
Liquid	5-8% v/v	75-110°F	1-3 minutes	Solution movement
Powder	4-24 oz/gal (30-180 g/L)	75-110°F (24-43°C)	1-3 min	Solution movement

Applications" describes specific acid treatments that supplement the information given in this chapter.

ACID DIP

This is the simplest type because the requirement is not complicated. The parts are conditioned as follows: alkaline cleaner film is neutralized and light oxide and/or rust is attacked and removed. Many parts fall into this category. This bath contains an inorganic acid, either hydrochloric or sulfuric. It may also include a surfactant to improve wetting of parts by lowering surface tension, accelerate the activation process, and emulsify trace oils and grease. Acid dips generally meet the operating criteria shown in Tables I and II. In the case of processing steel, brass, and copper together, the solution may contain a special inhibitor, preventing immersion copper deposits on steel.

For brass activation the acid typically contains a blend of sulfuric and hydrofluoric acids. Most brass parts have been formed, machined, or stamped; therefore, up to 4% lead can be incorporated into the metal to facilitate mechanical work. Fluoride is the best additive to dissolve lead smuts, leaving a clean surface for plating. (See Table III.)

Copper and copper alloys (beryllium, tellurium, etc.) activate well in formulas containing sulfuric acid and persulfates. This solution provides the preferred light etch to activate and desmut.

Most zinc alloys respond well to activation in sulfamic or sulfuric acid blends containing fluorides (preferably ammonium bifluoride). Fluoride effectively dissolves smuts, while the inorganic/organic acid mixture activates the surface.

ACID PICKLE

This process bath is most readily used to condition steel and stainless steel parts. It can be used as an immersion dip or cathodically. (See Tables IV to VI.) Some metal-

Table II. Acid Dip Operating Parameters for Steel & Stainless Steel

Acid	% v/v	Wetters, oz/gal	Deflocculents, oz/gal	Inhibitors, oz/gal
Hydrochloric	5-15	0.01-0.03	0.06-0.09	0.002-0.004
Sulfuric	7-20	0.01-0.03	0.06-0.09	0.002-0.004
Phosphoric	10-20	0.01-0.03	0.06-0.09	0.002-0.004

Table III. Acid Dip Operating Parameters for Nonferrous Metals

Metal	Sulfuric Acid Concentration, % v/v	Fluoride, oz/gal	Persulfate, oz/gal	Wetters, oz/gal
Brass	3-5	0.2-0.4[a]	—	0.01-0.03
Copper and Alloys	2-4	—	1-3	0.01-0.03
Zinc Alloys and Castings	1-2	0.1-0.3	—	0.01-0.03

[a] Fluoride source is typically fluoroboric acid or ammonium bifluoride. Sulfamic acid may also be added at 1-2 oz/gal.

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Table IV. Operating Parameters and Applications for Acid Pickling Steel and Stainless Steel by Immersion

Acid	*% v/v*	*Temperature, °F*	*Fluorides, oz/gal*	*Wetters, oz/gal*	*Inhibitors, oz/gal*
Hydrochloric	20-50	80-120	3-5	0.01-0.03	0.002-0.004
Sulfuric	20-40	90-150	1.5-3.0	0.01-0.03	0.002-0.004
Phosphoric	25-45	90-150	0.5-2.0	0.01-0.03	0.002-0.004

lic smuts and scales do not respond well to the acid dip. A more aggressive treatment is supplied by the acid pickle. Some heat-treat scales, weld scales, rusts, and oxides (formed by buffing or polishing operations) are readily attacked and removed in an appropriate acid pickle bath. The solution will also perform the functions of the acid dip. A typical acid pickle contains inorganic acids, such as hydrochloric, sulfuric, hydrofluoric, and phosphoric; and deflocculents, wetting agents, and inhibitors.

In some immersion or electrolytic applications scales are seen to literally peel off in sheets and rusted surfaces "whiten." The acid pickle, when used in double-cleaning cycles (immersion or electrolytic), is usually the first acid step, followed by the second electrocleaner and a final acid dip.

DESCALING ACID

This process bath is a step above the acid pickle in regard to chemical strength and application. The general focus is removal of heavy deposits: rusts, scales (hot forging or rolling, casting), and other heat treatments. The bath constituents are similar to the acid pickle, but contain higher levels of accelerators such as fluorides and chlorides. Operating parameters: concentration, temperature, and time, may be increased when compared to the acid pickle. Descaling acids can be used by immersion or electrolytically. These baths are sometimes used to pretreat parts off line before processing in a standard finishing line.

The pickling requirement is a critical factor of time, temperature, and concentrations of the components. Times may range from 5 to 30 minutes. This makes the incorporation of an inhibitor very important. Surface pickling can be accomplished with minimal attack on the base metal, while also greatly mini-

Table V. Operating Parameters and Applications for Acid Pickling Steel and Stainless Steel Cathodically

Sulfuric Acid, % v/v	*Temperature, °F*	*Fluorides, oz/gal*	*Chlorides, oz/gal*	*Wetters, oz/gal*	*Inhibitors, oz/gal*
5-10	90-120	1.5-3.0	3.0-4.0	0.01-0.03	0.002-0.004

4-6 V. 30-50 A/ft^2. Use chemically pure lead anodes or carbon.
For any cathodic acid application using carbon anodes in the presence of fluorides, the best resistant grade of carbon to fluoride attack should be used.

Table VI. Operating Parameters and Applications for Descaling Steel and Stainless Steel by Immersion

Acid	*Acid Concentration, % v/v*	*Temperature, °F*	*Fluorides, oz/gal*	*Chlorides, oz/gal*	*Wetters, oz/gal*	*Inhibitors, oz/gal*
1. Sulfuric	7-12	90-160	4.0-6.0	6.0-8.0	0.01-0.03	0.002-0.004
or						
2. Hydrochloric	7-12	90-160	4.0-6.0	—	0.01-0.03	0.002-0.004

mizing hydrogen embrittlement.

Stainless steels may be passivated as follows:

40% v/v of 42°Bé nitric acid at 75-145°F (24-63°C).
25% v/v of 42°Bé nitric acid, 6 oz/gal of molybdic acid at 70-150°F (21-66°C).

Aqueous solutions of citric acid at 120 to 140°F (49-60°C) may also be evaluated.

Note: Comprehensive information describing electropolishing (the anodic brightening and descaling of metals) and use of the Wood's nickel strike are in the chapter titled "Surface Preparation of Various Metal Alloys Before Plating and Other Finishing Applications."

ACID TREATMENT OF OTHER METALS AND ALLOYS

Aluminum

Bright Dipping

1. Nonetch aluminum soak cleaner.
2. Chemically polish in a special acid solution consisting of: 94% v/v of 85% phosphoric acid and 6% v/v of 42°Bé nitric acid at 180-185°F (82-85°), until desired surface polishing is achieved.

Descaling

1. Nonetch aluminum soak cleaner.
2. 3-5% sulfuric acid or phosphoric acid dip. Neutralizes and conditions the surface.
3. Chemically polish in 15-20% v/v sulfuric acid and 30-40% by wt. of ferric sulfate at 100-140°F (38-60°C). Solution is wetted and specially inhibited.
4. Tarnish inhibit in dip application using a soap (mechanical tarnish inhibit film) or apply on organic topcoat such as a lacquer.

Conditioning for Plating

Note: Comprehensive information describing aluminum alloys, castings, and suggested deoxidizer/desmutting baths is described in the chapter titled, "Surface Preparation of Various Metal Alloys Before Plating and Other Finishing Applications."

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Brass and Copper Alloys

Descaling—Bright Finish

1. Moderately alkaline soak cleaner.
2. 5% v/v sulfuric acid dip. Neutralizes and conditions the surface.
3. Chemically polish in solution consisting of: hydrogen peroxide at 20-25% v/v and 0.3-0.5% v/v sulfuric acid at 90-11°F (32-43°C). Solution is wetted and specially inhibited. A golden-brown surface film must develop with minimal surface gassing to obtain desired surface polishing. 2-5 minute immersion should cover most cycle applications.
4. 5% v/v sulfuric acid dip for 10-15 seconds to dissolve the protective brown film.
5. Tarnish inhibit in dip application using either a soap (mechanical tarnish inhibit film) or a benzotriazole (active surface antioxidant).
6. Optionally lacquer (dip or electrolytic) or apply electrolytic chromate.or

1. Moderately alkaline soak cleaner.
2. 5% v/v sulfuric acid dip. Neutralizes and conditions the surface.
3. Chemically polish in 15-20% v/v sulfuric acid and 30-40% by wt of ferric sulfate at 100-140°F (38-60°C). Solution is wetted and specially inhibited.
4. Tarnish inhibit in dip application using either a soap (mechanical tarnish inhibit film) or a benzotriazole (active surface antioxidant).
5. Optionally lacquer (dip or electrolytic) or apply electrolytic chromate.

If the scale is very heavy, the following mixed acid may be required.

1. Moderately alkaline soak cleaner.
2. Descale in a solution consisting of: 44% v/v of 66°Bé sulfuric acid, 20% v/v of 42°Bé nitric acid, balance water, containing 0.25 oz/gal of sodium chloride, 90-110°F (32-43°C). Monitor solution action to avoid etching, if a bright, polished finish is required.

Descaling—Matte Finish

1. Moderately alkaline soak cleaner.
2. Immersion treatment in solution consisting of 2-3% v/v sulfuric acid and 2-4 oz/gal of sodium or ammonium persulfate, at 80-95°F (27-35°C).or

1. Moderately alkaline soak cleaner.
2. Immersion treatment in solution consisting of: 75% v/v of 85% phosphoric acid and 25% v/v of 42°Bé nitric acid, 90-120°F (32-49°C).

Cast Iron

Standard alkaline soak clean, followed by alternate hot and cold rinsing to push solutions out of pores. Anodically electroclean in alkaline descaler. Parts exiting the electrocleaner should have a uniform light-yellow cast. Dip in 15 to 20% v/v hydrochloric acid or 5 to 10% v/v sulfuric acid to dissolve oxides, desmut, and form an active surface for plating. Control acid dip to avoid overtreatment. Cast iron

has a low hydrogen overvoltage, which can reduce electroplating efficiency. Extended immersion in the acid will further reduce this efficiency. Mass finishing may be a better option to remove rust and scale.

Gold and Gold Alloys

Brightening

1. Alkaline soak clean.
2. Anodic treatment at 6-12 V in a solution consisting of 20 oz/gal sodium citrate and 5 oz/gal Rochelle salts, 80-90°F (27-32°C).

Gold may be recovered by dummying at low current density onto stainless steel cathodes, also using stainless steel anodes.

High Carbon and Case-Hardened Steels

High carbon steel can be heavily scaled. Both metals are susceptible to hydrogen embrittlement. In addition pickling high carbon steels may generate heavy surface smuts. Solutions containing sulfuric acid, fluorides, organic acid complexors, inhibitors, pickle aids, and wetting agents are preferred to process these metals. The acid bath surface tension is reduced to promote superior wetting of the substrate. Once the scale or smut is removed an inhibitor film forms to prevent additional pickling. This prevents hydrogen embrittlement of critical parts, such as spring steel, and repeated smutting of high carbon steels. In some process cycles a follow-up electrocleaner is required to remove the inhibitor film following the acid treatment. The final preplate dip should be a dilute, 3-5% v/v sulfuric acid solution to neutralize alkaline films and provide a clean, water-break-free surface. Sometimes the parts can be cleaned in an off-line eletropolishing or mass finishing step before transfer to the actual process line.

1. Soak clean or preclean as described previously.
2. Anodically clean in an alkaline descaler.
3. Acid dip as described (see appropriate tables for suggested chemical constituents and operating conditions). In a double cleaning cycle the first acid may be an anodic electropolishing treatment.

Low Carbon Steel

1. Alkaline soak clean.
2. Anodically electroclean (moderate caustic, silicated, complexed, wetted blend). Use at standard operating parameters for rack and barrel.
3. Acid dip in either hydrochloric acid at 5-25% v/v or sulfuric acid at 3-10% v/v. Depending on surface condition, wetters, inhibitors, or deflocculents may be required. Use at standard operating parameters.

Magnesium Alloys

Removal of corrosion, heavy oxides, and mill scale:

1. Alkaline soak clean.
2. Acid immersion treatment in either of the following solutions: A. Hydrofluoric acid at 20-25% v/v, 75-90°F (24-32°C) or B. 20 oz/gal of 85% phosphoric acid, 2-3% v/v of 42°Bé nitric acid, and 0.2-0.3 oz/gal

ammonium bifluoride, 75-90°F (24-32°C).

or

Chromic acid containing solution consisting of: 44-48 oz/gal chromic acid, 3-4 oz/gal sodium nitrate, 1.5 oz/gal sodium chloride, 0.1 oz/gal sodium sulfate, 65-90°F (18-32°C).

Nickel and Cobalt Alloys

1. Alkaline soak clean.
2. Cathodically condition in a highly conductive electrocleaner blended for steel.
3. Acid dip in a solution consisting of 50% v/v of 70% hydrofluoric acid and 7% v/v of 42°Bé nitric acid at 75-90°F (24-32°C).

Silver and Silver Alloys

1. Alkaline soak clean.
2. Acid dip in either of the following solutions: A. 66% v/v of 42°Bé nitric acid at 75-160°F (24-71°C). B. 88% v/v of 66°Bé sulfuric acid, 75-90°F (24-32°C). C. 22% v/v of 42°Bé nitric acid at 75-90°F (24-32°C).

Titanium

1. Alkaline soak clean.
2. Acid treatment in solution consisting of 40% v/v of 42°Bé nitric acid and 2-3% v/v of 75% hydrofluoric acid, at 120-135°F (52-57°C).

Zinc and Zinc Alloys

Comprehensive information describing zinc alloys, castings, and suggested acid baths is described in the chapter titled "Surface Preparation of Various Metal Alloys Before Plating and Other Finishing Applications."

Activation of Bright Nickel Electroplate

There are two effective acid solutions for activating passive nickel deposits and to salvage reject parts. Their application is recommended for sulfur bearing electrolytic nickel deposits.

The immersion dip consists of 5 to 10% v/v sulfuric acid and 2 to 4 oz/gal of potassium iodide at 75 to 90°F (24-32°C), 1 to 5 minutes or as required. A cathodic activation of nickel consists of 5 to 11% v/v sulfuric acid, 1 to 3 oz/gal fluoride, 2 to 4 oz/gal chloride at 5 to 7 V for 1 to 2 minutes (as required) at 20 to 40 A/ft^2 and 75 to 120°F (24-49°C).

ELECTROPOLISHING

BY KENNETH B. HENSEL
ELECTRO POLISH SYSTEMS INC., MILWAUKEE; www.ep-systems.com

The electropolishing system smoothens, polishes, deburrs, and cleans steel, stainless steel, copper alloys, and aluminum alloys in an electrolytic bath. The process selectively removes high points on metal surfaces, giving the surface a high luster.

HOW IT WORKS

The metal part is immersed in a liquid media (electrolyte) and subjected to direct current. The metal part is made anodic (+) and a metal cathode (-), usually 316L stainless steel or copper, is used. The direct current then flows from the anode, which becomes polarized, allowing metal ions to diffuse through the film to the cathode, removing metal at a controlled rate. The amount of metal removed depends on the specific bath, temperature, current density, and the particular alloy being electropolished. Generally, on stainless steel, 0.0005 in. is removed in 1,500 amp-minutes per square foot. Current and time are two variables that can be controlled to reach the same surface finish. For example, 100 A/ft^2 electropolished for 5 min is 500 amp-minutes; 200 A/ft^2 for $2^1/2$ min is 500 amp-minutes. Both pieces of metal would have about the same surface profile. Current densities of 90 to 800 A/ft^2 are used in this process depending upon the part to be polished and other parameters. Electropolishing times vary from about 1-15 minutes.

ADVANTAGES

Conventional mechanical finishing systems tend to smear, bend, stress, and even fracture the crystalline metal surface to achieve smoothness or luster. Electropolishing offers the advantages of removing metal from the surface producing a unidirectional pattern that is both stress- and occlusion-free, microscopically smooth, and often highly reflective. Additionally, improved corrosion resistance and passivity are achieved on many ferrous and nonferrous alloys. The process micro- and macro-polishes the metal part. Micro-polishing accounts for the brightness and macro-polishing accounts for the smoothness of the metal part.

Deburring is accomplished quickly because of the higher current density on the burr, and because oxygen shields the valleys, enabling the constant exposure of the tip of the burr.

Because the metal part is bathed in oxygen, there is no hydrogen embrittlement to the part. In fact, electropolishing is like a stress-relieve anneal. It will remove hydrogen from the surface. This is important to parts placed under torque.

Another benefit is that bacteria cannot successfully multiply on a surface devoid of hydrogen, therefore, electropolishing is ideal for medical, pharmaceutical, semiconductor, and food-processing equipment and parts. The combination of no directional lines due to mechanical finishing, plus a surface relatively devoid of hydrogen, results in a hygienically clean surface where no bacteria or dirt can multiply or accumulate.

SUMMARY OF UNIQUE QUALITIES AND BENEFITS

Stress relief of surface
Removes oxide
Passivation of stainless steel, brass, and copper
Superior corrosion resistance
Hygienically clean surfaces
Decarbonization of metals
No hydrogen embrittlement
No direction lines
Low-resistance welding surface
Reduces friction
Both polishes and deburrs odd-shaped parts
Radiuses or sharpens edges depending upon rack position
Reduces annealing steps

SIMPLICITY OF THE SYSTEM

Practically speaking, three major process steps are necessary to electropolish most metal surfaces successfully:

1. Metal preparation and cleaning
2. Electropolish (electropolish drag-out rinse)
3. Posttreatment (rinse, 30% by volume of 42° Baumé nitric acid, rinse, deionized hot water rinse)

EQUIPMENT NEEDED FOR ELECTROPOLISHING

Electropolishing Tank

The electropolishing tank is generally constructed of 316L stainless steel, double welded inside and out. Stainless steel can withstand high temperatures, which are needed if too much water enters the electrolyte.

Polypropylene usually 3/4 to 1-in. thick, is another tank choice. This tank can withstand temperatures of 180-190°F.

Power Supply

The direct current source is called a rectifier. The rectifier is generally matched to the size of the electropolish tank. If the tank is to be cooled by tap water through a plate coil, no more than 5.0 A/gal should be used, therefore, in a 500-gal tank, the capacity of the rectifier should not be more than 2,500 A. If 3,500 A are needed, then the tank size must be increased to compensate for the increased wattage going into the tank (amps volts = watts).

Voltage is also determined by the number of amperes needed to electropolish the part. Generally, 600-3,000 A requires an 18-V DC output, and 3,500-10,000 requires a 24-V rectifier. Optimum running voltage is 9-13 V for stainless steel.

Aluminum requires a 30-40 V rectifier. Aluminum is run by voltage rather than amperage.

Racks

Electropolish racks for most metals are made of copper spines and crosspieces, which have been pressed in a thin skin of titanium. Copper, phosphor-bronze, or titanium clips are used and can be bolted on with titanium nuts and bolts.

Some racks are made of copper and copper spines and are coated with PVC. These racks are generally for electropolishing of aluminum, copper, brass, and bronze, although titanium can be used here instead.

When building a rack, remember that 1 in.^{2} of copper carries 1,000 A; therefore, if you use two spines of 1 +/÷ in., this rack will carry 500 A.

When large volumes of parts are to be processed, a specially constructed barrel may be used, or a tray.

Agitation

An air line is usually placed diagonally on the bottom of the electropolishing tank to stir up the solution, preventing temperature stratification. Air is not used directly under the parts to be electropolished because "white wash" can occur.

Mechanical agitation is the optimum method for part agitation. This brings fresh solution to the surface of the part for faster electropolishing. Other methods of agitation are mixer, filter-pump, or separate pump.

Filtration is used on many electropolishing systems. The solution lasts longer and the tank does not have to be cleaned as often. In high-technology operations this may be a requirement.

Temperature

Most electropolishing solutions must be heated and cooled during the operating period. Heating is accomplished by using quartz or Teflon-coated stainless steel electric heaters with controls. If steam is used, Teflon coils are used. Lead is no longer used because it is toxic.

Cooling is accomplished with 316L stainless steel plate coils. Stainless steel cannot be used for steam heating as most baths contain sulfuric acid, which attacks stainless steel at the high-temperature surface of the plate coil. Tank construction of 316L stainless steel is all right because excessively high temperatures (above 250°F) are not present.

Chillers are used when the tank solution will have 10-15 A/gal from the rectifier.

Heat exchangers are used when input amperage is above 5 A/gal.

TYPICAL SOLUTIONS

There are organic electropolishing baths, inorganic baths, and organic/inorganic baths. Some typical formulas are shown below.

Aluminum

Because it is amphoteric in nature, aluminum can be electropolished in both acid and alkaline electrolytes. The brightening process involves low rate of attack, use of high-purity aluminum, and requires prefinishing.

Alzac Process: First Stage (Brightening)

Fluoboric acid, 2.5%
Temperature, 85°F
Voltage, 15-30 V
Current density, 10-20 A/ft^2

The polarized film is stripped in hot alkaline solution. Anodizing, as usual, in the sulfuric acid bath follows. Only superpurity alloys (99.95%) should be used.

Polishing and brightening are obtained in concentrated acid-type solutions that feature greater stock removal and greater smoothing.

Battelle

Sulfuric acid, 4.7%
Phosphoric acid, 75%
Chromic acid, 6.5%
Al^{3+} and Cr^{3+}, to 6%
Current density, 150 A/ft^2
Temperature, 175-180°F
Voltage, 10-15 V

Chromic acid decreases the etching rate, but changes from the hexavalent to trivalent form in use. Sulfuric acid drops the cell resistance or voltage, but increases the etching rate.

Copper and Alloys

R.W. Manuel

Water, 100 parts by wt
Chromic acid, 12.5 parts by wt
Sodium dichromate, 37.5 parts by wt
Acetic acid, 12.5 parts by wt
Sulfuric acid, 10.0 parts by wt
Current density, 250-1,000 A/ft^2
Temperature, 86°F

H.J. Wiesner

Sodium tripolyphosphate, 14-16 oz/gal
Boric acid, 4-5 oz/gal
pH, 7-7.5 oz/gal
Temperature, 125-135°F
Current density minimum, 100 A/ft^2

S.B. Emery

Ammonium phosphate, 100 parts
Citric acid, 100 parts
Potassium phosphate, 25 parts
Water, 1,000 parts
Voltage, 6-25 V
Current density, 75-575 A/ft^2 (AC)

Nickel and Alloys

Sulfuric acid, 60% minimum
Chromic acid, to saturation
Water, as required

Sulfuric acid, 60% minimum
Glycerin, 200 ml/L
Water, as required

Nickel sulfate, 240 g/L
Ammonium sulfate, 45 g/L
Potassium chloride, 35 g/L
Orthophosphoric acid, 15-70%

Sulfuric acid, 15-60%
Water, balance

STEEL

Steel is more difficult to electropolish to the same degree of perfection as other metals, owing to variations. It has good potential in industrial applications, as well as for brightening and smoothing; however, results are not consistent because of great variations in composition and surface conditions from mills and/or heat treatment.

R. Delaplace and C. Bechard

Pyrophosphoric acid, 400 g
Ethyl alcohol to make 1 L
Temperature, 20°F
Current density, 300 A/ft²
Cooling of the electrolyte is required, and water must be absent.

C. Faust

Sulfuric acid, 15%
Phosphoric acid, 63%
Chromic acid, 10%
Current density, 50-1,000 A/ft²
Temperature, 125°F
This solution has a finite life.

Weisberg and Levin

Lactic acid, 33%
Phosphoric acid, 40%
Sulfuric acid, 15.5%
Current density, 100 A/ft²
Temperature, 65-90°F
Polishing rate is quite low; 1-2 hr are required.

Hammond, Edgeworth, and Bowman

Phosphoric acid, 55-85%
Trialkali metal phosphate, 1-15%
Alkali metal sulfate, 0.5% minimum

Stainless Steel

Stainless steel is the most popular electropolished metal today. It retains its finish, and no aftertreatment is required.

H. Uhlig

Phosphoric acid and glycerine, 90%
Glycerin, >50%
Current density, >20 A/ft²
Temperature, >200°F
J. Ostrofsky
Citric acid, 55%
Sulfuric acid, 15%

Current density minimum, 100% A/ft^2
Temperature, 200°F

This solution freezes below 130°F. Alcohol is recommended to reduce the freezing point.

C. Faust

Sulfuric acid, 15%
Phosphoric acid, 63%
Current density minimum, 50 A/ft^2
Temperature, 80-175°F

I. Clingan

Phosphoric acid, 56%
Sulfuric acid, 27%
Diethyleneglycolmonobutylether, 7%
Temperature, 125-165°F
Weisberg and Levin
Lactic acid, 33%
Phosphoric acid, 40%
Sulfuric acid, 13.5%
Current density, 75-300 A/ft^2
Temperature, 160-200°F

C. Faust

Phosphoric acid, 56%
Chromic acid, 12%
Current density, 100-1,000 A/ft^2
Temperature, 80-175°F

J. Kreml

Sulfuric acid, 10-60%
Glycolic acid, 20-80%
Current density minimum, 150 A/ft^2
Temperature, 175-212°F

CLEANING AND SURFACE PREPARATION

BY BRAD GRUSS
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The quality of coatings, regardless of the type, or process of application, vary greatly in terms of quality offered. One statement about pretreatment is becoming more true every day: "You can make a poor coating perform with excellent pretreatment, but you can't make an excellent coating perform with poor pretreatment!" The point is that today, with the emphasis on quality coupled with new technology in coatings (powder, electrocoat, water-based, and high solids), the shift of burden of performance is pointed directly at pretreatment. Having a solid process, which meets or exceeds expectations, must be all encompassing to address soils, metals, water quality, and the process, control, and maintenance of the pretreatment system. Here we provide a broad stroke on the basics, and hope to promote further investigation by our readers depending on the specifics of each product and their needs. The best way to begin pretreatment is with a series of questions designed to promote both specifics and generalities that have impact on the process.

FINISHER FACT-FINDING QUESTIONNAIRE

1. What base metals are pretreated?
2. What soils are on incoming metals?
3. What soils are applied to metals in-house?
4. What is the production flow of the products?
5. What production assemblies are premanufactured and stored? Do they corrode in storage? Do the soils age or become more difficult to remove?
6. What are the physical size limitations of your products? Can they be classified as to percentage of small or light, medium or large, and heavy or bulky?
7. How many of what part must be finished per shift?
8. During welding and fabricating are soils entrapped or sandwiched between metals?
9. Do you preclean prior to welding? If not, how much carbonaceous residue is left on or near weldments?
10. Do you physically abrade via wire brush, grind, steel shot, or sandblast those corroded, carbonaceous areas?
11. If you have weld spatter, does it interfere with finishing?
12. What paint specifications are in-house?
13. What paint specifications do your customers have?
14. Do you currently meet your expectations on production parts?
15. Do your currently purchased coatings meet your specifications on production parts?
16. Do your currently purchased coatings meet your specifications on test panels?

17. What is your current pretreatment process? Does it provide a quality base for adhesion and salt spray?
18. What are your current process controls for pretreatment and finishing? Do they get done? Are they logged, recorded, and reviewed?
19. What preventative maintenance steps are taken? Is it by poundage, hours, weeks, or need?
20. What space limitations do you have for expanding pretreatment and finishing?
21. What are the local, state, and federal laws and regulations for effluent emissions? Do you currently meet these?
22. What safety program do you have? What products can be replaced? What energy sources do you have? What are the limitations?
23. What manpower resources are available?
24. What type of training do you or your vendors offer?
25. What are your financial resources or limitations?
26. What is your competition doing in the marketplace and where do you fit in the market niche? Where do you want to be? What do you have to accomplish to be there from a finishing perspective?

THE MECHANISMS OF AQUEOUS CLEANING

Wetting: Cleaners contain surface-active agents (surfactants) that "wet out" the soil. This loosens the soil-surface bond by a reduction of surface tension. Wetting is actually the first requirement for soil removal.

Emulsification: This occurs following wetting. Simply stated, emulsification is the dispersion of two mutually immiscible liquids (i.e., oil and water). Primary factors affecting emulsification are type of oil encountered and choice of surfactants used in th cleaner. Secondary factors include pH, temperature, and concentration of the cleaning solution.

Neutralization (saponification): A reaction where in fatty acid soils (oils) are neutralized in the presence of alkali. The result is generation of water-soluble soaps that assist in cleaning and rinsing. Examples of fatty oils are vegetable (corn), animal fats (lard), and marine (whole).

Solubilization: "Like dissolves like." This simply means that the solubility of water-insoluble soils (oil) is increased in the presence of surfactants.

Displacement: Soil is displaced from the surface as a result of select surfactant activity. This is particularly desirable in spray applications where the soil can be removed using oil-skimming techniques.

Mechanical Action: This can greatly increase the speed and efficiency of soil removal in aqueous cleaning systems. It can be accomplished by solution movement or movement of the part itself. Examples include air, impeller, ultrasonic, spray, and gas scrubbing (electrolytic).

Sequestration: Water must be properly conditioned or softened in order for effective cleaning and rinsing to occur. Hard water consists of divalent calcium, magnesium, and iron ions that must be complexed to avoid generation of insolubles that would otherwise interfere with cleaning and rinsing. In effect, cleaners with adequate sequestering ability obtain better surfactant performance.

Deflocculation: A cleaning mechanism whereby soil is peptized or broken down into very fine particulates and maintained in a dispersive phase to prevent ag-

glomeration (coming together).

DETERMINING A CLEAN SURFACE

A *clean surface* is one that is free of oil and other unwanted contaminants. The degree of cleanliness required is dependent on the operation or process to which the part or product must pass. Manufacturers utilizing the cell cleaning concept or workstation cleaning are typically cleaning between process steps. Situations like these usually do not require the degree of cleanliness needed for final prepaint preparation.

A *water break-free surface* tells you that you have removed all organic soils. The parts exiting the last pretreatment or rinse stage prior to drying will show a uniform sheeting of the rinse water indicating an organically clean surface. The water break-free surface has been *the* long-standing test for cleanliness. The key to this test is using fresh uncontaminated rinsewater. Detergent additives or rinse aids used in a final rinse may hide poor cleaning. Additionally contaminated rinses due to poor overflow may also mask poor cleaning due to the surfactant's wetting ability.

A *water break surface* tells you that you have not sufficiently cleaned and that organic soils are still present. The part will exhibit a surface that resembles a freshly waxed car surface after a good rain. There will not be uniform sheeting of the water but beading. Normally, poor cleaning is most often found on or near weldments, or in areas that receive poor spray impingement to the part.

Another test of a clean surface is the *white towel test*. Wiping a white towel across clean and dry surfaces will indicate the effectiveness of inorganic soil removal. Check flat surfaces and those areas most likely not to receive direct spray impingement.

In the *tape pull test*, apply scotch tape to a clean and dry surface, then remove the tape and place on a white piece of paper. This will also indicate the effectiveness of inorganic soil removal as the contrast allows for easy identification of remaining soils.

The *ultraviolet (UV) detection* requires soiling with a fluorescent oil, cleaning, and inspecting under ultraviolet light. The degree of cleanliness can be quantified by a numbering system. This is accomplished through photoelectron emission or reflectance. The higher the reflectance, the cleaner the surface is.

THE IMPORTANCE OF CLEANING

Cleaning of metals and other finishing-related substrates is the single most important consideration to successful coating application. Achieving clean surfaces has applications throughout a manufacturing facility: for corrosion protection, for welding operations, for part handling, for part inspection, and for metal finishing. All of these cleaning applications can and should have a quantitative degree of cleanliness required. The degree can vary from gross soil removal to a high degree of cleanliness, which surpasses the standard water-break-free test of cleanliness. The ultimate requirement is dictated by the requirements of the part, the process, the chemical type, and control of process parameters. With today's new coatings, a greater emphasis is placed on achieving a totally clean surface.

Factors That Affect Aqueous Cleaning

The success of a cleaner relies on more than just the functional chemistry that

comprises it. Effective cleaner-to-surface contact must be made. A number of factors must be considered, understood, and properly implemented and maintained for effective results. Failure to utilize a workable combination of these factors will often produce marginal results and render the cleaning system less effective.

There are several factors that directly impact aqueous cleaning. Because of their significance, each should be addressed: (1) application methods and equipment, (2) history and configuration of part, (3) soil, (4) type(s) of substrate(s), and (5) cleaner selection and operation parameters.

APPLICATION METHODS AND EQUIPMENT

Several questions must be answered in conjunction with the equipment and the application of the cleaner. The method of and amount of agitation must be determined. Chemicals must be selected in either the high-, medium-, controlled-, or low-foam category. More severe agitation or pressure at the nozzle, for example, would place your chemical choice in the least foaming category to prevent excessive foaming.

The temperature range of the process equipment should be known. Cleaners tend to be formulated with surfactants and detergents that offer optimal cleaning within a given temperature range. Typically, low temperature ranges from 90°F to 120°F, medium temperature ranges from 120°F to 140°F, and high temperature ranges from 140°F to 160°F. The trade-off becomes this. If you are using a cleaner designed for high temperatures, but the equipment can only maintain process heat at 120°F, the chances for poor cleaning and foaming are present. On the other hand if your chemistry is designed for low temperature and the process heat cannot be lowered to that range, you may experience stratification of the solution, and in severe cases oiling out of the cleaner's detergent package.

The length of time that the solution is in contact with the part must also be decided. Pretesting the parts with the cleaner for the allotted time is always advised. The process equipment, based on the length of each stage and the speed of travel, will yield a total contact time. Typically these times for cleaners range from 60 to 120 seconds; however, many coil lines operate in a range from 3–15 seconds. The chemical choice for cleaning should be made only when the process contact time is known.

History and configuration of the part play a key factor in not only cleaner choice, but also the application. Multiconfigured parts, for example, may be best suited for immersion cleaning rather than spray. Usually, machined castings, or parts with ports, threads, extensions, blind holes, etc., are very difficult to clean because the part positioning is typically fixed. In these cases, immersion, or immersion spray combinations, or rotating fixtures may be required. In addition to the configuration of the part, what is the history of the part? Is it a component, finished product, or subassembly? Will it be cleaned once, twice, or more before leaving the factory as a finished product?

Finally, how long may the part be staged, or stored? Will the surface corrode or tarnish, and will the in-process soil or rust inhibitor adequately protect without becoming more difficult to remove if the part is not in a just-in-time, or on a first-in, first-out inventory schedule?

SOIL AND SUBSTRATE AUDIT

Soils

There are many different types of soils used in a manufacturing facility. It is often assumed that all soils will be easily cleaned.The cleaning operation would be less difficult if all the individual soils were understood more completely. Soils are generally shop dirt, smut, oils, metal chips, and drawing, stamping, and buffing compounds.Upon completion of a soil audit, and the determination of a suitable cleaner, every effort should be made not to introduce new soils without pretesting.

Soils can be classified as organic or inorganic. *Organic soils* are oily, waxy films such as mill oils, rust inhibitors, coolants, lubricants, and drawing compounds. Alkaline cleaners should be used to clean organics. *Inorganic soils* include rust, smut, heat scale, and inorganic particulate, abrasives, flux, and shop dust. These inorganic soils are most easily removed by acidic cleaners.

Soils can also be classified by the degree of difficulty present in cleaning. Soils that are very difficult soils to remove include chlorinated lubricants, sulfurized lubricants, heavy-duty rust-inhibiting compounds, honey oils, buffing compounds, stearates, diecast release agents, and oxidized soils. Those that present a moderate degree of difficulty include fatty oils, waxy oils, heavy-duty hydraulic oils, mill oils, lapping compounds, and water-displacing rust inhibitors. Lastly, those soils that are relatively easy to clean are soluble oil-cutting fluids, synthetic cutting fluids, spindle oil, lightweight machine oils, mill oils, water-soluble and rust inhibitors, and vanishing oils.

The very difficult soils tend to be heat sensitive. Soils falling into the napthenic, paraffinic, chlorinated paraffin blends, or those containing waxes are generally heat sensitive to some degree. When you encounter this type of soil, it limits the variable of temperature. A heat sensitive soil of say 160°F requires you to adjust upward accordingly.

Specially formulated low-temperature cleaners rely on both soil displacement and slight emulsification. The blend of detergent systems built into the low-temperature cleaners is designed to reduce surface tension at the soil–metal interface. This unique factor enables removal of soils sensitive to heat at a low temperature; lower than the melting point of the waxes of that soil. This fact also produces less contamination if properly skimmed, resulting in longer tank life.

Substrates

The composition or chemistry of the base metal is one of the key limiting factors in cleaner choice. The cleaner must be chosen so as to be compatible with the metal being processed. In multimetal cleaning lines, nonferrous metals are typically the limiting factor. With these metals it is important to choose a cleaner that either does not attack or overetch the metal and where the attack is controllable or desirable.

A common mistake by both chemical vendors and manufacturers is when a base metal audit is made for cleaner selection, but not done completely. Most aluminum and zinc alloys with slightly different alloy content can vary widely in their ability to withstand either alkaline or acidic cleaner attack. In some cases, where minute etch is desirable, slightly more or less is unacceptable.

Substrates should be classified to make cleaner choice easier.

1. Ferrous or Iron Bearing: Cold-rolled steel, hot-rolled steel, stainless steel, and

Table I Cleaner Selection	
Alkaline Cleaner Characteristics	*Choice Relationship*
High Alkalinity pH 11-13.5	Noncausticsensitive metal processing only. Ferrous, stainless and yellow metals. Composites.
High Alkalinity (buffered) pH 10.5-12.5	Multimetal lines ferrous/nonferrous.
Low alkalinity pH 6-9	Nonferrous, aluminum, zinc, also effluent sensitive or restricted cleaning operations.
High-foam surfactants	Static tank cleaning, immersion systems, and spray wand nonrecirculating systems.
Controlled-foam surfactants	Agitated and oxidized soils of a waxy nature, heavy accumulations and short process contact time.
High temperature 140°F and above	Aged and oxidized soils of a waxy nature, heavy accumulations and short process contact time.
Medium temperature 120-140°F	Controlled soils. Light to heavy accumulations. Short to medium contact time.
Low temperature 90-120°F	Light to medium soils. Typical for medium contact time

Table II Typical Cleaner	
Part Type	*Dragout gal/1,000 ft²*
Vertical parts, well drained.	0.4
Vertical parts, poorly drained.	2.0
Vertical parts, very poorly drained.	4.0
Horiziontal parts, well drained.	0.8
Horiziontal parts, very poorly drained.	10.0
Cup shaped parts, very poorly drained	8 to 24 or more

ferrous castings.

2. Nonferrous: Aluminum, sheet, coil, castings, extrusions, zinc castings, galvanized, terne plate, and zinc plated.
3. Yellow Metals: Copper and brass.
4. Mixed Metals: Combinations of the above.
5. Composites: Mixtures of metals with other materials.

CLEANER SELECTION AND OPERATING PARAMETERS

Cleaner selection is codependent on the other aqueous cleaning factors discussed. Table I provides alkaline cleaner characteristics and the typical choice relationship.

POSTCLEANING RINSING STAGES

The purpose of rinsing is to remove or flush the remaining peptized soil, to neutralize the remaining alkaline salts, and to maintain a wet surface prior to entering the subsequent chemical stage. Initial rinsewater quality is very important as the part or product in question will only be as clean as the water is pure. Deionized or reverse osmosis treated water is used where a high degree of surface cleanliness is required.

Part configuration, drain vestibules, and adequate time are important con-

siderations in reducing overall water usage. Table II shows typical cleaner dragout that can be expected from various part configurations. Many improvements in rinse stages have been tested and employed to reduce the volumes of effluent to be treated. A common practice is the backflow rinses in a conventional five or more stage pretreatment system. The process is as follows:

1. Clean
2. Rinse
3. Phosphate
4. Rinse
5. Seal

Finishing system organizations have introduced unique design improvements to utilize rinsewater more efficiently and to assist in maintaining rinse cleanliness. Counterflow rinsing provides the cleanest possible water as the last contact with the part, and allows for multiple use rinse effectiveness.

The major control mechanisms for rinse tanks remain the control of pH and total dissolved solids (TDS). These tools have been automatically incorporated into washers, which allow sensing devices to either increase the overflow rate or reduce or drop TDS by automatic draining, thus maintaining consistency in water quality without regard to part shape, drag-in or drag-out.

VAPOR DEGREASING WITH CHLORINATED SOLVENTS

BY JAMES A. MERTENS
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Degreasing is an essential part of the modern production process, particularly in industries fabricating or assembling metal parts including aircraft, appliance, automotive, electronics, and railroad manufacturers. The process is widely used to remove oils and oil-borne soils, such as chips, metal fines, and fluxes, from objects that have been stamped, machined, welded, soldered, molded, or die-cast. Parts ranging from tiny printed-circuit assemblies to diesel motors can all be safely, completely, and quickly cleaned with modern vapor degreasing techniques, in most cases more effectively than with aqueous or semiaqueous processes, particularly when a high level of cleanliness is required.

Vapor degreasing is ideal for reaching into small crevices in parts with convoluted shapes to remove stubborn soils. Parts degreased in chlorinated solvent vapors come out of the process dry; there is no need for an additional drying stage, as in aqueous and semiaqueous processes.

The chlorinated solvents trichloroethylene, perchloroethylene, and methylene chloride are the solvents most commonly recommended for the vapor degreasing process for the following reasons:

- The chlorinated solvents have high solvency for organic materials, as well as good chemical compatibility with a wide range of materials (e.g., metals, glass, plastics, elastomers, etc.), so that parts consisting of several materials can be effectively cleaned in these solvents.
- They are virtually nonflammable in most end-use conditions (consult MSDS) because they have no flash point as determined by standard test methods.
- They have low latent heat of vaporization, resulting in relatively low energy requirements.
- They have relatively high stability and are noncorrosive. Further, vapor degreasing grades of the chlorinated solvents contain stabilizing additives that prevent the buildup of corrosive material and inhibit the formation of oxidation products.
- Because the vapors of the chlorinated solvents are heavier than air they can be contained relatively easily in degreasing equipment.
- The chlorinated solvents can be readily recycled, thus reducing waste and permitting high solvent "mileage" in a continuous degreasing operation.
- The latest generation of vapor degreasing equipment permits fully enclosed operation, thus virtually eliminating the loss of solvent vapors to the environment.

PRINCIPLES OF VAPOR DEGREASING

The traditional vapor degreasing process is carried out in either a batch or an in-line degreaser. The standard batch degreaser is an open-top tank into which the dirty parts (the "work") are lowered (see Fig. 1). Solvent in the bottom of the tank is heated to produce vapor, and since the vapor is heavier than air it remains in the tank. Cooling coils below the lip of the tank create a cool zone, which forms the upper boundary of the vapor zone.

On contact with the cooler work the vapor condenses into pure liquid solvent, which dissolves the grease and carries off the soil as it drains from the parts into the reservoir of solvent below. The cleaning process continues until the work reaches the temperature of the vapor, at which point condensation ceases and the work is lifted out of the vapor, clean and dry.

The degreasing process may be supplemented by adding a spray lance to the open-top degreaser so that hard-to-remove soils can be flushed off by the operator. In addition many degreasers also contain one or several immersion tanks below the vapor zone so that parts can be lowered into liquid solvent — often in a tumbling basket — before being raised into the vapor for final rinsing.

If scrubbing is required to remove heavy oil deposits and solid soils, ultrasonic cleaning can be added by installing transducers in the degreaser. When ultrasonic energy is transmitted to a solution, it produces cavitation — the rapid buildup and collapse of thousands of tiny bubbles, which impart a scrubbing ac-

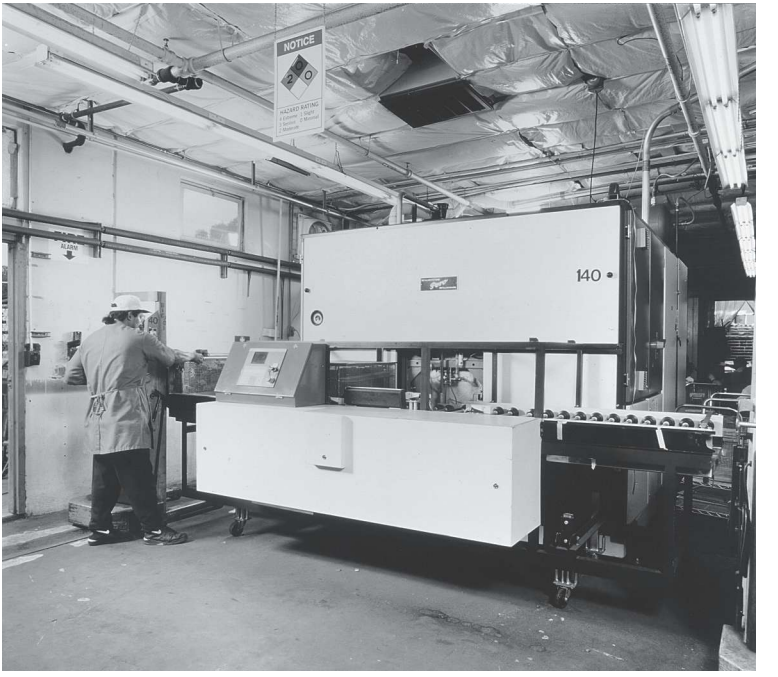


Fig. 1. Typical batch open-top vapor degreaser.

tion to the surface of soiled parts.

Although the vapor generally stays below the cool zone of an open-top degreaser there is always some solvent loss. Drafts in the area around the degreaser will cause solvent vapor to be pulled out. Parts loading causes losses as work to be cleaned disturbs the solvent/air interface. In addition cleaned parts may also carry solvent with them when removed from the degreaser. Up to 70% of the solvent in a traditional open-top degreaser can be lost through these factors over a year. Consequently, procedures are called for to minimize this loss, in order to provide a working environment in which vapor exposure is below the levels permitted by Occupational Safety and Health Administration (OSHA) regulations and an industrial environment, which meets requirements set by the EPA. These procedures are outlined below.

In-line vapor degreasers include several types of conveyorized equipment — large, automatic units, which can handle a large volume of work and are enclosed to provide minimal solvent loss. These units include the monorail, cross-rod, and vibratory degreasers.

The monorail conveyorized degreaser uses a straight-line conveyor to carry parts into the degreaser, lower them into the vapor zone, raise them into a cooling zone, and finally out of the degreaser. This process is ideal when production rates are high and large parts to be cleaned can be suspended from hooks or hangers.

The cross-rod conveyorized degreaser is generally used for processing small parts in baskets, trays, or even mesh cylinders. In this equipment the parts are placed in the degreaser and removed from it at the same opening, while the conveyor carries the work through immersion dips, vapor zones, and drying zones. The vibratory degreaser is a patented unit. In this process the work is dipped in solvent then rises on a vibrating spiral elevator trough through a counterflowing rinse of clean solvent distillate, a vapor zone, and finally a drying section.

Although these units are enclosed there is still some solvent loss through the openings where work enters and leaves the equipment, and through the joints and seams of the equipment.

CHARACTERISTICS OF CHLORINATED SOLVENTS

For many years 1,1,1-trichloroethane (methyl chloroform or MCF) was the solvent of choice for vapor degreasing because of its status as a non-VOC; it was not classed as a VOC compound under federal regulations because it does not contribute to the generation of ground-level ozone and the consequent production of urban smog. This situation changed drastically at the end of December 1995, when MCF was phased out of production for all uses except chemical feedstock, under the provisions of the U.S. Clean Air Act and the international Montreal Protocol, due to its action as a depleter of stratospheric ozone.

This led to a misunderstanding in many quarters that all chlorinated solvents were coming under a ban. In fact corporate edicts in some companies required their manufacturing divisions to cease using chlorinated solvents for degreasing as soon as practicable. This unfortunate misunderstanding has led a number of companies to experiment with a variety of alternate cleaning technologies.

The fact is, chlorinated solvents are still very viable products and remain one of the best choices for surface cleaning and vapor degreasing. Trichloroethylene, perchloroethylene, and methylene chloride are not regulated for ozone-de-

Table I: Physical Properties of Chlorinated Solvents[a]			
Properties	***Trichloriethylene***	***Perchloroethylene***	***Methylene Chloride***
Chemical formula	C_2HCl_3	C_2Cl_3	CH_2Cl_2
Molecular weight	131.4	165.8	84.9
Boiling point	189°F	250°F	103.5°F
	87°C	121.1°C	39.7°C
Freezing point	–124°F	–9°F	–139°F
	–86.7°C	–22.8°C	–95°C
Specific gravity	1.456	1.619	1.32
Density (lb/gal)	12.11	13.47	10.98
Density (kg/L)	1.456	1.619	1.32
Vapor density	4.53	5.76	2.93
Viscosity	0.54	0.84	0.41
Flash point	None	None	None
Flammable limits (volume of solvent in air)	8-9.2% (saturation)	None	14-22%
Kauri butanol value	129	90	136
Solubility (g/100g)			
Water in solvent	0.04	0.0105	0.17
Solvent in water	0.10	0.015	1.70

pleting potential (ODP). In fact these three solvents have been approved under the U.S. Environmental Protection Agency's Significant New Alternatives Policy (SNAP) as replacements for 1,1,1-trichloroethane. When the EPA published its SNAP ruling for ozone depleting substances on March 18, 1994 (see *Federal Register* 59 FR 13044-13161), it gave industry the official go-ahead to consider the three chlorinated solvents as acceptable alternatives to 1,1,1-trichloroethane in surface cleaning as well as other applications.

This policy also pointed out that worker exposure and environmental emissions of these solvents should be controlled properly and in accordance with other workplace, environmental, and consumer regulations established by the EPA and other agencies. The policy is particularly applicable, however, in cases where nonflammability is a critical prerequisite for safety and where effects on personal health and the environment are reduced to a minimum by engineering and operating design.

Each of the three chlorinated solvents has its own advantages for specific applications, based on its physical profile (see Table I for physical properties).

Trichloroethylene (TCE) is a clear, heavy liquid (12.11 lb/gal) with excellent solvency. Long recognized for its cleaning power, TCE boils at 189°F (87°C) and freezes at -124°F (-86.7°C). The high density of TCEs vapor (4.53 times that of air) assures low vapor loss and easy recovery from vapor degreasing systems.

TCEs aggressive solvent action works well on the oils, greases, waxes, tars, lubricants, and coolants generally found in the metal processing industries. It is especially effective in removing difficult soils such as semicured varnish or paint films, heavy rosins, and buffing compounds.

Perchloroethylene (PCE or perc, also called tetrachloroethylene) is a clear, colorless liquid with a distinctive, somewhat ether-like odor. It has the highest boiling point (250°F, 121.1°C) and freezing point (-9°F, -22.8°C), weight (13.47 lb/gal), and vapor density (5.76 times that of air) of the chlorinated solvents.

The high boiling point of PCE makes it especially effective in removing high-melting pitches and waxes and for cleaning grossly contaminated parts.

The high temperature of PCE vapors also permits complete and thorough drying of work by vaporizing moisture entrapped in porous metals, deeply recessed parts, and blind holes.

Methylene chloride (MEC, also called dichloromethane) is a powerful and versatile chlorinated solvent known for its high solvency capabilities. MEC has the lowest boiling point (103.5°F, 39.7°C) and freezing point (-139°F, -95°C) of the chlorinated solvents, as well as the lightest vapor density (2.93 times that of air) and weight (10.98 lb/gal). Because of its low boiling point MEC is often used for degreasing sensitive parts such as thermal switches and thermometers, which would be damaged by high temperatures. It is also chosen when parts must be near room temperature after cleaning for immediate handling or for tolerance testing and measurements.

These three solvents are widely used in surface cleaning, particularly in the vapor degreasing process. They are also used in cold cleaning, both dip and wipe methods, but the need to keep workplace vapor levels and environmental vapor losses low, in accordance with federal, state, and local regulations, limits their use in cold processes.

HEALTH CONSIDERATIONS

Health effects from exposure to chlorinated solvents have been studied extensively. Exposure to vapor concentrations within recommended guideline levels will not result in any known adverse effects on most people. Acute overexposure to vapors, however, may cause anesthetic or narcotic effects (solvent drunkenness) and death at high enough concentrations. Central nervous system effects and liver and/or kidney effects can result from chronic overexposure.

Proper ventilation when using chlorinated solvents is essential. Because chlorinated solvent vapors are heavier than air, high concentrations can accumulate in poorly-ventilated and low-lying areas, such as pits, causing dizziness, unconsciousness, and eventually death.

The chlorinated solvents have been subjected to a great many animal tests as well as epidemiological studies on humans to determine their health profile and so far the available scientific data indicate that they are not human carcinogens.

On the basis of animal tests, however, the chlorinated solvents, like many other chemicals, have been given cancer classifications by different agencies. The U.S. EPA classes all three solvents as B2, "Probable Carcinogen," while the American Council of Governmental Industrial Hygienists (ACGIH) classes PCE and MEC in Category A3, "Animal Carcinogen," and TCE in Category A5 "not suspected as a human carcinogen." All three solvents are listed under California's Proposition 65 as "Known to the State of California to cause cancer."

On the international scene the International Agency for Research on Cancer (IARC) places TCE and PCE in Group 2A, "probably carcinogenic to humans" and MEC in Group 2B, "possibly carcinogenic to humans." The German MAK commission lists PCE and MEC in Category IIIB, "possible carcinogen" and TCE in Category IIIA, "human carcinogen."

WHAT REGULATIONS APPLY

Users of chlorinated solvents for parts cleaning are aware of the regulations affecting the use, handling, transportation, and disposal of these solvents. They are regulated at the U.S. federal level under the Clean Air Act, the Clean Water Act,

Regulation	*Trichloroethylene*	*Perchloroethylene*	*Methylene Chloride*	*1,1,1-Trichloroethane*[a]
Ozone depletion (CAAA, Montreal Protocol)	No	No	No	Yes
VOC (Votatile Organic Compounds)	Yes	No[2]	No[3]	No[4]
state-to-state differences	<100 tpy marginal[1] <50 tpy serious <25 tpy severe <10 tpy extreme			
Permits	Yes	Yes	Yes	Yes
CAA Title V	10 tpy or combination of 25 tons HAP	10 tpy or combination of 25 tons HAP	10 tpy or combination of 25 tons HAP	10 tpy or combination of 25 tons HAP
HAP (Hazardous Air Pollutants NESHAP	Yes	Yes	Yes	Yes
Clean Water Act	Yes	Yes	Yes	Yes
OSHA	Yes	Yes	Yes	Yes
PEL (Permissible Exposure Limit)	50 ppm[5] Worker right to know Training Record keeping Reporting	25 ppm[6] Worker right to know Training Record keeping Reporting	25 ppm[7] Worker right to know Training Record keeping Reporting	350 ppm Worker right to know Training Record keeping Reporting
RCRA (Resource Conservation and Recovery Act Hazardous Waste)	Yes <100 kg: Cond. exempt 100-1,000 kg: Small quantity generator >1,000 kg: Large quantity generator	Yes <100 kg: Cond. exempt 100-1,000 kg: Small quantity generator >1,000 kg: Large quantity generator	Yes <100 kg: Cond. exempt 100-1,000 kg: Small quantity generator >1,000 kg: Large quantity generator	Yes <100 kg: Cond. exempt 100-1,000 kg: Small quantity generator >1,000 kg: Large quantity generator
CERCLA (Superfund reportable quantities)	Yes 100 lb Reportable quantity spill	Yes 100 lb Reportable quantity spill	Yes 100 lb Reportable quantity spill	Yes 100 lb Reportable quantity spill

[a]1,1,1-Trichlorothane included for comparison.

[1]In areas of the country classed as having marginal smog problem up to 100 tpy emissions are allowed to a facility. Allowable emissions are lower in areas with more serious problems.

[2]Perchloroethylene listed as exempt February 7, 1996, Federal Register, 4588.

[3]Methylene chloride listed as exempt July 8, 1977, Federal Register, 35314

[4]1,1,1-trichloroethane listed as exempt July 8, 1977, Federal Register 35314

[5]This limit in OSHA's 1989 rule has been overturned. dow continues to use these 1989 PELs in MSDS and labels.

[6]This limit in OSHA's 1989 rule has been overturned. dow continues to use these 1989 PELs in MSDS and labels.

[7]Currently challenged by industry ACGIH recommends 50 ppm, and Dow supports this limit.

Occupational Safety and Health Administration (OSHA) rulings, the Resource Conservation and Recovery Act (RCRA), and the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), as well as under state and local regulations aimed at controlling emissions.

Fortunately, these regulations are manageable because a great deal of assistance is available to help companies reach full compliance.

The following are the federal regulations governing the chlorinated solvents (see Table II). The *Clean Air Act Amendments* (*CAAA*) of 1990 legislated the phase-out of 1,1,1-trichloroethane as an ODS as of December 31, 1995.

VOC regulations under the Act apply to TCE and limit its emissions, particularly in ozone-nonattainment areas, in order to reduce smog formation. Exact requirements vary by state but generally include obtaining a permit allowing a specific amount of VOC emission from all sources within a facility.

The CAAA also calls for MEC, PCE, and TCE to be regulated as hazardous air pollutants (HAPs), but a complete set of regulations has not yet been issued for their control. EPA has, however, issued National Emission Standards for Hazardous Air Pollutants (NESHAP) for solvent cleaning with chlorinated solvents (*Federal Register*, Vol. 59, No. 231, 61801-61820). Other NESHAPs have been issued governing dry cleaning with PCE and the use of MEC in aerospace manufacture and rework, while NESHAPs governing the use of chlorinated solvents in wood furniture manufacture and asbestos brake cleaning are still awaited.

Clean Water Act. The Federal Clean Water Act defines chlorinated solvents as toxic pollutants and regulates their discharge in to waterways.

The *Occupational Safety and Health Administration (OSHA)* has set permissible exposure limits (PELs) for chlorinated solvents based on an 8-hour time-weighted average (TWA). The PEL for MEC is 25 parts per million (ppm), for PCE 100 ppm, and for TCE 100 ppm.

OSHA also specifies a minimum element of training for people working with the solvents. This includes how to detect the presence or release of a solvent, the hazards of the solvent, and what protective measures should be used.

OSHA's Hazard Communication (HAZCOM) standard regulates the labeling of all hazardous chemicals. Labels must contain a hazard warning, the identity of the chemical, and the name and address of the responsible party. Guidelines are provided by an OSHA compliance document [OSHA Instruction No. CPL-2-2.38 C (1990)] and by the American Standards Institute (ANSI) publication on precautionary labeling (ANSI Z129.1-1994).

Under the federal *Resource Conservation and Recovery Act (RCRA)*, wastes containing chlorinated solvents from solvent cleaning operations must be considered hazardous waste. Generators, transporters, and disposers of such hazardous waste must obtain an EPAID number.

According to the *Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund)*, if are portable quantity of a chlorinated solvent is released into the environment in any 24-hr period, the federal, state, and local authorities must be notified immediately. Reportable quantities are 1,000 lb of MEC and 100 lb of PCE or TCE.

This is only a checklist of regulations. It is important to confer with your environmental consultant or your legal counsel to determine just how these regulations apply to your business.

Other sources of help and advice are also available. For example the CAAA mandated a Small Business Ombudsman under EPA and a Small Business Assistance

Program (SBAP) in each state. State SBAPs provide a Small Business Ombudsman and a Technical Assistance Director to facilitate communications between the EPA and small businesses and to provide information on new and existing environmental regulations and policies. To qualify as a small business, a company must have fewer than 100 employees and must not be "dominant in its field." The federal Small Business Ombudsman provides literature and a toll-free hot-line to answer questions. Primary assistance for a business comes from the state SBAP office, and a small business can find out who to contact on a state level by calling the federal Small Business Ombudsman's hotline: 1-800/368-5888.

The Halogenated Solvents Industry Alliance (HSIA), a trade association of producers of chlorinated solvents, provides legislative and regulatory news for the solvent industry, sponsors research on chlorinated solvents, and presents information from research to the EPA and other solvent regulators. Users of chlorinated solvents can obtain information from this organization, as well as literature on the use of the solvents and how to comply with regulations, by calling HSIA at 202/775-0232.

Help is also available from the producers of chlorinated solvents. Producers and distributors are required by law to provide a MSDS, containing complete information on safety and handling, to all customers. In addition many producers also supply other forms of assistance.

PROCEDURES FOR REDUCING EMISSIONS

Emission standards for chlorinated solvent degreasing operations are now governed by EPA's NESHAP for new and existing halogenated solvent cleaning operations. These standards cover both vapor degreasing and cold cleaning with TCE, PCE, and MEC, as well as with chloroform. The goal of the NESHAP regulation is an overall reduction in solvent emissions of 50 to 70% of current nationwide emissions.

The NESHAP provides a number of control procedures for reducing solvent emissions from equipment. Operators of batch vapor degreasers and in-line cleaning machines may choose from a series of combinations of two or three of the procedures, which include:

- Freeboard ratio of 1.0: The height of the freeboard above vapor level must be equal to the width (shorter dimension) of the degreaser.
- Freeboard refrigeration device: This is a refrigerated system that supplements or replaces the traditional water cooling system and creates a cold air blanket above the vapor zone.
- Reduced room draft: Wind speed above the freeboard must not exceed 50feet per minute (15.2 m/min).
- Working-mode cover: This is defined as any cover or machine design that shields the cleaning machine from outside air disturbances during the parts cleaning cycle.
- Dwell: This refers to the time in which cleaned parts remain in the freeboard area above the vapor zone after cleaning. The EPA defines proper dwell time as 35% of the time required for the parts to cease dripping in the vapor zone.
- Superheated vapor (vapor temperature maintained 10°F above the

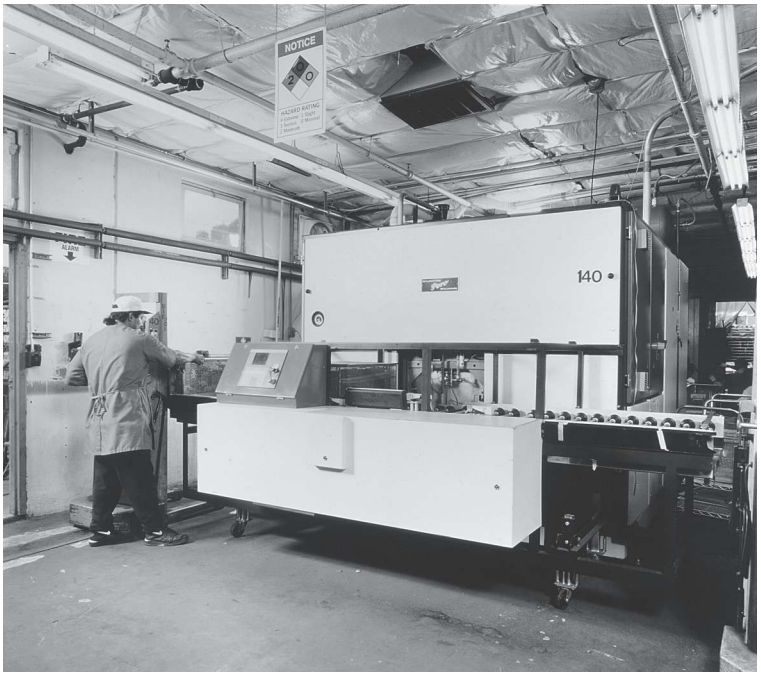


Fig. 2. Totally enclosed vapor degreaser can meet stringent environmental regulations.

boiling temperature of the solvent): This promotes more thorough drying of the work before it is removed from the degreaser.

- Carbon adsorption equipment in the ventilation system connected with the degreaser.

In addition vapor degreasing operators must employ an automated hoist or conveyor that carries parts at a controlled speed of 11 fpm or less through the complete cleaning cycle.

Each of these procedures used alone will reduce solvent loss by a respectable amount while combining two or three procedures reduces loss even further. For example creating a freeboard ratio of 1.0 in an open-top degreaser will reduce loss by 30 to 40% over the traditional process. Combining an increased freeboard ratio with superheated vapor or reduced room draft increases the control level to 60%. And in most cases, if a user combines three of the procedures, this will bring the control up to 70%. Table III illustrates how these incremental improvements can be brought about.

Many companies have found it cost effective to adopt one of the new degreasers, which have no air/vapor interface. These sealed and virtually emissionless units were first introduced in Europe to meet the stringent environmental regulations of some countries (see Fig. 2).

Typically these degreasers perform the cleaning operation in a sealed chamber into which solvent is introduced *after* the chamber in closed. Solvent vapor

Table III. Incremental Value of Upgrades[a]

NESHAP Option or Control Combination	Primary Control Option	Secondary Control Option	Tertiary Control Option
1	Freeboard ration = 1 30%	Superheated vapor +30%	Automatic cover +10% = 70%
2	Freeboard refrigeration 30%	Superheated vapor +30% = 60%	
3	Freeboard refrigeration 30%	Automatic cover +20% = 50%	
4	Freeboard ration = 1 30%	Superheated vapor +30%	Reduced room draft +10% = 70%
5	Freeboard refrigeration 30%	Reduced room draft +20% = 50%	
6	Freeboard refrigeration 30%	Freeboard ration = 1 +30% = 60%	
7	Freeboard refrigeration 30%	Dwell time +20% = 50%	
8	Freeboard ration = 1 40%	Reduced room draft +20%	Dwell time +10% = 70%
9	Freeboard refrigeration 30%	Carbon adsorption +30% = 60%	
10	Freeboard ration = 1 30%	Superheated vapor +30%	Carbon adsorption +10% = 70%

[a]All values are approximate, compiled from tests at a number of companies

is introduced as the final rinse and all vapors are exhausted after each cycle and passed into a solvent recovery system. With the sealed chamber control of solvent loss exceeds 90%; in other words virtually no solvent escapes.

Programmed automated operation permits a variety of cleaning programs including cold or warm solvent dipping, as well as vapor degreasing. Solvent recovery cycles make use of advanced methods of carbon adsorption and hot air desorption. The manufacturer of one such unit, a "closed open-top degreaser" with a large cleaning chamber, claims that solvent emission losses average less than 100 lb/yr. Solvent concentrations in the work area of the "closed open-top" unit average between 5 and 10 ppm, well below the permissible exposure limits set by OSHA for the chlorinated solvents.

Although these "emissionless" units can be costly, a number of plants in the U.S. have found them economical because they provide excellent compliance with safety and environmental regulations,conserve solvent, save floor space, and provide excellent parts cleaning performance. Several brands of these "emissionless" degreasers are available in North America today.

Most producers and distributors of chlorinated solvents provide support for solvent users. The Responsible Care initiative of the Chemical Manufacturers Association, to which all solvent producers subscribe, and the Responsible Distribution code of the National Association of Chemical Distributors require members to share product stewardship information, safety training, and regulatory data with customers. When selecting a supplier be sure to review what kind of support is provided.

NON-PHOSPHATE TRANSITION METAL COATINGS

BY BRUCE DUNHAM AND DR. DAVID CHALK, DUBOIS CHEMICALS, SHARONVILLE, OHIO

INTRODUCTION

Traditional iron phosphate and zinc phosphate conversion coatings have been used for more than a century as pretreatments for painting over a variety of metals. These "legacy" phosphate pretreatments have served well; however, environmental regulations restricting phosphate discharge, increased phosphate and zinc costs, and higher corrosion-resistance requirements have provided impetus for the development of non-phosphate alternatives. During the evaluations of the various technologies, it was discovered that these new non-phosphate pretreatment conversion coatings conferred significant cost savings and operational benefits along with their promised decreased environmental impact.

Considered new and experimental in the New Millennium (Y2K), these non-phosphate conversion coatings have gained significant traction in the pretreatment market and are rapidly becoming the technology of choice for paint and powder coating pretreatment. The purposes of this article are to provide background information for those new to non-phosphate pretreatments, and to answer some frequently asked questions about the non-phosphate conversion coatings.

WHAT ARE TRANSITION METAL COATINGS?

If iron phosphate and zinc phosphate can be referenced as "Traditional Metal Phosphates", the new non-phosphorus pretreatments can rightly be called "Transition Metal Coatings" (and will be referenced as "TMC" coatings in the remainder of this paper).

The term "transition metal" refers to a metal's position in the Periodic Table of the Elements, and is a term chemists use to describe the location of a group on the Table.

Zirconium (Zr) is at the center of a group of elements in the Periodic Table that are considered relatively environmentally friendly. (See Figure 1) Oxides of zirconium, titanium, and/or vanadium are the most commonly used transition metal coatings, with zirconium as the most frequently encountered transition metal. Note the location of these metals relative to chromium. The closer two given elements are to each other on the Periodic Table, the more similar their properties.

The first recorded application of zirconium oxide on steel was in 1996, when the first non-chrome seal rinse based on zirconium was introduced. Applied over a traditional metal phosphate conversion coating, the sealer conferred corrosion resistance that was close to that offered by the chromium seal rinse that had traditionally been used.

The chemistry was then modified in 1998 to serve as a chromium replacement for conversion coating on aluminum. The first applications for steel arrived in 2002.

WHAT IS THE APPEARANCE OF A TRANSITION METAL COATING PRETREATMENT?

Zirconium oxide is a very versatile material, taking on such varied forms as

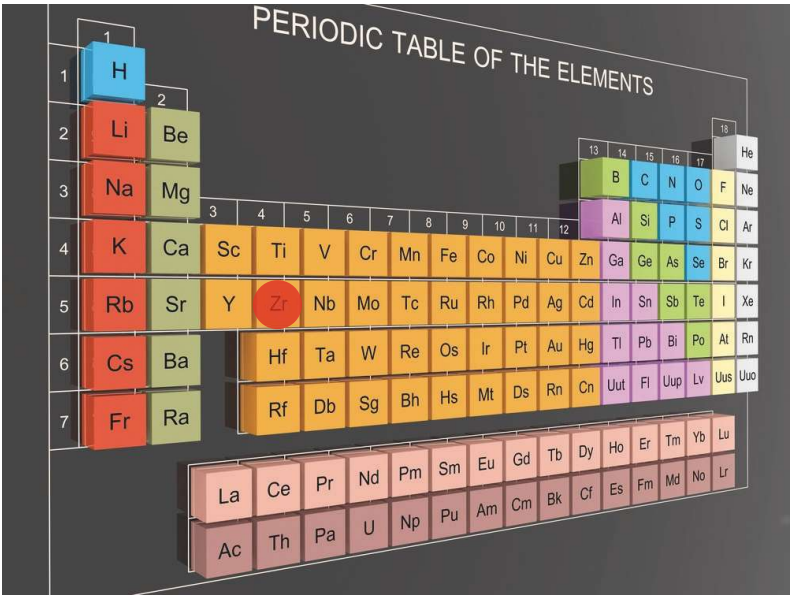


Figure 1. Periodic Table of Elements—note Zirconium's position.

ceramic bake ware, or when fused as jewelry, cubic zirconia. Imagine cladding a reactive metal in an inert substance like cubic zirconia, then applying a corrosion-resistant organic coating. This is the promise of the modern transition metal coatings, once referenced as nano-ceramic.

Figure 2 shows the relative thicknesses of the pretreatments. When gauging relative thickness of applied pretreatments, zinc phosphates are by far the heaviest and thickest pretreatments, depositing a mineral layer of some 1000 to 5000 nanometers (nm) in thickness. (Footnote 1) Iron phosphate applies typically a 250 to 500 nm thick coating. TMC pretreatments are approximately 50 nm, with some approaching 200 nm in thickness. They are the smallest, thinnest of the pretreatments, and are much thinner than the traditional metal phosphates they replace.

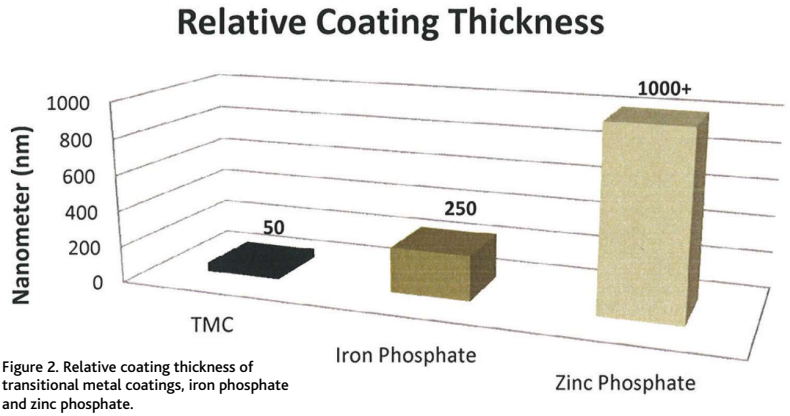


Figure 2. Relative coating thickness of transitional metal coatings, iron phosphate and zinc phosphate.

Figure 2a. Pretreatment comparison.

	TMC*	Iron Phosphate	Zinc Phosphate
Coating Structure	Amorphous	Amorphous	Crystalline
Typical Coating Thickness	~50 nm	~250 nm	1000 nm
Typical Coating Weight	50-150 mg^2 5-15 mg/ft^2	300-700 mg/m^2 25-65 mg/ft^2	2-3 g/m^2 180-300 mg/ft^2
*TMC = Transitional Metal Coating			

Much like traditional phosphates, TMC pretreatments can exhibit an array of colors, from nearly colorless, to tan, gold, and iridescent blue. Investigation has revealed that the appearance of pretreated metal is related to the thickness of applied coating. When the substrate is mild steel, the coating color goes from the original appearance of the substrate to light gold or tan, to a deep gold, to light blue and gold, to blue, to deep iridescent blue as the coating becomes more complete and increases in coating weight or thickness. As with traditional phosphates, the coating will become higher with increases in one or more of the following variables: chemical concentration, contact time, pressure (spray) or agitation (immersion), or temperature.

Another significant variable that impacts appearance of the coating is the type of steel a finished good is made from and the fabrication steps required to produce it. Heat treatment, welding, grinding, bending, blasting and other common manufacturing processes impact the amount of carbon (or scale) and iron at the surface of the part. The more carbon at the surface, the less reactive the surface is to the pretreatment solution. The more iron at the surface, the more reactive the surface is to the pretreatment solution. The photos below show a mild steel and hot rolled steel panel. Both panels were processed through a five-stage pretreatment process (Clean, Rinse, TMC, Rinse, Final Seal). The cold rolled steel is an even deep blue and the hot rolled steel is an even grey color because of the high carbon content at its surface.

WHAT ARE THE BENEFITS OF REPLACING PHOSPHATE CONVERSION PRETREATMENTS?

The primary benefit of replacing traditional metal phosphate pretreatments is significant and measurable cost savings in the operation/application of TMC pretreatments.

A significant benefit of replacing traditional metal phosphate with TMC pretreatments is the elimination of phosphorus from the waste stream. Phosphorus is becoming increasingly regulated, especially in areas near large bodies of fresh water such as the Great Lakes region; watersheds such as the Chesapeake Bay; and other areas where municipalities are trying to reduce phosphates in the water they discharge back into the environment. Minimizing

Footnote 1 - Note that a nanometer is on one billionth of a meter so the "smallness" of the concept is difficult to grasp. Put more succinctly, a nanometer is to a meter, what a marble is to the earth.



Figure 3 Top: Heavy zirconium oxide coating on hot rolled steel. Bottom: Heavy zirconium oxide coating on cold rolled steel.

phosphates in water is a strategy aimed at reducing eutrophication (Footnote 2). Adopters of TMC pretreatments often claim a green pretreatment strategy; the disposal procedures are generally inexpensive and uncomplicated.

TMC pretreatments are very reactive so heat is not needed to drive the reaction of the zirconium with the metal at the surface of the part. Thus, TMC pretreatments can run at ambient temperature, whereas the traditional metal phosphates require significant heat to drive the deposition reaction. This saves significant energy cost.

Most TMC pretreatments operate between 90 and 105°F. The heat carried in by the parts coming from the heated cleaner stage and the energy generated by the pump in a spray system are typically enough to maintain this temperature range.

Early adopters of TMC pretreatment technology enjoyed a minimum of 15%, to as much as 40% lower costs when converting from traditional metal phosphate pretreatments. These kinds of savings persist with the modern renditions of TMC pretreatments.

Another key benefit of TMC pretreatments is much better corrosion performance in service, as well as in accelerated testing, when compared to the legacy metal phosphates (10% to 30% longer salt spray hours and more intervals of cyclic corrosion testing have been observed with the first versions of this new class of chemistry). Several suppliers of pretreatment chemistry have developed TMC pretreatments that are approaching the performance of zinc phosphate. Because of high operational and disposal costs associated with running a successful zinc phosphate process, OEM's are investigating substituting TMC for zinc phosphate pretreatment, and several organizations have successfully made the transition.

There are several reasons why TMC pretreatments provide excellent corrosion protection. As previously noted, TMC contain elements that are near chromium on the period table; the oxides of these elements are relatively chemically inert so they do not dissolve as easily as phosphate metal coatings. Zirconium oxides are so stable that hydrofluoric acid, which is extremely corrosive and aggressive, is needed to dissolve them. Secondly, TMC are made of much smaller particles than amorphous iron phosphate coatings or zinc phosphate crystals. Because the par-

Footnote 2: Eutrophication: or more precisely hypertrophication, is the ecosystem response to the addition of artificial or natural substances, such as nitrates and phosphates, through fertilizers or wastewater, to an aquatic system.

ticles are so small, they are able to pack closer together. This results in less void space within the matrix of the TMC when compared to conventional phosphate metal coatings, so there is less room for air, moisture, and salts to travel to the substrate and cause corrosion. These coatings also inhibit galvanic corrosion because the transition metal has electrons that would be sacrificed prior to the electrons of the iron in the base metal.

Paint/powder coating adhesion and corrosion resistance also benefit because of the efficiency of the reaction. As stated, the efficient reaction results in very little sludge formation, so there is much less suspended solids in the pretreatment solution. As the pretreatment bath ages and the level of insoluble suspended solids increases, they can become incorporated in the phosphate coatings and/or dry down on top of them despite rinsing. The result is a powdery appearance on the parts that provides an inferior surface for adequate paint or powder coating adhesion. If you have managed an iron or zinc phosphate pretreatment process, you have likely made the decision to dump the bath at the end of its useful life due to powdery part appearance in your past.

The reader may be thinking, "If it saves costs, increases environmental compliance, and gives better performance, what's not to like?" The market agrees, and adoption of TMC pretreatments is therefore rapidly increasing in the marketplace.

HOW ARE TRANSITION METAL COATINGS DIFFERENT (FROM TRADITIONAL PHOSPHATE)?

New users observe several differences when converting from the legacy phosphate pretreatments.

- **TMC are best applied at cool temperatures, not warm-to-hot like phosphate.**
- **TMC are MUCH more reactive than phosphates during application, yet they sludge much less. They benefit from a continuous filtering regimen to remove iron solids.**
- **TMC can be (and are) used in mild steel washers, but are best applied from stainless equipment.**
- **TMC are equally as well applied via spray, immersion, and pressure wand.**
- **TMC require excellent rinsing and low-salt content applications along with a very clean surface.**

HOW ARE TRANSITION METAL COATINGS THE SAME (AS A PHOSPHATE)?

New users of TMC pretreatments are delighted to find that there are many similarities with the traditional metal phosphates.

- **TMC pretreatments are usually applied from a washer and generally will change the color of the metal substrate (if it's steel). The color change can give a good visual indication of a properly running process.**
- **The application mechanism of TMC pretreatments is somewhat similar to phosphate, with pickling of metal and depositing of coating. There is a bit of a difference in that the substrate metal is not generally believed to be a participant in the deposition reaction**

Table 1. Five-Stage TMC Sytem

	Process Stage					
	1	2	3	4	5	Comments
Option 1	Clean	Rinse	TMC	Rinse	Seal	Legacy Iron Conversion
Option 2	Clean	Rinse	Rinse	TMC	Rinse/Seal	New TMC Line Design
Option 3	Clean/TMC	Clean/TMC	Rinse	Seal	Rinse/Seal	Clean-Coater TMC

mechanism.

- **The application requires some measure of control and attention to the process. Typical measurements are for pH, acidity, and perhaps a colorimeter to measure the transition metal concentration.**
- **TMC pretreatments work by passivating the substrate with respect to corrosion, and enhancing mechanical/physical paint bonding—the same as traditional pretreatments.**

CONVERTING FROM PHOSPHATE TO TMC

There are generally two types of conversions: the washer is an existing traditional metal phosphate application, or the washer is newly constructed for application of TMC pretreatments. The two applications require different approaches.

A legacy metal phosphate washer will typically feature a cleaning stage, one rinse, a pretreatment application stage, one or more rinses and perhaps a seal rinse.

The best practice for TMC is stainless steel for the TMC stage, good cleaning, very good rinsing, and perhaps provision for a seal rinse. At first glance it would be considered fairly straightforward to simply replace the traditional metal phosphate stage with a TMC stage. Unfortunately, this overlooks the need for very thorough rinsing ahead of the TMC stage. More frequently, a conversion of the legacy metal phosphate stage to a rinse, followed by conversion of a legacy rinse to a TMC stage is more successful. New washer construction takes into account the requirement of sufficient rinsing ahead of pretreatment by inserting an extra rinse after cleaning.

Three-stage washer configurations present a particular challenge because the process must both clean the metal and provide a conversion coating. Surfactants cannot be incorporated into zinc phosphate baths so the cleaning and pretreatment must be in separate stages, separated by a minimum of 1 rinse. Zinc phosphate requires a minimum of 5 stages and more typically 7 stages. Iron phosphate is commonly applied in a three-stage process, where the cleaning and conversion coating is accomplished in the first stage. The cleaning is achieved the addition of both the surfactant and/ or solvent into the formula. When parts are heavily soiled with mill oils and other metalworking fluids, it is not uncommon to use a tank side additive to improve cleaning and extend the useful life of the bath.

As previously stated, TMC do not contain phosphate. While this is an environmental benefit, it diminishes the cleaning capability of the chemistry because phosphates are a detergent and help cleaning. TMC must rely solely on surfactants and solvents in the formula to degrease the metal. cleaner-coater TMC products are available and are best used when the soil load is light and consistent.

Table II. Three-Stage TMC System

	Process Stage			
	1	2	3	Comments
Option 1	Clean	Rinse	TMC	For dry-in-place time TMC
Option 2	Clear/TMC	Rinse	Rinse/Optional Seal	Clean-coater TMC

Table III. Three-Stage Spray Application Methods

	Stage One	Stage Two	Stage Three
Process	Clean	Rinse	TMC (Dry-In-Place)
Time	90 sec	30-45 sec	45-60 sec
Temperature	95-130°F	Ambient	Ambient
Concentration	2%-4%	n/a	2%-4%
pH	Alkaline	Neutral	Acidic

The most common way of using TMC in three-stage pretreatment processes is to apply them in the final stage. The clean, rinse, coat configuration is ideal for manufacturers that have tough to remove soils and inconsistent sources of steel. A custom coater with 3-stage washer is a good example of an organization that could benefit.

Users of these technologies report varying degrees of satisfaction, but with creative use of vestibule space for misting risers to provide better rinsing, and good chemical product selection, a 3-stage washer can give satisfactory service. The 5-stage washer configuration will give much more flexibility in the application of TMC pretreatments.

Of particular interest are conversions of legacy zinc phosphate systems to TMC pretreatments. With performance of TMC pretreatments approaching that of zinc phosphate, without the detriments of heavy sludge, high process cost, and need for onsite waste water treatment, these old washers are being converted with increasing frequency. The most important consideration is the removal by acidic descaling of the old sludge and activator products from the washer surfaces. Using a hot recirculating solution of muriatic acid will dissolve old zinc phosphate scale, corrosion products, titanium salts, and other deposits, leaving the washer ready to accept the new TMC pretreatment. Failure to descale the washer will cause contamination and compromise performance of the new pretreatment.

CONCLUSION

TMC are now widely used across the globe by hundreds of users in a broad range of industries. This technology is the fastest growing powder coating and paint pretreatment and is firmly established in the finishing market. It is no longer considered "new". The technical support to convert existing metal phosphate pretreatment systems is well established. The newest TMC products are easy to run, so there are no barriers to enjoying the benefits to your process offered by TMC. If you are interested in improving the corrosion resistance of your product and the environmental profile of your pretreatment program, you may consider TMC.

ZINC PHOSPHATING

BY JOHN DONOFRIO
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The phosphating of steel, galvanized steel, zinc, and sometimes aluminum represents an essential stage in many areas of surface finishing. It is employed for the purpose of pretreatment prior to painting, increasing corrosion protection, assisting cold forming, and improving the sliding friction properties of components in sliding contact. Each of these areas will be covered with application examples.

Zinc phosphate is a crystalline conversion coating that is formed on a metal substrate utilizing the chemical reaction between metal ions that have been dissolved in mineral acids and then diluted with water to form the process solution. Contrary to traditional plating operations where electrical current forces the coating formation, zinc phosphating processes rely on the basic pickling reaction that occurs on the metal substrate when the process solution comes in contact with the metal. The mineral acids that are normally used to dissolve the metal ions are nitric acid and phosphoric acid.

Metals, such as zinc, nickel, and manganese, are dissolved depending on the process necessary. Several other metals can be dissolved to create specific characteristics. Nickel plays a major role in achieving an acceptable corrosion resistance of the coating as well as accelerating the process chemistry. More recent developments have created nickel-free processes that can compete with the nickel-containing processes.

Accelerators are added to phosphating processes for specific reasons such as reaction speed, hydrogen elimination, and sludge formation control. Accelerators can be used as single materials or they can be mixed to achieve the most effective combination. Several materials can be used including nitrite/nitrate, chlorate, nitroguanidine, hydroxylamine, peroxide, and organic compounds such as sodium nitrobenzene sulfonate (SNBS).

Other additives are used such as free and/or complex fluorides when, for example, hot-dipped galvanized and/or aluminum substrates are treated. Figure 1 shows some phosphate crystal structures created by different processes.

REACTION MECHANISMS

Pickling Reaction

The first reaction that occurs when the zinc phosphate solution comes into contact with the metal surface is the pickling reaction, which will dissolve some metal from the surface. On steel, depending on the process solution used, the pickling rate is in the range of 1–3 g/m^2 of surface area treated; however, it can be much higher for higher coating weights.

This pickling reaction is essential for the coating formation since this can be said to be a chemical cleaning of the surface and, as such, will affect the adhesion of the coating to the base metal.

During the pickling reaction, for free acid of the solution close to the metal surface is consumed because of the dissolution of the metal surface. Metal ions are transferred into the process solution. The type of metal ion depends on the type of sub-

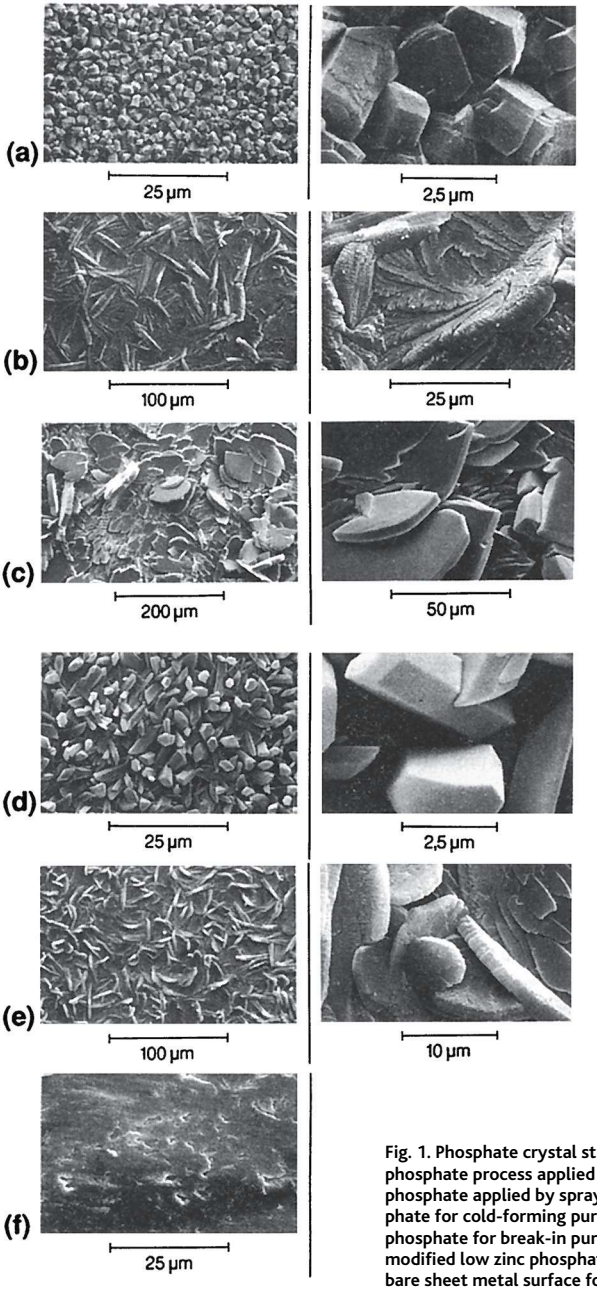


Fig. 1. Phosphate crystal structures. (a) low zinc phosphate process applied in dip; (b) low zinc phosphate applied by spray; (c) heavy zinc phosphate for cold-forming purposes; (d) manganese phosphate for break-in purposes; (e) manganese modified low zinc phosphate applied by spray; (f) bare sheet metal surface for reference.

strate mix being treated. Minimization of hydrogen development occurs by the use of oxidation agents (Ox) (accelerators).

Steel surface

$$Fe + 2H^{+1} + 2Ox \rightarrow Fe^{+2} + 2HOx$$

Zinc-coated steel surface

$$Zn + 2H^{+1} + 2Ox \rightarrow 2HOx$$

Aluminum surface

$$Al + 3H^{+1} + 3Ox \rightarrow Al^{+3} + 3HOx$$

Coating Reaction

The second reaction that occurs is the coating reaction. Because of the consumption of the free acid in the liquid-metal interface, pH rises and the metal cations cannot stay soluble in the solution. They react with the phosphate in the solution and deposit on the metal surface as crystalline zinc phosphate.

Depending on the process chemistry involved, several crystal structures are possible:

$$3Zn^{+2} + 2H_2PO_4^{-1} + 4H_2O \rightarrow Zn_3(PO_4)_2 \cdot 4H_2O + 4H^+$$

$$2Zn^{+2} + Fe^{+2} + 1H_2PO_4^{-1} + 4H_2O \rightarrow Zn_2Fe(PO_4)_2 \cdot 4H_2O + 4H^+$$

$$2Mn^{+2} + Zn^{+2} + 2H_2PO_4^{-1} + 4H_2O \rightarrow Mn_2Zn(PO_4)_2 \cdot 4H_2O + 4H^+$$

$$2Zn^{+2} + Mn+2 + 2H_2PO_4^{-1} + 4H_2O \rightarrow Zn_2Mn(PO_4)_2 \cdot 4H_2O + 4H^+$$

Sludge Reaction

The metal ion (Fe^{+2}) that is dissolved from the pickling reaction is oxidized using the accelerator (e.g., nitrite/nitrate, chlorate, or peroxide) and will precipitate out as sludge. In the case of zinc ions (Zn^{-2}) they are incorporated in the coating reaction and will not form any sludge. Aluminum ions (Al^{+3}), by the use of fluoride, react to form a fluoroaluminate complex. This complex is precipitated as kryolith.

$$Fe^{+2} + H^{+1} + Ox \rightarrow HOx\ Fe^{+3}$$

$$Fe^{+3} + H_2PO_4^{-1} \rightarrow FePO_4 \text{ (sludge)} + 2H^+$$

$$Al^{+3} + 6F^{-1} \rightarrow AlF_6$$

$$AlF_6^{-3} + 3Na^+ \rightarrow Na_3AlF_6 \text{ (sludge)}$$

The created sludge in the process is normally filtered out from the solution utilizing some sort of filter media or equipment, such as lamella clarifiers or settling tanks, direct feed through a filter press, or hydromation filter technology. The system to be used is a matter of discussion and preference of customer or line manufacturer.

ZINC PHOSPHATING PRIOR TO PAINTING

To increase the durability and service life of painted parts where maximum performance is essential, zinc phosphating is widely used. Today's zinc phosphate

Table I. Materials for Sheetmetal Constructions

Steel:
Soft, unalloyed
High strength, micro alloyed, dual phase P-alloyed
Steel coated with molten metals:
Zinc + 0.1%-0.2% aluminum (galvanized)
Zinc + 0.1%-0.2% brushed (1/2 galvanized)
Zinc + 0.1%-0.2% aluminum + app. 10% iron (Galvanneal)
Zinc + app. 5% aluminum + app. 1% mix metal (Galfan)
Zinc + app. 30% aluminum + app. 0.2% magnesium (Lavegal)
Zinc + app. 55% aluminum + app. 1.5% silicon (Galvalume)
Steel electrolytically
Zinc
Zinc + app. 10% nickel
Zinc + app. 16% iron
Zinc + app. 16% iron (as base coat) [zinc + app. 83% iron (as a top coat)]
Aluminum:
Aluminum–magnesium
Aluminum–magnesium–silicon
Aluminum–magnesium–manganese

coatings are developed to meet the increasing demands placed on the total finish of the parts; therefore, a close working relationship has been formed with the paint industry to create processes requested by the market.

Also, a more widespread use of zinc coated steel and aluminum substrates has forced the manufacturer of zinc phosphate processes to develop processes that can treat a wide variety of metal mixes through one and the same process. Some of the commonly used substrates in the prepaint operations are discussed below. A
properly performed zinc phosphate coating prior to paint application will create the following: good bonding of the zinc phosphate coating with the metal; good bonding of the paint film in the microporous zinc phosphate coating; reduction of electrical corrosion currents underneath the paint; chemical resistance of the zinc phosphate coating; reduction of electrical corrosion currents underneath the paint; chemical resistance of the zinc phosphate coating; and a diffusion barrier against water and oxygen. All of these create retardation of corrosion underneath the paint coating starting at a paint chip.

SUBSTRATES

The principal material to which zinc phosphate is applied is steel as well as, in varying proportions according to the particular part, precoating steel and aluminum. Precoated steel is used to improve the corrosion protection of the part, whereas aluminum and thin-walled, high-strength steels are employed to save weight. Table I surveys the industrial materials employed

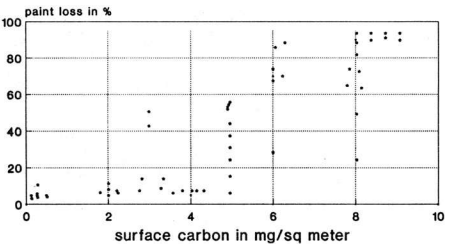


Fig. 2. Percent paint loss related to surface carb on content on steel after gravelometer test and 480 hours of salt spray.

in manufacturing.

With bare steel, the particular alloy, soft or high strength, does not affect zinc phosphating as much as the condition of the surface. Excess residual carbon left on the surface after the annealing process where recrystallization takes place, or after the steel has been cold rolled, will cause poor corrosion resistance (see Fig. 2).

This residue cannot be removed effectively by the most mild alkaline cleaners on the market and action should be taken so that the steel used for production has a controlled low level of residual carbon.

Hot-dipped galvanized steel strip is produced by applying molten zinc on the strip. The metal mix in the bath specifies the alloy that will be applied on the strip and metals, such as lead, tin, antimony, and aluminum, can affect phosphatability.

In particular, aluminum will form on aluminum oxide film that has a thickness less than 5 nm on the surface, which negatively influences the surface reactivity during zinc phosphating. Zinc-aluminum alloy coatings, such as Galvalume, have similar but more severe problems with aluminum oxide surface coatings. These require zinc phosphate processes that are specially designed to treat larger amounts of aluminum surfaces. Most of those processes add controlled fluoride to the bath.

Galvanneal is a substrate that is produced by heat treating the hot-dipped, zinc-coated steel sheet. This causes iron from the sheet to diffuse into the zinc coating and form an alloy consisting of 10–15% iron. This substrate has better weldability and is not as reactive in the zinc phosphating process to form "white spotting" as do pure zinc coatings.

Electrogalvanized steel sheets are made by plating zinc onto the steel strip utilizing electroplating technology. Different electrolytes will create different zinc coatings and alloys, which can vary the physical properties as well as the corrosion resistance of the substrate itself. Most of those alloys are easily zinc phosphated. Zincated steel surfaces can be damaged by corrosion forming white rust on the surface (zinc carbonate/zinc oxide). Normally, this coating cannot be effectively removed by using mild alkaline cleaners; therefore, the surface will not be properly zinc phosphated and will create a poor paint finish with little corrosion resistance.

To avoid the surface corrosion, protection by an oil or passivation by using a chromium treatment can be used. Care should be taken that no passivated substrates are used for parts that should be painted; however, in coil coated operations, the processes are adjusted so that this substrate can be treated with success.

Aluminum, aluminum alloys, and zinc-coated steel with high aluminum content (Galvalume) can be treated very successfully with zinc phosphating processes, thereby creating a substrate that will show as good corrosion protection as traditionally used chromate conversion coatings when painted and tested in different corrosion environments. Studies have shown that when the aluminum substrate is ground and the aluminum alloy includes silicon, poor corrosion resistance and paint adhesion will occur, if the zinc phosphating process does not create a uniform crystalline coating on the substrate. It is recommended that zinc phosphating processes consisting of controlled fluorides be used when aluminum substrates will be treated. Table II shows the effects.

ZINC PHOSPHATE PROCESS TECHNOLOGIES PRIOR TO PAINTING

Over the years different zinc phosphating processes have been developed to address corrosion resistance and adhesion as well as the demand from the indus-

Table II. Corrosion Test Results for Aluminum Compared with Cold-Rolled Steel and Electrogalvanized Steel

Test Method	Aluminum[a]				Steel (Trication Process + F)	Electrogalvanize Steel (Trication Process + F)
	Trication Process, No Fluorides, No Crystalline Layer		Trication Process with Fluoride Crystalline Layer			
	+S	-S	+S	-S		
Salt spray test DIN 50021 1008 hr (mm)	0(–4)	0(–2)	0	0	<1	5–9
Salt spray–humidity cycle VDA 621-415 10 weeks (mm)	0–8 (Filiform)	0–8 (Filiform)	0–1	0–1	1	3–6
Outdoor exposure + NaCl (VDA 621-414) 1 year (mm)	25–27	0–9 (Filiform)	0–3	0–1	1.5	<1
Chipping corrosion VW specification (% paint loss)	0	0	0	0	0	1
Condensing humidity (240 hr + cross hatch (index)	0	0	0	0	0	0

[a]Material: A1MgO•4Sil•2: passivation, Cr(VI) and Cr(III): coated with cathodic paint, primer, topcoat: +S, sanded surface: S nonsanded surface

Table III. Results of Corrosion Testing

Phosphating Process	Steel	Electrogalvanized Steel
Salt spray test (SS DIN 50021) mm creepage from scribe after 1008 hr+-		
Low zinc, phosphate	1–1.5	1–7(480 hr)
Low zinc, manganese-modified	<1–1	1–12 (480 hr)
Cycle test (VDA 621-415 paint creepage from scribe after 10 weeks in mm		
Normal Zinc	5–8	3–7
Low zinc, phosphate	1–1.5	1–6
Low zinc, manganese-modified	1	1–7
Accelerated outdoor exposure test paint creepage from scribe after 12 months in mm		
Normal Zinc	>13	2
Low zinc, phosphate	2.5–3	1
Low zinc, manganese-modified	1–2	1
Cross hatch combined with humidity after 240 hr GT note and paint loss (%)		
Normal Zinc	5(80%0	5(80 to 100%)
Low zinc, phosphate	1–2(5–15%)	2(15%)
Low zinc, manganese-modified	0–1(0–5%)	<1(<5%)
Metal: Steel and zinc-coated steel sheet Phosphate process: Low zinc phosphating with and without manganese modifying Post rinse: Cr(VI) and Cr(III) Paint system: Cathodic electrocoat epoxy primer and topcoat		

try to handle mixed metal production. The traditionally used, so-called normal zinc processes have, in several cases, been replaced by the use of low zinc or low zinc-manganese-modified processes that create an outstanding performance in all corrosion testing environments (Table III).

The differences between the processes used as pretreatment prior to painting involve the process chemistry. Whereas in normal zinc phosphating baths, approximately 2,000–4,000 ppm zinc and approximately 6,000–14,000 ppm phosphate are present, the corresponding concentrations in low-zinc baths are approximately 400–1,700 ppm zinc and 16,000–22,000 ppm phosphate. The low zinc phosphate technology has further been developed by incorporating a third metal, namely manganese, in the process bath.

These processes are known as manganese-modified, low-zinc phosphate processes and are characterized by their outstanding performance. A comparison of zinc phosphating technologies is given in Table IV.

Coating weights that are recommended prior to painting depend on the application and the subsequent paint process. As a rule of thumb, the coating weight is in the range of 100–500 mg/ft^2.

CRYSTAL STRUCTURE

Depending on the process and the substrate, different crystal structures are possible. For the "normal zinc" technology the crystal structure is the same on all substrates.

$$Zn_3(PO_4)_2 \cdot 4H_2O \text{ (hopeite)}$$

The low zinc technology shows a better coating performance because of sev-

Table IV. Comparison of Zinc Phosphating Technologies

Property	Normal Zinc	Low Zinc	Low-Zinc Manganese
Phosphating speed	Higher	Lower	Modified higher
Coating weight	Higher/same	Same/lower	Same/lower
Crystal size	Higher/same	Same/lower	Lower
Chemical consumption	Same	Same	Same
Corrosion protection with cathodic E-coat	Poor	Good	Excellent
Chip corrosionresistance	Poor	Good	Excellent
Wet adhesion of cathodic E-coat	Poor	Good	Excellent

eral factors: A longer pickling reaction and thereby a better chemical cleaning of the metal surface; slower deposition reaction and thereby a denser phosphate structure; and an increased amount of zinc-iron phosphate (phosphophyllite) on steel surfaces.

The following are the crystal structure of various substrates.

Steel surfaces

$$Zn_3(PO_4)_2{\cdot}4H_2O \text{ (phosphophyllite)}$$

Zinc-coated steel

$$Zn_3(PO_4)_2{\cdot}4H_2O$$

Aluminum

$$Zn_3(PO_4)_2{\cdot}4H_2O$$

With the development of manganese-modified, low-zinc phosphate processes a further step was taken to increase corrosion protection as well as paint adhesion. Zinc is partially replaced by nickel and/or manganese in trication phosphate processes. Some of the advantages are lower coating weights with better thermal stability that provide improved adhesion and corrosion protection under paint.

The following represents the crystal structure on various substrates:

Steel surfaces

$$Zn_2(Fe \text{ or } MN)(PO_4)_2{\cdot}4H_2O$$
$$Mn_2Zn(PO_4)_2{\cdot}4H_2O$$
$$Zn_3(PO_4)_2{\cdot}4H_2O$$

Zinc-coated steel

$$Mn_2Zn(PO_4)_2{\cdot}4H_2O$$
$$Zn_3(PO_4)_2{\cdot}4H_2O$$

Aluminum

$$Mn_2Zn(PO_4)_2{\cdot}4H_2O$$
$$Zn_3(PO_4)_2{\cdot}4H_2O$$

Another process technology that has been widely used in the appliance in-

dustry is the calcium-modified normal zinc technology. This technology has an advantage in that the process does not need a grain refiner or activation compound prior to phosphating, but because of its disadvantages with high process temperature as well as heavy sludge development, the process has been replaced by the use of the manganese-modified, low-zinc phosphate processes.

ACTIVATION OF PHOSPHATE COATING FORMATION

The phosphating rate, thickness, and crystal size of the zinc phosphate coating depend not only on the composition and form of the phosphating bath, but also on the pretreatment of the metal surface prior to phosphating. Strong alkaline cleaner and acid pickling processes frequently produce a coarsening of the coating texture and prolong the time required for the formation of a phosphate coating with uniform coverage.

Mechanical treatments, for example, grinding or polishing, brushing, and even simply wiping, produce marked refinement of the subsequent zinc phosphate coating. The reason for this phenomenon lies in the different number of nuclei on the metal surface at which crystallization of the phosphate coatings can begin.

Special prerinses applied to the metal surface prior to phosphating provide a considerable increase in the number of nuclei for phosphate crystallization. This is termed activation of the phosphate coating formation. It is manifested in the subsequent phosphating process by an increase in the number of phosphate crystals per unit surface area; a decrease in the dimensions of the individual crystals of the coating; a reduction in coating weight; and a reduction in the minimum phosphating time.

Titanium phosphate produced according to a special process has been found to be a highly effective nucleating agent. In industrial practice, the activating agent is added either directly to the rinse bath prior to phosphating or to preliminary alkaline cleaning baths. Since the lifetime of the activation agents is affected by several factors, such as pH, water hardness, and temperature, they are normally added (replenished) on an ongoing basis during production. New liquid processes offer advantages such as increased lifetime (better process stability).

NITRITE-FREE PHOSPHATING

The usual practice for most of the zinc phosphate processes to painting is to employ nitrite as a primary accelerator. Nitrite, however, in the acid phosphating baths, always produces a small quantity of volatile nitrous gases. On the other hand, zinc phosphating processes accelerated with organic nitro-accelerators will not create nitrous gases.

In the event the line is shut down for a comparatively long time, steel surfaces may become rusty due to the effect of the atmosphere surrounding the work. This process is accelerated and reinforced by the presence of nitrous gases. Organic nitro-accelerators have less tendency to rust. This type of process can also create coating weights in a very narrow and controlled band, 100–200 mg/ft^2. Coatings in this range are distinguished by especially high flexibility under bending load.

Other accelerators have been developed and are increasingly used in production. Hydroxylamine has the advantage of being soluble in the zinc phosphate replenisher; therefore, no separate accelerator package is needed. Hydrogen peroxide-accelerated processes can provide very low coating weights; however, the

Table V. Process Examples

	Spray Process	Dip Process	Spray/Dip Combination
Cleaning	60 sec, 110–130°F	120 sec, 120–140°F	30–60 sec spray, 120–140°F
Cleaning	60 sec, 110–130°F	120 sec, 120–140°F	60–90 sec spray, 120–140°F
Rinse	30–60 sec ambient	60–120 sec, ambient (two rinses preferred)	30–60 spec spray, ambient 60 sec dip, ambient
Activation	30 sec, ambient	60–120 sec	60 sec dip, ambient
Zinc Phosphating	60–120 sec, 120–140°F	120 sec, 120–140°F	120–180 sec dip 120–140°F
Rinse	30–60 sec, ambient	60–120 sec, ambient (two rinses preferred)	30–60 sec, ambient
Rinse			60 spec dip, ambient
Seal	30–60 sec, ambient	30–60 sec, ambient	30–60 sec, ambient
DI water rinse	30–60 sec, ambient	30–60 sec, ambient	(Recirculating) 30–60 sec dip, ambient
DI water rinse			Fresh DI water riser spray, ambient

phosphate crystals tend to be larger in comparison to other accelerators. Since peroxide accelerators do not produce any side products other than water, these are the most compatible where environmental issues are of concern. Recently, nitroguanidine has been introduced into low-zinc phosphate technologies. This is the only accelerator in use that is not self-decomposing. Another major benefit is its wide working range, which provides a very robust process.

NICKEL-FREE PHOSPHATING

Nickel has long been known to significantly improve paint adhesion and corrosion protection; however, nickel compounds are noxious and closely regulated in the effluent stream. Nickel-free processes, therefore, are desirable to satisfy health and environmental demands. Nickel-free processes are available and in use. Most processes replace the nickel with very low concentrations of copper. The corrosion protection of these copper-modified processes on steel is excellent; however, further progress is still needed if hot-dipped galvanized steel is part of the treatment mix. The paint adhesion under cathodic electrocoat as in use in the automotive industry is not sufficient with these processes to match the performance of nickel-containing processes on hot-dipped galvanized steel.

PROCESS SETUP PRIOR TO PAINTING

Several different processes can be utilized with zinc phosphating. Straight spray installations are popular as well as straight dip operations; combinations of both are also used to make them advantageous. When complex parts are being processed where a lot of recessed areas have to be treated and painted, a combination of spray

and/or straight dip operations is preferred. In a combination installation, spray can be utilized in areas such as first cleaner stages, rinse stages, and final rinse stages; however, if dip cleaning is used, then rinsing should be done in the dip as well as in the activation, phosphating, and sealing operations.

Because the spray utilizes the kinetic energy of the spray pressure, concentrations and treatment times can be kept lower in spray operations compared to dip. As for the phosphate process, treatment time for a spray installation should be a minimum of 60 seconds and for a dip 90 seconds, but 120 seconds is preferred. Typical process examples are given in Table V.

HEAVY ZINC PHOSPHATING FOR RUST PROTECTION

Zinc phosphating or manganese-phosphate processes are also widely used for corrosion protection purposes where the phosphate coating works as a carrier for the specific oil or wax film that is applied over it. Typical applications where the technology is used include screws, nuts, bolts, plain washers, brake components, clutch components, engine parts, and several others.

The processes are applied in dip operations, either in bulk processes utilizing tumblers, or in a specific rack design. The coating weight produced by the processes can vary in the range of 1,000–4,500 mg/ft^2. With no further after-treatment, these processes create a salt-spray resistance (SS DIN 50021) of 0.5 to 2 hours. Application of a sealant process can create salt-spray resistance of up to 24 hours. Application of a rust-preventive oil or wax impregnation can further increase the salt-spray resistance of the respective products in the range of 48 to 720 hours.

The process technology is based on the same reaction as described earlier. Several accelerators can also be used in the process chemistry. The heaviest coatings are developed by the nitrate-accelerated processes, which are working on the "iron side," meaning that divalent iron is present in the process solution. This technology has a limit in that the iron content has to be controlled because it can inhibit proper coating reaction and spontaneous sludge formation. The nitrate-accelerated processes cannot create the heavy coatings but they phosphate faster than the nitrate processes. Coating weights with the nitrite processes are also lower than the nitrate-accelerated processes.

The crystal structure of the coatings is mainly hopeite and phosphophyllite for the zinc phosphating processes and if a manganese-phosphate process is used, a manganese-iron phosphate crystal is developed.

The process specifics for the processes will vary but some guidelines are as follows: (1) Phosphate coatings with coating weights up to 4,500 mg/ft^2 are deposited by processes with long immersion times and high temperatures. Tines can be as long as 60 minutes and temperatures are in the range of 180–205°F. (2) Phosphate processes containing accelerators, such as nitrates, produce zinc or manganese phosphate coatings with coating weights in the range of 1,000–3,500 mg/ft^2 with treatment times in the area of 5 to 15 minutes. Temperature range is between 130°F and 200°F depending on the process. The coatings can also be treated with coloring agents so that the appearance of the parts can be varied to customer demands. (Fig. 3 shows a summary of the possible sequences.).

COLD-FORMING PROCESSES FOR TUBE WIRE, COLD EXTRUSION

The application of chemical processes for the purpose of assisting the cold forming of metals was already in general use at the beginning of this century. The in-

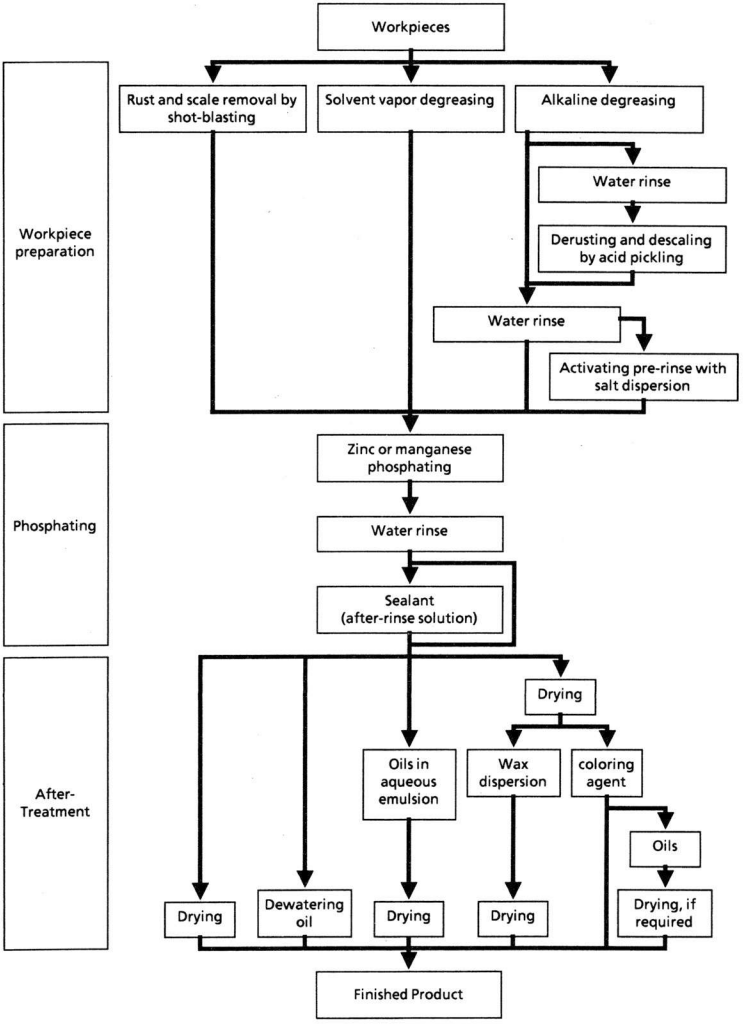


Fig. 3. Sequence of operations for heavy zinc or manganese phosphating.

dustrial importance of cold-forming technology for the entire steel working industry sector today would be inconceivable without the metal surface technology including zinc phosphate and lube.

The expression *cold forming* implies that the change of form is effected without preheating the workpiece. The noncutting of a workpiece is performed under the action of outside forces (tensile, compressive, and shear stresses), which strain the material beyond the yield point and then force the material, now in the plastic state, to assume the form imposed on it by the tool. During this process the mass and composition of the material remain unchanged.

The internal processes taking place in the material consist of permanent changes in the position of the atoms within the crystal lattice. The crystallo-

graphic changes produced within the interior of the material find expression internally in the form of so-called strain hardening. An example is an increase in tensile strength and hardness. Characteristic of the cold forming of steel compared with other metals is the high amount of mechanical energy required.

This means that high temperatures occur in the forming zone where workpiece and tool come into contact with each other, which may impair or even completely nullify the effect of normal lubricants. Another factor is that the change in form of the workpiece may in some circumstances entail a considerable increase in the specific surface, so that additional stress is imposed on the lubricant. The character of friction prevailing in the forming zone under industrial conditions of cold forming largely corresponds to the concept of mixed friction. That is, in the range of the roughness peaks, there is an extensive lubricant coating up to several molecule layers deep, which because of its texture can prevent galling and seizing in the case of pressures that are not too high (boundary friction). In the depression between the roughness peaks occur hydrostatic pressure areas, which may be regarded as a lubricant reservoir.

The lubricant forced out of these pressure areas or cavities during forming produces locally limited hydrodynamic friction states. The tendency of one surface to become bonded by galling and seizing on direct contact with the other surface is a major problem in cold-forming operations. The chemical and physical-chemical properties of the surfaces of the tool and workpiece have a considerable influence on the tendency to galling and seizing. Under favorable conditions the workpiece surface can be altered to such an extent that galling and seizing during the cold-forming process practically never occur. To achieve this is one of the main aims of chemical surface treatment.

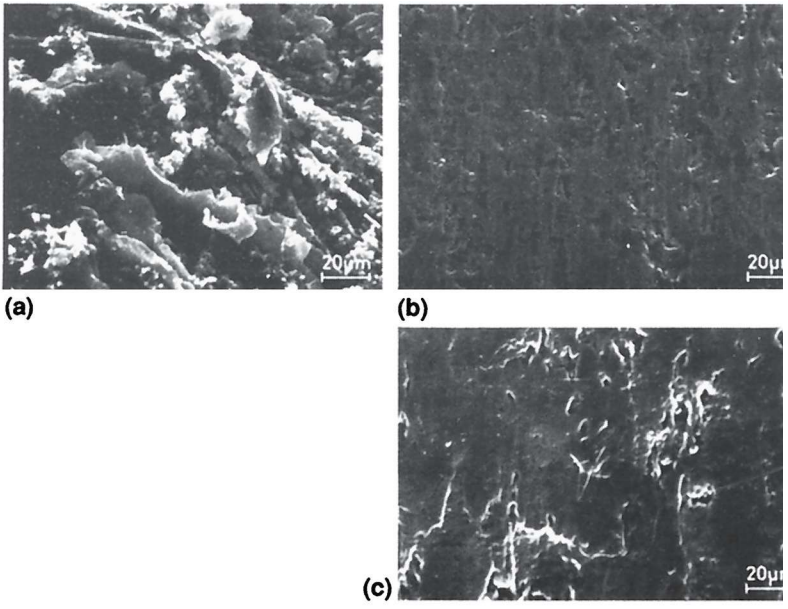


Fig. 4. These SEM pictures show the internal surface of a steel pipe before (a) and after (b) drawing and also after cleaning (c).

Table VI. Examples of Metallurgical Finishing Process, in which Workpieces are Subjected to Chemical Surface Treatmetn Prior to Cold Forming.

Finishing of Seamless Tubes	**Finishing of Welded Tubes**	**Finishing of Cold-Heading Wire**	**Finishing of Spring Steel Wire**	**Finishing of Cold-Extruded Parts (in several stages)**
Production of tube blank, M Pickling, C Rinsing, C Phosphating, C Rinsing, C Application of soap-based lubricants, C Initial pass, M Bright annealing, M Application of RS lubricants, C Final drawing, M	Welding of tubes, M Annealing, M Pickling, C Rinsing, C Phosphating, C Rinsing, C Application of soap-based llubricants, C Initial pass, M Bright annealing, M Application of RS* lubricants, C Final Drawing, M	Production of rod wire, M Pickling, C Rinsing, C Phosphating, C Rinsing, C Application of soap-based lubricants, C Initial pass for cold heading, M	Production of rod wire, M Pickling, C Rinsing, C Phosphating, C Rinsing, C Liming, C Drying, C Initial drawing, M Patenting, M Pickling, C Rinsing, C Phosphating or copper-coating, C Rinsing, C Liming, C Drying, C Final drawing, M	Production of slugs, M Pickling, C Rinsing, C Phosphating, C Rinsing, C Application of soap-based lubricants, C Drying, C Cold extrusion, M Cleaning, C Rinsing, C Drying, C Annealing, C Pickling, C Rinsing, C Phosphating, etc., C

M, metallurgical process step; C, chemical process steop; RS, reaction lubricants.

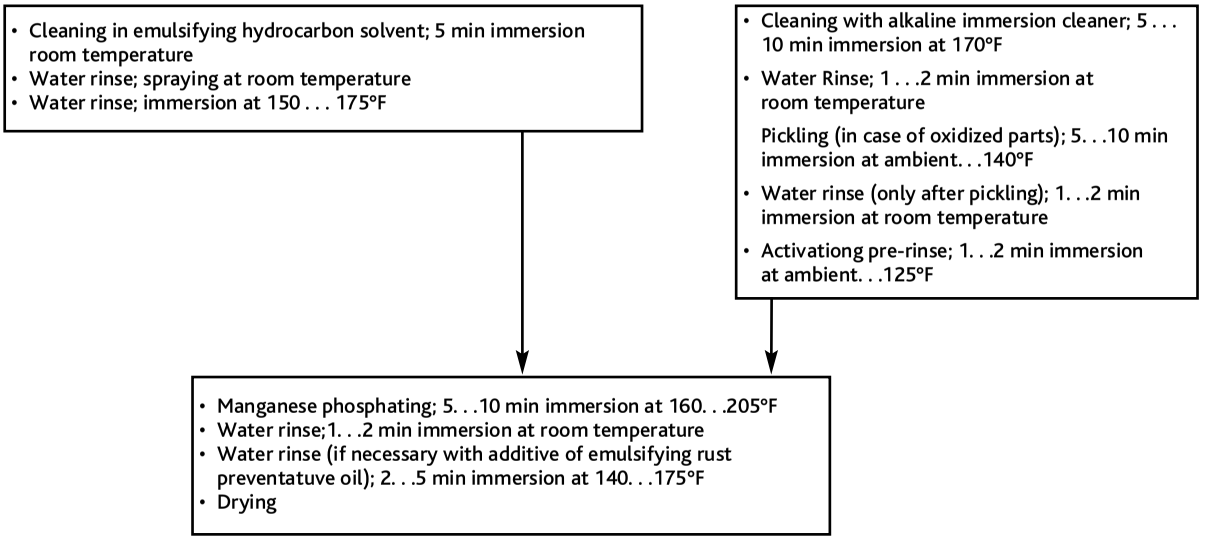


Fig. 5. Treatment process flow chart for manganese phosphating.

ZINC PHOSPHATE COATINGS

Coatings composed of zinc phosphate have been successfully used in all areas of the cold forming of nonalloy and low-alloy steels. The main reasons for the special suitability of zinc phosphate as a separating medium and as a wear-reducing material are as follows: zinc phosphate coatings are associated with strong binding forces with the iron surface; the specific structure of the zinc and zinc-iron crystal structure enables the plastic deformation of crystals under the action of the compressive and shear stresses arising during forming operations; zinc phosphate coatings are able to react with alkali metal soaps to give high-efficiency lubricant systems; the actual phosphating process is performed by immersion or by an in-line method. The workpieces are treated for a period of 5 to 10 minutes (dip process) or 20 to 30 seconds (in-line process) with zinc phosphating processes working on the "iron side" or accelerated with nitrite. Coating weights can vary as much as 300 to 2,500 mg/ft^2.

The properties of the zinc phosphate coatings produced are mainly determined by the following factors: type of phosphate forming the coating (zinc phosphate, zinc-iron phosphate, and zinc-calcium phosphate); type of accelerators used (nitrite/nitrate, chlorate, and nitrate); concentrations of components of the process (total acid, free acid, metal components in the bath, and accelerators); process parameters such as process temperature and process time; type of application (dip operation versus in-line process); application of activation prerinses; type and mode of previous pickling processes; and type and mode of previous annealing.

Lubrication and its different processes will not be discussed in detail here. Plastic forming of a zinc phosphate coating after being treated with metallic soap is shown in Fig. 4. The SEM pictures show the internal surface of a steel pipe before and after drawing and also after cleaning. Some application differences are listed in Table VI.

MANGANESE PHOSPHATE COATINGS TO IMPROVE SLIDING PROPERTIES

Manganese phosphate coatings are extensively employed to improve the sliding properties of engine, gear, and power transmission systems. Manganese phosphating is capable of application to carbon steels with a maximum extraneous element content (i.e., Ni + Cr + Mo + V, etc.) of approximately 5% to 6%, and also to cast iron. The additive quantities of the individual alloying components here amount to a maximum of approximately 1.5% manganese, 0.4% silicon, 0.2% chromium, 4% nickel, and 0.6% molybdenum. In the case-hardening steels the carbon content amounts to approximately 0.2%, whereas in the tempering steels it is between 0.2 and 0.5%. Of the elements mentioned, chromium and molybdenum, particularly in the upper concentration range, may interfere with the phosphating process. The existing surfaces in many cases are in the carburized or nitrided state, without significantly affecting the phosphating capacity. In contrast, a working layer produced by mechanical means seriously affects the formation of the phosphate coatings.

The Process

The manganese phosphate process is performed by immersion using water solution, which, besides the necessary free acid for setting the phosphating equilibrium, contain primary manganese phosphate as the determining compo-

nents. Nitrates and nickel compounds and possibly other additives are also included for acceleration and modification of the coating formation. The phosphate layers precipitated mainly consist of $(Mn,Fe)_5H_2(PO_4)_4 \cdot 4H_2O$ and manganese or iron hureaulith mixed crystal and varying contents of manganese and iron.

When adapted to the particular application and the permissible dimensional tolerances, manganese phosphate coatings are produced with a coating weight between 500 and 2,200 mg/ft^2. The coating weight and crystal size of the manganese phosphate coatings are influenced to an even greater extent than in zinc phosphating by the mechanical, thermal, and chemical pretreatment of the workpiece surface prior to phosphating. For example, cleaning in alkaline aqueous cleaning agents or pickling in acids produces coatings with a much coarser texture. Even after such treatments, however, fine crystalline phosphate coatings are still obtainable if the workpieces are prerinsed in an activation rinse prior to the phosphating process. A typical flow chart for the process would be as shown in Fig. 5.

PAINT PRETREATMENTS FOR ALUMINUM

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Chemical conversion coatings are the most widely used prepaint treatment processes for metal substrates. Processes specifically designed for aluminum are of recent origin. These include accelerated chromate phosphates, chromate oxides, anodizing and, very recently,nonchromate formulations. Historically, however, phosphoric acid cleaners, wash primers, and iron and zinc phosphates have all been utilized as paint pretreatments with satisfactory results. Among these,the chromate types provide the most reliable under film corrosion protection and paint adhesion. Anodized coatings, especially unsealed sulfuric and chromic acid types, are also comparable in performance, but fall far short of the productivity and cost effectiveness of the chromate processes.

A careful evaluation of critical product requirements is essential in selecting the right conversion coating for anticipated field performance. Paint pretreatments must assure these corrosion protection functions: passivation of base aluminum, action as a barrier against moisture, oxygen, and other corrosive agents, electrochemical insulation, and protection against mechanical erosion. In addition,conversion coatings must provide other essential interfacial properties complementary to the paint top coat, including an effective and continuous bonding site; chemical stability during the service life of painted products; remaining insoluble, impervious, and flexible; providing a wettable subsurface for paint application; and maintaining adhesive integrity between the base metal and painted film. See Table I for typical performance data.

CRYSTALLINE PHOSPHATES

These are primarily accelerated iron and zinc phosphate processes adapted from iron and steel pretreatment. Phosphating solutions typically contain metal hydrogen phosphate salts with limited free acidity. The metal phosphates are soluble in strong acids but crystallize out when the acidity is reduced. This mechanism occurs as the acid ions react with the aluminum surface, become neu-

Table I. Comparative Performance Data

Conversion Coating	Film Weight (mg/ft^2)	Paint Adhesion	Salt Spray Resistance Painted	Humidity Resistance Painted
Iron Phosphate with chrome seal	20–30	Fair	Good	Good
Zinc Phosphate with chrome seal	100–300	Good	Very Good	Very good
Anodize	1000–3000	Very good[a]	Very Good	Good
Primer	3000+	Excellent	Excellent	Good
Chromate	15–70	Excellent	Excellent	Excellent
Chrome Phosphate	30–100	Excellent	Excellent	Excellent
Alkaline chromate oxide	10–30	Very Good	Excellent	Good

[a]Chromic acid anodized, unsealed sulfuric films, and chromate sealed films.

tralized, and produce an integral crystal growth on the metal surface. The aluminum surface is therefore converted to a finely crystalline phosphate film with acceptable texture for paint bonding. Crystalline phosphate films may be iridescent to gray. Coating weights range from 10 to 50 mg/ft^2 for iron phosphates and 100 to 300 mg/ft^2 for zinc phosphates.

Properly applied, this group of phosphates provides good corrosion protection. Iron and zinc phosphates find widespread use in mixed steel and aluminum product lines. They are popular because of low operational costs and mild environmental toxicity. Bath life is, however, very limited due to low tolerance for aluminum ion accumulation. Application is by immersion at 125 to 140° for 1 to 4 minutes, or spraying at 125 to 160°F for 30 seconds to 2 minutes. Product selection should be restricted to moderate field service environments.

CHROMATE PHOSPHATES

Chromate-phosphate coatings enjoy a privileged position in aluminum prepaint treatment. They have a historic significance as being the first pretreatment specifically developed for aluminum in 1945. Since then, these products have performed remarkably well for the architectural metal and beverage can industries. Demand for cans,however, is on the decline. Recently introduced high-performance topcoats are more forgiving toward nonchromate prepaint treatments.

Chromate-phosphate coatings are applied by spray or immersion.Immersion times range from 30 seconds to 3 minutes at 110 to 130°F, whereas spraying is done at 15 to 45 seconds at 95 to 130°F. These baths produce crystalline or amorphous coatings of 15 to 1,000 mg/ft^2. The film is iridescent to grayish green. Thickness can be as high as 0.1 to 0.4 mil. A typical air-dried coating is given as 50% to 55% chromic phosphate, 17% to 23% aluminum phosphate, 22% to 23% water, and a trace of fluorides.

Performance properties of chromate-phosphate films are generally very close to chromic acid anodizing films and those of chromate-oxide films to be discussed later. Adhesion and corrosion protection increase with coating weight up to a point, then fall off. The best range is between100 and 200 mg/ft^2.

Because of its excellent qualities, the American Architectural Manufacturers Association (AAMA) has designated the chromate-phosphate process as a standard prepaint treatment. It also meets U.S. military specifications. Generally, this process is recommended for severe and long-term service conditions.

CHROMATE-OXIDE COATINGS

Chromate-oxide films are more versatile and widely applied than the chromate-phosphate treatments. They comprise the bulk of treatments for the coil stock and transportation industries. In applications where anodizing is not feasible, for example, where parts are too long or assembled with dissimilar metals, chromate treatments of this type have been used in place of anodizing.

Typically, a chromate-oxide bath consists of three principal constituents: acid chromates, etchants and accelerators or complexing agents.

Application may be by spray, immersion, or brush at 70 to 110°F for 15 to 45 seconds. The aluminum surface is converted to an iridescent golden yellow color. The film is tightly adherent, amorphous, and mixed with metallic oxide products. Film thicknesses range between 0.005 and 0.04 mil. Coating weights are from 15 to 100 mg/ft^2. A freshly formed film can be leached to a nearly

colorless appearance.

Chromate-oxide films have superior performance ratings compared to chromate-phosphate coatings. Unpainted films have almost twice the salt spray resistance of a chromate-phosphate coating. Chromate parts are known to have passed 2,000 hours of salt spray. Such performances are partly explained by the fact that these films retain hexavalent chromate ions in their structures. In corrosive environments, they trigger a repair mechanism into action. Chromate films are capable of withstanding very severe service conditions. They comply with military specification MIL-C-5541 and AAMA 605.2.

ALKALINE CHROMATES

These are among the oldest coating processes analogous to the phosphate treatments described earlier. One ingredient serves to attack the aluminum substrate to a limited degree, while a second functions to form an oxide coating on the reactive substrate. Alkaline chromates are primarily solutions of 2% to 3% sodium carbonate and 0.5% potassium dichromate. Immersion times range from 10 to 20 minutes at 180 to 190°F. Thin (0.04 to 0.1 mil) gray and porous films made up of aluminum oxide and dispersed chromate oxides are produced. Maximum corrosion resistance is achieved by sealing in hot 5% potassium dichromate. Consistent coating action depends on the correct ratio of carbonate to dichromate in the treatment solution.

MISCELLANEOUS TREATMENTS

No survey of prepaint treatment is complete without mention of numerous other products being successfully used in diverse applications. Some of the older successful ones include wash primers, chemical oxide films, and mechanical treatments such as wire brushing and sandblasting. Wash primers are primarily pigmented polymeric organic chromate compounds similar to paint. They have excellent corrosion protection and adhesion properties. Humidity resistance is poor.

Environmental restrictions of the last decade have generated exciting interest in chromium-free products. A substantial number of these have met acceptable requirements for the beverage can industry. Testing is in progress in coil coating and architectural segments. There is a strong indication that chromium-free products will eventually meet the stringent requirements of the architectural and transportation industries. Some of the shortcomings of current products are being gradually eliminated. New high performance top coat paints such as silicones, fluoropolymers, and powder coats can minimize performance requirements for these prepaint treatments. Advances in application technology of electrocoat systems are also proving beneficial.

PROCESS GUIDELINES

Conversion coating processes are essentially multistep operations. Preconditioning stages, such as cleaning, rinsing, and postrinse treatments are significant factors in assuring critical final results. Spray and immersion systems usually show the same order of operation. Stages consist of the following:

1. Clean
2. Rinse

3. Acid deoxidize (optional)
4. Rinse
5. Conversion coat
6. Rinse
7. DI/Acidulated/Seal rinse (optional)
8. Dry.

In the basic five-stage operation, the deoxidize and seal rinse stages are often omitted. The chromate bath initially functions as a deoxidizer before reacting to produce the desired conversion coating. Many installations easily meet this design criteria, but others, utilizing alkaline cleaners loaded with dissolved aluminum, generally produce poor quality and powdery films.

Cleaning, on the other hand, is very critical. General dirt, surfaces oils, grease, debris, and natural oxides must be removed in the cleaning process to achieve uniform coating and paint adhesion. Nonetch and etch-type cleaners may be applied with satisfactory results. Slight etching is desirable. Timely rinsing prevents soil dry-on and redeposition.

Rinse stages require fresh water input to neutralize, dilute and prevent cross-contamination between the stages. Water quality requirements for the chromate and final rinse stages are even more critical. Excessive hard water salts and soluble contaminants are detrimental to coating performance. Very often, these contaminants have been known to precipitate on the chromated film and cause paint blistering or corrosion problems when moisture penetrates the paint film in the field. The water supply should not exceed the following impurity limits. Total dissolved solids should not exceed 150 ppm, chlorides 15 ppm, sulfates (as SO4) 25 ppm, and total hardness (as CaCO3) 200 ppm. Deionized water is recommended for the chromate and final rinse stages if the incoming water quality falls below these limits.

TESTING AND QUALITY CONTROL

Testing and quality control are important parts of any manufacturing process. A large majority of the prepaint processes are proprietary. Supplier recommendations on equipment and bath maintenance must be observed to produce acceptable results consistently. Frequent bath analysis or on-line process control greatly reduces rejects and lowers cost.

COATING WEIGHT PROCEDURE

Coating weight and occasional salt spray determinations on the unpainted parts are important tools in evaluating work quality. The coating weight procedure is as follows:

1. Solvent degrease and blow dry a 3- x 3-inch panel. Weigh accurately to ± 0.2 mg.
2. Immerse for 2 to 5 minutes in a molten salt bath (temperature 620 to 670°F) consisting of reagent grade sodium nitrite (NaNO2). Aged panels may require up to 15 minutes for stripping.

Table II. Coating Weight Classifications

Specification	Color	Coating Weight, mg/ft^2	Application
ASTM B 499			
Class 1	Yellow to brown	30–100	Maximum protection
Class 2	Iridescent to yellow	10–35	General purpose
Class 3	Yellow to colorless	Less than 1 or 2	Decorative, contract resistance
MIL-C-5541			
Class 1A	Unspecified	Greater than 40	Maximum protection
Class 3	Unspecified	Greater than 40	Corrosion and contact resistance
AAMA 605.2	Yellow to brown	30–100	Maximum corrosion resistance
AAMA 603.8	(Unspecified coating properties		

3. Remove from the salt bath and carefully rinse in cold water.
4. Dip for 30 seconds in equal parts by volume of concentrated nitric acid and water at room temperature.
5. Rinse thoroughly in cold water and blow dry.
6. Reweigh.
7. Repeat steps 2 through 6 until the weight loss is less than 0.6mg.
8. Calculate the costing weight as follows:

Coating weight = total weight loss/total area

Verify that the observed coating weight meets the required specifications. Manufacturing specifications for coating weights differ for various applications. Guidelines for quality manufacturing practices are covered by specifications from agencies such as American Society for Testing and Materials (ASTM), American Architectural Manufacturers Association (AAMA), military specifications (MIL), and AeroSpace Material Specifications (AMS). See Table II for typical examples.

Other Test Requirements

Salt spray resistance tests are also required as standard quality-control practices. Comprehensive testing procedures listed in the following standards and specifications evaluate the performances of the composite film consisting of the conversion coating and paint topcoat.

ASTM D 1730: Standard practices for preparation of aluminum and aluminum-alloy surfaces for painting.
ASTM B 449: Standard practice for chromate treatments on aluminum.
MIL-C-81706: Chemical conversion materials for coating aluminum and aluminum alloys.
MIL-C-5541: Chemical conversion coatings on aluminum and aluminum alloys.
AAMA 603.8: Voluntary performance requirements and test proce dures for pigmented organic coatings on extruded aluminum.
AAMA 605.2: Voluntary specification for high-performance organic coatings on architectural extrusions and panels.

AMS 2473: Chemical treatment for aluminum-base alloys, general purpose coating.

What then are the critical factors in a coating system? Under film corrosion protection is an independently quantifiable property of prepaint treatments. You can measure the unpainted salt spray or humidity resistance and assess performance and quality.

On the other hand, top coat paint adhesion, as it relates top pretreatment quality can sometimes be difficult to measure. This property is jointly dependent on the two coating systems considered. A third factor is substrate metal. Alloy quality significantly affects the overall performance of the coating system.

Other factors being equal, paint quality should be reviewed for inclusion in quality planning, especially if an adhesion problem occurs. Significant quality defects may be contributed by high levels of low-molecular-weight resin and additive fractions in the formulation. These fractions usually have poor wetting properties. This results in weak boundary layers along the underlying substrate. Closely related to the adhesion properties of the paint system is moisture permeability. Corrosion and loss of adhesion is accelerated by poor permeability properties of the paint topcoat.

PREPARATION OF NONFERROUS METALS FOR PAINTING

BY EARL GROSHART
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Metals to be painted should be cleaned to remove oily soils and loose materials. It may not be necessary to remove the natural oxides if they are solid, such as the blue scale on heated steel; however, for many active metals it may be advantageous to remove the natural oxides and replace them with artificially formed oxides by "anodizing." For the preparation of aluminum, see both "Paint Pretreatments for Aluminum" and "Anodizing as a Pretreatment for Aluminum," in this section of the *Guidebook*. The preparation of cadmium, chromium, cobalt, copper, lead, magnesium, molybdenum, nickel, silver, stainless steels, titanium, zinc, and alloys of zinc-nickel and tin-zinc are covered here.

Each metal requires its own processing, but a few general steps are the same for all metals.

GREASE REMOVAL

"Degreasing," i. e. , the removal of oils, greases, waxes, and corrosion-inhibiting compounds, which have in the past been removed in vapor phase degreasers with chlorinated solvents, should now be removed in an environmentally approved manner. These include closed vapor degreasers, solvent (vat) washing, parts washers with cleaning agents in water, and emulsion degreasers. There are a number of closed-loop vapor degreasers that can safely be used with chlorinated solvents. These satisfy and offer the least disruption to production that in the past has used vapor degreasers. Solvent washing with a hydrocarbon solvent, usually a blend of several solvents and a combined low-vapor pressure (below 45 mm Hg at 20°C for the aerospace industry), has replaced some degreasers. If properly covered, these will meet environmental requirements. The parts washers and the emulsion cleaners can be selected so that they leave the work with a water-break-free surface and, thus, would not require further cleaning. The solvent cleaning methods will require alkaline cleaning to provide this water-break-free surface if other processing, such as conversion coating, is to be applied. If not further wet processed, the emulsion cleaning and washer cleaning will require an extra drying step prior to painting.

HAND SOLVENT WIPING

As painting is generally done after the cleaned parts have been exposed, i. e. , after assembly or storage, most parts will require a hand solvent wipe just prior to painting. This is especially true prior to painting with the new environmentally designed high-solids and water-reducible paints. Because they have little or no organic solvent, they cannot tolerate even small amounts of organic contamination on the surface of the substrate. To exacerbate the problem further, as the Clean Air Act of 1990 becomes more defined for various industries, fewer solvents are being allowed for cleaning and their vapor pressures are going down, making them more difficult to remove. Solvents and wipe cloths should be clean. A level of 100-ppm dissolved contamination in the solvent with clean, lint-free wipes should be maintained. Before the solvent dries, it should

be wiped off with a clean dry wiper. This way the soil is removed, not just spread around. Because these solvents find their way into the atmosphere, the wipers should be placed into closed containers until sent to reclamation or to hazardous waste disposal. Sealed plastic bags will work.

"Old work," which is defined as having previously been painted or primed, generally requires different handling, in general. If the work is to be stripped of the coating and started over, one should proceed with the stripping and, when completed, remove or arrest the corrosion and start as if it were new work.

If it is not necessary to remove the old paint, the surfaces can be prepared by mechanically removing any loose material. Wire brushing by hand or with a motor or a light brush-off blast are all methods that work well. The wire brushes should be devoted to a substrate. Although stainless steel can work on all substrates, if it has been used on iron or copper, it should not be used on aluminum or magnesium unless thoroughly cleaned including an acid pickle to remove all foreign metal. Iron wire and copper or brass brushes should only be used on like substrates.

Finally, hand sanding, using sandpapers or mat abrasives, or "dust blasting" should be used on the surface of good materials to roughen the surface and to remove the surface oxidized layers of materials. This will promote better adhesion between the old and the new paint.

After any of the above mechanical treatments, the work should be solvent washed or wiped to remove all of the loose materials, and it should then be final wiped as described above just prior to painting.

WASH PRIMER

This paint preparation goes by a number of names. In addition to wash primer, it is known as pretreatment coat, resin-acid coat, and acid-etch primer, and it has a number of military and commercial specifications that describe the material. The coating is a two-part mixture. The first part is composed of a (polyvinyl) butyl resin dissolved in ethyl and butyl alcohol with small amounts of zinc chromate and magnesium silicate added. The second part, which makes up 20% of the volume, is composed of phosphoric acid (85% ortho), ethyl alcohol, and water. The two parts are mixed just prior to application. The purpose of the phosphoric acid is to react with the metal surface, forming an in situ metal phosphate. As the water and alcohol evaporate, the very thin resin forms a stabilizing coating over the phosphate and promotes adhesion of subsequent coats. This system is only good when the metal substrate will react with the phosphoric acid to form the phosphate. If the acid is not essentially neutralized by the reaction, the coating may appear satisfactory upon drying; but on aging, as water vapor penetrates through the coating, the acid will be reformed and will cause failure of the coating in service. The coating, nevertheless, is useful as an adhesion promoter on some metals and will be recommended for use when appropriate. There are some low-solvent wash primers on the market; these should be investigated if the material usually used will not meet the local air quality district's requirements.

CADMIUM

Cadmium surfaces should be stabilized with a conversion coating prior to painting. A phosphate coating is the usual way of doing this, but chromate coatings, though usually used for corrosion protection, can be painted. Because chromi-

um (hexavalent) poses a health hazard, however, its use is discouraged. Phosphate coatings are usually applied from proprietary baths, all of which should be satisfactory as a paint base. Immersion for 2 to 4 minutes in the following solution will leave the cadmium surface stable enough for painting:

Phosphoric acid (85% ortho), 10 oz/gal
Zinc phosphate, 3 oz/gal
Room temperature

CHROMIUM

A fine sandblasting with one of the hard abrasives — aluminum oxide, silicon carbide, etc. — to provide a matte but smooth finish, followed by solvent wiping to remove dust and a thin coat of primer, will develop satisfactory adhesion. Keep the time between blasting and priming as short as possible.

COBALT

Light sand blasting with aluminum oxide or silicon carbide to provide a matte finish, followed by solvent wiping to remove dust, will be adequate for priming. Wash primer may add additional topcoat adhesion if a traditional primer is not used.

COPPER

Conversion coatings on copper are usually not necessary; however, the black oxide treatments used for adhesive bonding of copper are also paintable. Removal of oily soils, followed by wash primer, will give sufficient topcoat adhesion.

LEAD

Cleaning to remove all oily soils will be satisfactory for lead. The dull natural surface resulting from atmospheric exposure should not be removed. Wash primer or a very thin coat of traditional primer is recommended but not required, provided the first topcoat is applied thin.

MAGNESIUM

Magnesium must be conversion coated or anodized before painting. Products used in mild environments and not subject to mechanical abuse can be conversion coated. The following treatment can be used:

Immerse parts for 1 1/2–2 minutes with agitation in the following solution:

Ammonium phosphate monobasic($NH_4H_2PO_4$), 16 oz/gal
Ammonium sulfite [$(NH_4)_2SO_3 \cdot H_2O$)], 4 oz/gal
Ammonia (30%), 2 fl oz/gal
Room temperature

After rinsing in cold water, immerse for 1 to 2 minutes in the following solution:

Sodium hydroxide, 16 oz/gal
Temperature, 160–190°F
Mild agitation

Hot water rinse and dry and the part is ready for priming. This treatment provides less corrosion protection than the chromates used in the past, but when used with a corrosion-protective paint system, it is satisfactory.

Anodizing should be done on products used in a severe environment or subject to mechanical abuse that may damage the paint. The following solution is recommended:

Potassium hydroxide, 22 oz/gal
Aluminum hydroxide (see note 1), 4.5 oz/gal
Potassium fluoride (anhydrous), 4.5 oz/gal
Trisodium phosphate ($Na_2PO_4 \cdot 12H_2O$), 4.5 oz/gal
Potassium manganate [or permanganate (see note 2)], 2.5 oz/gal
Room temperature
Current density, 18–20 A/ft^2
Voltage, 0–60 VAC
Time, ~8 min

Note 1: Aluminum (1100 alloy to prevent impurities in the bath) can be dissolved into part of the potassium hydroxide in a separate tank and then decanted (or filtered) into the tank.

Note 2: Dissolve permanganate in water prior to adding to the tank.

Make the parts one electrode and the tank the other electrode, or (in a plastic tank) divide the load into approximately equal areas and make each half a separate electrode.

MOLYBDENUM

After cleaning, to provide a water-break-free surface, the paint coatings can be applied. Wash primer can be used but is not necessary.

NICKEL

Nickel will respond to the wash primer pretreatment before applying the topcoat. A light sandblasting to produce a matte surface, which can be primed with the wash primer or a regular primer, will produce satisfactory topcoat adhesion.

SILVER

The cleaned surface can be painted without further processing. Silver that has been chromate conversion coated will also paint satisfactorily. The conversion coating stabilizes the silver from sulfide tarnishing. Surfaces with sulfide tarnish will accept paint so long as the tarnish is not powdery.

STAINLESS STEEL

Stainless steel should be cleaned and can then be given one of the passivation treatments followed by wash primer, or it can be sandblasted and followed as soon as possible with either a wash primer or a regular primer.

Heat-treated materials that have been put through an alkaline scale conditioner and have then either been acid cleaned or hydroblasted to remove scale residues can be painted without further processing.

TITANIUM

Untreated titanium exists in the atmosphere as a passive material, and as such, it is paintable; however, adhesion is only moderate. A conversion coating or an anodize coating is recommended. A phosphate–fluoride conversion coating is applied by immersion for 2 to 3 minutes in the following solution:

Sodium phosphate (Na2PO4), 6–7 oz/gal
Potassium fluoride (KF.2H2O), 2–3 oz/gal
Hydrofluoric acid, 2–3 fl oz/gal
Room temperature

Anodizing can be accomplished by making the part anodic at 10 VAC for 20 minutes in a 70 to 80 oz/gal solution of potassium hydroxide. Steel tanks can be used as cathodes and to hold the solution. Titanium will heat and the solution will produce a caustic spray, so it should be covered and handled carefully.

Both of the treatments will provide satisfactory paint adhesion.

ZINC

A phosphate coating applied after electroplating will render zinc-plated parts paintable. A solution containing 10% phosphoric acid (85% ortho) and zinc phosphate or dissolved zinc (0.5–2.0 oz/gal) will provide a coating satisfactory for painting; however, the proprietary processes intended for heavy phosphate coating are also satisfactory.

New galvanize should be thoroughly washed and given a phosphate conversion coating prior to painting. An alkaline resisting primer will give best results for outdoor exposures. Assembled and weathered galvanize can be washed with a solution of 25% phosphoric acid (85% ortho), 25% isopropyl alcohol, 0.25% wetting agent, and balance water. Allow the solution to stay wet on the part for a few minutes, then wash off by spraying with water (hose or spray bottle, depending on size), and then dry and paint.

Wash primer can also be effective on weathered galvanize, but it may not work well on new work.

ALLOYS

The zinc-nickel and tin-zinc alloys that are emerging as cadmium replacements will respond to both chromate and phosphate conversion coats. Owing to environmental pressures the chromates are not recommended; hence, the phosphate coatings are excellent. Wash primer without conversion coating also works well for a pretreatment.

ENSURING READINESS FOR PHOSPHATE-FREE CONVERSION COATINGS

BY KEN KALUZNY, PRODUCT MANAGER,
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Most everyone involved with metal finishing processes is aware of the new pretreatment technologies available. Several names have been used to identify these alternatives to phosphate-based treatments. Within this article I will use the acronym TMC, transitional metal conversion, as it describes what is on the substrate after treatment similar to using the terms iron or zinc phosphate.

There are dozens of companies that have this technology. Anyone who mixes hydrofluorozirconic and/or hydrofluorotitanic acid in water can say they have the new pretreatment technology. However, there is more to the formulation for success. What matters is performing on your line day after day. It is very important that you roll smoothly into this change. Most TMC line conversions are made without incident. However, there are situations that can create issues for a successful TMC implementation. All I am asking you is to know why you're changing and that it is a sound business decision.

CONSIDERING CHANGE

The features and benefits of the new pretreatments are hard to ignore. Who doesn't want to reduce energy consumption, phosphate usage and washer maintenance? Increasing water discharge regulations and energy costs make TMCs very appealing. Before changing your pretreatment to a TMC, it is prudent to know your current pretreatment cost per unit as well as your first-pass efficiency. If your goal is to reduce cost, then you need to know your current costs to determine if you were successful. The cost to treat or haul away waste is also a factor. If your pretreatment change is motivated by environmental restrictions then perhaps there is no reason to take the time to calculate your operating costs.

Identify Benefits and Savings

Unless your goal is to become a "greener" neighbor or manufacturer, if there are no significant benefits or savings then why change your process? Phosphate restrictions and POTW surcharges could motivate a change in pretreatment technology. If you're operating a wastewater treatment system, then the change to TMC will reduce and possibly eliminate your wastewater treatment costs. Newly imposed environmental restrictions may require your company to treat your wastewater. The capital investment for a wastewater treatment system might be avoided by changing to a TMC.

Cost savings are really what drive the change to TMC. Unless you are using a zinc phosphate process, the savings from switching to TMCs are usually from process-related savings rather than from the TMC product cost and consumption. Energy savings is heavily marketed and realized from eliminating applied heat to the treatment stage and potentially from reduced heating requirements

from the dry off oven. The TMC treatment has a lower surface tension than phosphate surface conversions due to lower TMC coating weights requiring less heat to dry the parts.

Maintenance-related costs are generally lower for a TMC. The absence or extreme reduction of phosphate in the treatment solution significantly reduces the formation of precipitates that accumulate as sludge that makes scale. If you have particulate filtration for your phosphate system, then this cost is virtually eliminated. Washer descaling frequency will by substantially reduced and perhaps eliminated as you won't have the sludge that forms scale.

Product – Process Research

Start your research by determining potential vendors and products. Get references—good and bad. I wouldn't be shy to ask the hard questions of where they have had problems and how they were resolved. We're talking about new technology and manufacturing—stuff happens. You need to find ways to shorten your TMC learning curve. This is one of the reasons I think you should ask for "bad" references. It is helpful to know what has gone wrong and how those issues were resolved. You also want to know how your vendor will respond in times of need. It may or may not relate to your situation. At the very least, the discussion can motivate questions that need addressing prior to implementation. If your risk is substantial, you should consider taking some tours.

Somewhere in the same time frame you should conduct testing of the chosen TMCs. You can use laboratory panels as control panels but should include production substrates to make sure the process is viable. If possible, treat your own parts through an existing TMC production pretreatment system. When you compare lab-prepared TMC panels to a production phosphate panels you are not only comparing the pretreatment technologies but also the washers.

You need to also research the requirements of the chosen TMC. Will the construction of your existing washer be compatible with the TMC's chemistry? Some products require stainless steel construction and all products have better bath life when used in acid-resistant construction. Water quality is also an issue. Most TMCs will require RO or DI water. Solution control equipment and procedures should also be reviewed to make sure you have, or are capable of conducting, pertinent solution control procedures.

Successful implementation requires vendor support. Prior to implementation you need to define support for the start-up and in the following days or weeks. Generally you don't need a representative for weeks but a plan for the vendor to check in on the process is warranted.

Implementation Strategy

Once you have a viable product and process, you should conduct some training prior to charge-up. Include wash line operators as well as painters and appropriate management to familiarize them with the TMC operation as well as the treatment's appearance. The appearance will most likely be different from what they are accustomed. There will probably be several questions that would be better addressed prior to charging up the TMC. Discuss your and your vendor's concerns. They know their product, requirements and limitations. You know your system, requirements and constraints. These need to be fully discussed to make sure that all the necessary steps are taken to ensure a successful implementation.

Those who have used iron phosphates for a substantial time have probably seen

Process Time Sequence	Adhesion	Creepage From Scribe
Normal Time Sequence	5B	0.1 mm
3-Minutes in Stages	5B	0.2 mm
3-Minutes in Drain Zones	5B	2.9 mm
3-Minutes in Stage & Drain Zones	5B	0.4 mm

Table 1. Adhesion Test Results

something unusual and perhaps unexplainable despite the long history of iron phosphating. The chance for something unforeseen with TMC is possible. If there is still uncertainty about how the new technology will perform on your line, then conduct a short-term trial. Consider a 5-stage pretreatment system with the traditional alignment of cleaner, rinse, phosphate, rinse, final rinse. With some effort and a garden hose for auxiliary rinsing you can conduct a short-term TMC after a shift or on a weekend by putting the TMC in stage 4. Run for an hour or two or set a number of parts to treat, test and set the rest on the side for eventual use. In other words, try it on for size to see if it fits your operation. This will help reassure that a change over has a chance of success or whether some modifications are required. If you have multiple paint lines then perhaps you can start your testing on the smallest line or the line with the least amount of risk.

WHAT CAN GO WRONG

Water quality is very important for most if not all TMCs. Cations such as calcium, iron, and magnesium can precipitate vital ingredients of TMCs. If the water hardness isn't too hard then you might not need it. Even if the TMC can tolerate some water hardness, there is concern about its use in the final rinse. The water cations dried on the substrate are hygroscopic and will absorb moisture to form blisters in moist environments, compromising paint adhesion which leads to corrosion. The anions such as sulfate and chloride can initiate corrosion.

Poor rinsing and excessive carry over can also create performance issues. The TMC products operate with very low solids in the treatment solution. In other words, they don't handle contamination very well especially alkaline carry over as it precipitates the active metals in the TMC solution. Lines with insufficient rinsing from lack of stages, poor riser/nozzle performance, or short drain zones lead to quality or product usage issues. High chemical usage can also occur if the solution control procedures aren't adequate.

Insufficient cleaning causes most finishing issues. Obviously all organic soils need to be removed. Inorganic soil removal is more important for TMCs than for phosphating. Phosphate-based surface conversions are more forgiving for metal variations simply due to the phosphate reaction etching the substrate to start the phosphate conversion. The TMCs do not etch the substrate to this extent to produce a surface conversion. If there is a thin layer of organic or inorganic soil, the phosphate etching will undermine the residual soil to give you a passivation. Inorganic compounds formed on the substrate from aging or from reaction with certain lubricant components can interfere with the continuity of the surface conversion. The inorganic compounds and transitional metal oxides are electro-chemically different. The electro-chemical difference



Figure 1. Uniform coating on HRPO rims.

can create corrosion cells. All that is needed is water or moisture and corrosion initiators such as chloride or sulfate commonly found in untreated water. Depending on the quality of your paint and your product's service environment this may be an issue.

WAR STORIES

I'm not going to mention any names of companies or vendors. The TMCs have been around long enough that the stories have made it around our metal finishing world. Vendors are more in tune to this as we are all competing for business with new technology. There is an adage used by pretreatment vendors: every line is unique. As much as suppliers do research, it would be unreasonable to expect a research chemist to anticipate every unique situation. Before I start relating war stories, I want you to understand that I'm telling you about the bad things. My intent is not to make you paranoid but rather prepared for a TMC. Most TMC installations go without incident if there is sufficient planning and resources.

The quality issues aren't always unique to TMCs as they also happen with iron phosphating. Adhesion issues generally stem from improper cleaning and rinsing. Loose deposits will cause paint adhesion issues. Line stops can create flash rusting that is loosely bonded. Ergo, flash rusting can cause paint adhesion issues. A quick test for TMC adherence can be simply done with tape. If you can pull the coating off exposing silver metal underneath, then you will have a paint adhesion problem. This is pretty obvious but leads into a situation where a metal finisher had over a dozen consecutive line stops due to paint color changes. The question was posed: was there a particular area of the 5-stage washer where line stops create adhesion issues.

Laboratory testing was conducted to determine if there was a particularly bad area for parts during a line stop. Lab variations simulated 3-minute line stops in the process stages with normal transfer times, 3-minute line stops in the drain

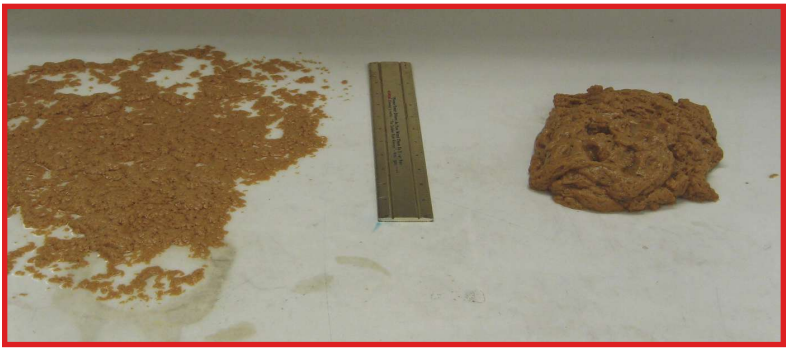


Figure 2. TMC implementation changes how coagulants work in treating wastewater.

zones with normal stage exposure, and three minute stops in both the stages and drain zones. A fourth set was prepared with normal sequence times as a control. Used production TMC solution was utilized for the lab treatment. The time increment of 3 minutes was used as this was the time it took to hand spray a rack of parts and change colors. Adhesion testing and salt spray testing was performed to compare the variations.

To my surprise, all of the cross- hatch adhesion (ASTM D3359) results were perfect. This was not expected and was most likely due to the differences between the laboratory and the production washers. The neutral salt spray (ASTM B117/D1654) results at 336 hours demonstrated better variation. The test data suggests that the line stops in between stages have a greater impact on performance than stopping in the stages that continued to spray solution. Spray impingement prevents the formation of loose deposits that can interfere with paint adhesion and corrosion resistance.

Other process-related issues include flash rusting. Figure 1 illustrates a uniform coating on HRPO rims and an appearance that is not uncommon with TMCs. The HRPO substrates were treated in a 5-stage washer with the TMC in stage 4, followed by a reverse osmosis rinse. As the parts continued towards the e-coat tank their color changed. You couldn't wipe off the TMC coating, although it was evident that the reaction continued. About the same time the e-coat ultra-filters were beginning to plug with an iron containing residue. Drippings were collected to determine how much iron was in the residual water entering the e-coat tank. A high number was 10 ppm and values were typically 2–3 ppm. Assuming 10 ppm of iron was constant, it would have taken 52,000 gallons of iron containing water dragged into the 7,000 gallon e-coat tank to match the amount of iron in the e-coat tank. The metal finisher was conducting TMC trials with multiple vendors. It was unknown how much came from the first or second vendor.

Based on material balance, there was no way that water on parts alone established the iron levels in the e-coat tank. High iron loading had to be related to line stops, and I suspect that the parts were rusty due to line stops in pretreatment and then dissolved in the cathodic e-coat tank. A power and free conveyor would eradicate this situation. Iron entering an e-coat tank is a concern you need to consider. Not all lines have this issue, but I have heard of at least four e-coaters having this issue. In one instance, the e-coat solution had to be replaced. Iron accumulation in rinse tanks has also been seen. In as much as I've heard of this problem, one would think that it could be remediated with better rinse overflow. This is not always the case and generally leads to the use of "rinse aids" or rust preventatives.

High operating cost has also been observed. High water usage was seen on a line where the total RO water usage in the stage before and after the TMC was 52 gpm. This metal finisher also had extreme TMC usage as well. There was high carry-over from the parts processed on this line. High carry is a concern not only for product usage but for quality as well. Phosphate discharge wasn't a concern for this finisher. They were solely interested in energy savings. Once they converted to an ambient iron phosphate they reduced chemical purchases by 58%.

This is the crux of this article. I believe in being green. I reduce, reuse, and recycle whenever I can. But I also believe you need to run your line efficiently to survive and prosper. You need to make good decisions so that you aren't the guy at yet another company saying the conversion to TMC "was a mistake."

Ancillary processes associated with your pretreatment line may also be affected by changing to the new technology. If you continue to treat your wastewater

after implementing a TMC you need to consider the water treatment chemistry. The implementation of TMC changed how the coagulant worked. Figure 2 shows what happened to the right and how the sludge should look on the left. The result was that the sludge became dense and sticky making a mess in the clarifier and sludge thickening tank.

WRAP UP

Transitional metal conversions potentially can save you money while improving quality. I believe in the new technology. However, in the last two years I've seen lines converted in many ways from iron or zinc phosphate to TMC and some went back to phosphating. The common denominator for failed implementation is carry-over contamination and in-process rusting from slow transfer times. I have also seen TMCs replace with competitive TMC's. The reason for this transition is that the original product's capabilities were oversold. It is these situations that motivate my topic.

In closing, do your research, make a plan and roll with the changes with open eyes.

BIO

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SURFACE PREPARATION OF VARIOUS METALS AND ALLOYS BEFORE PLATING AND OTHER FINISHING APPLICATIONS

BY STEPHEN F. RUDY
HUBBARD-HALL, WATERBURY, CONN.

There are three basic considerations for selecting the right cleaning and activation solutions: what to use, when to use, and how to use. These are supported by specific guidelines to help us make the right choices:

- Identify the base metal (type, alloy, surface characteristics)
- Limitations (process line, chemistries, temperature, time)
- Rinsing characteristics (parts, equipment, process line)

The next set of considerations addresses the concern for sufficient, complete soil removal. Focus on condition of the parts, soils, and existing surface coatings.

- Types of soils (oils, grease, shop dirt, buffing and polishing compounds, smuts, scales)
- Existing finishes (chromates, electroplated coatings, phosphates, rust inhibitors)

This issue of the Metal Finishing Guidebook contains additional discussions, references, and suggestions for cleaning and activation, as well as more detailed information regarding filtration, rinsing, analysis, testing, and related subjects.

SOAK CLEANING

Practical soak cleaning should efficiently remove organic soils. But it should also meet F006 sludge reduction mandates, OSHA safety regulations, facilitate analysis control, and simplify waste treatment. More chemically diverse oils in stamping, forming, extruding, and rust proofing, coupled with reduction in solvent cleaning, make the soak cleaner selection more challenging. Liquid concentrates and powder blends are formulated to meet the specific demands of most soak-cleaning requirements. This includes cleaning ferrous and nonferrous metals in the same solution. In some cleaning applications strong alkalis, such as sodium and potassium hydroxide, are beneficial. Conversely, these may be detrimental for removing certain soils, such as chlorinated paraffin oils, or chemically attack nonferrous metals. Factors influencing soak cleaning—time, concentration, and temperature—should be determined by appropriate trial and evaluation, adhering to any specific limitations of the cycle or process. Displacement and emulsification mechanisms remove oils, grease, and shop dirt in this first step of surface preparation. In recent years displacement cleaning has become more preferred to extend cleaner bath service life and simplify waste treatment. Automatic skimming devices, such as belts, coalescers, ultrafiltration, tank weirs, and overflow dams, are mechanical aids to facilitate oil and grease removal

Table I. Operating Criteria for Soak Cleaners

Cleaner Type	*Concentration Range*	*Temperature*	*Time*	*Agitation*
Liquid	4-8% v/v	120-185˚F (49-85˚C)	2-10 min	Solution movement
Powder	4-10 oz/gal (30-75 g/L)	120-185˚F (49-85˚C)	2-10 min	Solution movement

Table II. Soak Cleaner Operating Parameters—Bath Chemistry (oz/gal)

Metal	*Caustic*	*Silicate*	*Gluconate*	*Phosphate*	*Borates*	*Wetters*
Steel	1.8-2.2	1.5-3.0	0.16-3.2	0.4-0.8	—	0.4-0.8
Stainless steel	1.8-2.2	1.5-3.0	0.16-3.2	0.4-0.8	—	0.4-0.8
Brass	0.0-0.8	2.0-4.0	0.16-0.32	0.8-1.6	0.0-0.8	0.4-0.8
Copper	1.6-3.2	1.2-2.4	0.16-0.32	0.8-1.6	0.0-0.8	0.4-0.8
Zinc	0.0	0.8-1.6	0.16-0.32	1.2-2.4	—	0.4-0.8
White metal	0.0	0.8-1.6	0.16-0.32	1.2-2.4	—	0.4-0.8

Multiply oz/gal by 7.5 to convert to g/L
Wetters are usually a balanced blend of anionic and nonionic surfactants.

from displacement and emulsifying cleaners. Most soak cleaners meet the operating criteria shown in Table I. Aluminum requires a specialized, different approach to cleaning, which will be dealt with separately.

Bulk parts may be soak cleaned in line or off line in basket or barrel operations. Table II provides an example of general soak cleaner constituents and applicable concentration ranges. Trial evaluation and testing is required to determine which specific formulation meets the soak-cleaning requirements within the specified cycle limitations.

These are some appropriate cleanliness tests to confirm removal of soils:

- Absence of water breaks on parts rinsed after a weak post acid dip
- Flash rusting of ferrous parts
- White towel wipe cleaned surface, confirming absence of smuts, oils, and grease
- Absence of UV light fluorescence on cleaned surface previously coated with UV fluorescing oils.
- Immersion bronze, copper, or tin deposits on the cleaned, active, appropriately reactive substrate
- Mechanical deformation, bending of finished part or grinding of plated deposit
- Measure the contact angle of a drop of water on the cleaned metal surface.

ELECTROCLEANING

This method uses a DC rectifier to provide current, generating gas bubbles that mechanically scrub the part. This is a powerful cleaning method that complements the previous soak-cleaning step. Parts are predominantly positively charged, resulting in anodic or reverse current cleaning. To a lesser degree parts may be negatively charged, resulting in cathodic cleaning. A third option is periodic reverse, which takes advantage of anodic and cathodic cleaning mechanisms. Electrocleaning can be classified into four groups, meeting most cleaning applications.

1 .Anodic. If preceded by a soak cleaner the electrocleaner's main

Table III. Electrocleaner Operating Parameters

		Current Density, A/ft²		*Voltage*		
Base Metal	*Cleaning Type*	*Rack*	*Barrel*	*Rack*	*Barrel*	*Time (min)*
Steel	Anodic	50-100	10-20	4-8	8-2	1-5
Stainless steel	Anodic	50-100	10-20	4-8	8-12	1-5
Brass[a]	Anodic	15-30	5-10	6-9	9-13	1-3
Copper[a]	Anodic	20-50	5-15	6-9	9-13	1-4
Zinc	Anodic	10-20	5-10	6-9	9-13	1-4
White metal	Cathodic	10-20	5-10	2-4	5-7	1-2

[a]Polished brass and copper may also be cathodically cleaned as per the specifications given for white metal.

function should be effective removal of metallic fines and oxide deposits. Oil and grease removal should be secondary since an effective soak cleaner removes these soils as a primary function. The electrocleaner concentrate can be either liquid or powder. The main ingredient is either sodium or potassium hydroxide as the source of solution conductivity. Desmutters, descalers, and water hardness conditioners are also present. Buffers and inhibitors control the surface action, moderate pH, and protect the base metal against the harmful effects of the process itself and buildup of solution bearing contaminants. Wetters and surfactants provide secondary cleaning to remove organic soils. They also form a light foam blanket to significantly suppress the effects of corrosive fumes during electrolyzing. The bath may also contain reducing agents to control certain contaminants such as hexavalent chromium.

2. Cathodic electrocleaning generates twice the volume of gas bubbles versus anodic electrocleaning. The scrubbing action on parts is essentially doubled. This method is preferred for highly buffed and polished nonferrous metals such as brass, other copper alloys, and white metal. It prevents oxidation, tarnish, and surface attack, which would mar or destroy the desired surface brightness, leveling, and luster.
3. Periodic reverse (PR) is a specialized treatment for descaling and derusting steel. This procedure uses a switch on the rectifier (automatic or manual) that changes polarity on the work between anodic and cathodic in specific time cycles for optimum cleaning. Parts usually exit the process bath anodic, deplating any metallic smuts deposited in the previous highly scrubbing cathodic mode. This oxidation/reduction/oxidation surface treatment softens scales, rust, and oxides, permitting chelates and complexors to dissolve them. These electrocleaners are also referred to as alkaline descalers.
4. Combination soak/electrocleaners meet the requirements of soak

Table IV. Electrocleaner Operating Parameters—Bath Chemistry (oz/gal)

Metal	*Caustic*	*Silicate*	*Gluconate*	*Phosphate*	*Borates*	*Wetters*
Steel	5-7	2-4	1-3	2-4	—	0.1-0.3
Stainless steel	5-7	2-4	1-3	2-4	—	0.1-0.3
Brass	1.5-2.5	1.2-2.4	0.2-0.4	0.8-1.6	0.8-1.6	0.1-0.3
Copper	1.6-3.2	1.2-2.4	0.2-0.4	0.8-1.6	0.4-1.8	0.1-0.3
Zinc	1.2-2.4	1.6-2.4	0.08-0.16	0.4-0.8	—	0.1-0.3
White metal	0.8-1.2	1.6-2.4	0.16-0.32	1.2-2.4	—	0.1-0.3

Multiply oz/gal by 7.5 to convert to g/L
Reducing sugars at 0.2-0.4 oz/gal (1.5-3.0 g/L) reduce hexavalent chromium to the insoluble chromium hydroxide.
Polished brass and copper may also be cathodically cleaned as per the specifications given for white metal. The exception is omitting caustic in the electrocleaner solution.

and electrocleaning in one step, one tank, or in separate process tanks. In many applications this provides three advantages: simplifies product inventory, eliminates a rinse between soak and electrocleaner, and accomplishes both cleaning steps in one tank. A disadvantage would be shorter service life of the electrocleaner due to oil and grease buildup.

Based on the metals electrocleaned, the alkalinity level is critical relative to the caustic (sodium or potassium hydroxide) content. Nonferrous metals, such as copper alloys, brass, and zinc, are best suited to electrocleaning in low- to mid-range caustic solutions. These solutions must also contain inhibitors, such as silicate in ratio with caustic, for optimum conductivity with sufficient inhibition of the zinc surface to prevent etching; Borax buffer and silicate inhibitor for copper alloys and brass to prevent dezincification of brass and excess oxidation of copper alloys; high caustic for steel electrocleaning requirements such as conductivity.

Table V. Acid Dip Operating Parameters

	Temperature			
Base Metal	*°F*	*°C*	*Time (min)*	*Acid Type*
Steel	75-95	24-35	1-3	Hydrochloric/sulfuric
Stainless steel	75-95	24-35	1-3	Hydrochloric/sulfuric
Brass	75-85	24-29	2-4	Sulfuric/sulfamic
Copper	75-85	24-29	2-4	Sulfuric
Zinc	75-85	24-29	1-4	Sulfuric/sulfamic
White metal	75-85	24-29	1-4	Sulfuric/sulfamic

Table VI. Acid Dip Operating Parameters—Bath Chemistry (oz/gal)

Base Metal	*% v/v (H & S) Acid Concentration*	*Fluorides*	*Chlorides*	*Wetters*	*Inhibitors*
Steel	H(5-50), S(5-15)	0.3-0.7	0.8-1.2	0.03-0.05	0.01-0.03
Stainless Steel	H(5-50), S(5-15)	0.3-0.7	0.8-1.2	0.03-0.05	0.01-0.03
Brass	S (3-5)	0.2-0.5	—	0.03-0.05	—
Copper	S (5-7)	0.2-0.5	—	0.03-0.05	—
Zinc	S(1-2), Sul(0.5-0.7)	0.3-0.5	—	0.03-0.05	—
White metal	S(1-2), Sul(0.5-0.7)	0.3-0.5	—	0.03-0.05	—

H = hydrochloric acid; S = sulfuric acid; Sul = sulfamic acid.

Table VII. Cathodic Acid Operating Parameters for Steel and Stainless Steel

Anode	Temperature °F	Temperature °C	Time (min)	Cathode Current Density (A/ft^2)	Voltage
Pure lead	85-120	29-49	2-7	20-60	3-6
Graphite	85-120	29-49	2-7	20-60	3-6

Use lead anodes in solutions that do not contain any fluorides. Otherwise, graphite anodes are required.

The optimum caustic level also dissolves the iron hydroxide surface film that forms, preventing splotchy brown stains and burning due to low conductivity.

Current densities are related to the base metal and whether the application is rack or barrel. (See Table III.) Double cleaning cycles are ideally suited to cleaning and activating welded parts, such as wire goods, or heat-treated parts. Typical operating parameters are given in Table IV.

Sufficiently electrocleaned parts should be free of smuts, oils, and grease. Scales and rust can be removed or softened prior to removal in the acid.

ACID TREATMENT

A more comprehensive discussion of this subject is found in the chapter "Pickling and Acid Dipping."

The consideration of knowing the metal or alloys processed remains a critical factor in selecting the optimum acid solution. Sensitive metals (brass, copper alloys, and zinc) require milder acid treatments. (See Tables V and VI.) Steels can be scaled and rusted, needing more aggressive treatment, even cathodic action. The acids used can be grouped into inorganic (hydrochloric or sulfuric) and organic (sulfamic, citric, gluconic, etc.). Accelerators, such as chloride and fluoride, provide extra "bite" to improve pickling. Fluorides activate brass by dissolving lead smuts. Inhibitors prevent over pickling steel that would result in raising excessive surface smuts or detrimental hydrogen embrittlement. Pickle aids help two ways: lower solution surface tension to improve wetting and increase contact action. Wetting agents generate a light foam blanket to minimize corrosive sprays and mist and emulsify residual oils on parts or dragged into the acid bath. Deflocculents prevent the redeposition of soils.

Double cleaning cycles may employ an aggressive first acid to meet pickling demands. The second acid should be a milder type sufficient to neutralize the second electrocleaner film while activating the surface as a last step before plating. One note of caution! Hydrochloric acid or chloride salts in the first acid presents a special problem. Insufficient rinsing and draining of parts after this dip can drag chloride, a contaminant, into the anodic second electrocleaner. A sufficient buildup of chloride (measured in part per million levels) in the electrocleaner results in corrosive pitting of parts during the reverse anodic cleaning cycle. Specially inhibited electrocleaners minimize this condition, increasing solution tolerance to chloride. Alternatively, a chloride-free acid, if appropriate, should be used before the second electrocleaner. Heavily scaled or rusted steel parts may benefit from cathodic acid treatment. (See Table VII.) This process combines scrubbing action with activity of the acid solution to dissolve scales and rust.

Inhibitors are special amines, substituted ureas, and glycol-based organic compounds. Wetters may be anionic or nonionic types. Some wetters and inhibitors provide a filming action to inhibit attack on the base metal. Good

Table VIII. Operating Parameters for Electropolishing Different Metals and Alloys

Metal/Alloy	*Temperature*		*Anodic Current Density (A/ft^2)*	*Voltage*
	°F	*°C*		
Aluminum	150-200	66-93	10-60	10-30
Copper	65-160	18-71	20-300	6-18
Nickel	85-125	29-52	100-200	10-18
Stainless steels	110-190	43-88	50-500	6-18
Carbon steels	110-140	43-60	100-300	10-18
Titanium	60-105	16-40	80-500	3-10

rinsing is required to remove any films, or in a double cleaning cycle use an inhibited/wetted acid as the first acid, followed by a simple mineral acid as the second acid.

Some modifications are made to cathodically remove heavy scales and rust.

Acid dipped or pickled parts should be free of any organic soils, rust, scale, and smuts. This is the last process treatment bath before plating, painting, chromating, or final topcoat application.

ADDITIONAL CLEANING OPERATIONS

Electropolishing

This is an electrolytic process by which the substrate's surface can be improved using a specific solution. Burrs, belt lines, scratches, scales, and other imperfections anywhere on the surface that is immersed and anodically charged will be polished and refined. Electropolishing is current-density specific. In this regard surface improvement occurs more readily than by mass finishing. A wide variety of common metals and alloys are successfully electropolished, especially the nickel-rich 300 series stainless steels. The electrolyte is typically a mixture of mineral acids. Parts are predominantly racked. The ranges in the operating parameters shown in Table VIII reflect the use of more than one type of electrolyte.

Table IX. Liquid and Powder Spray Cleaner Operating Parameters

Cleaner Type	*Concentration Range*	*Temperature*		*Time (min)*	*Agitation*
		°F	*°C*		
Liquid	2-5% v/v	100-160	38-71	0.5-3	15-35 psi
Powder	3-6 oz/gal[a]	100-160	38-71	0.5-3	15-35 psi

[a]22.5-45 g/L

Table X. Spray Cleaner Operating Parameters—Bath Chemistry (oz/gal)

Metal	Caustic	Silicate	Complexor	Phosphate	Glycols	Wetters
Aluminum	—	0.05-0.1	0.08-0.12	0.10-0.17	0.10-0.14	0.06-0.09
Steel	0.4-0.8	0.3-0.6	0.10-0.14	0.10-0.17	0.10-0.14	0.06-0.09
Stainless steel	0.4-0.8	0.3-0.6	0.10-0.14	0.10-0.17	0.10-0.14	0.06-0.09
Brass	0.0-0.06	0.3-0.6	0.12-0.17	0.2-0.4	0.10-0.14	0.06-0.09
Copper	0.0-0.17	0.15-0.3	0.12-0.17	0.2-0.4	0.10-0.14	0.06-0.09
Zinc	—	0.3-0.6	0.12-0.17	0.1-0.2	0.10-0.14	0.06-0.09
White metal	—	0.3-0.6	0.12-0.17	0.1-0.2	0.10-0.14	0.06-0.09

The cleanliness criteria are the same as described in the soak cleaning section.

Table XI. Mass Finishing Media Shapes and Applications

Media	*Application*
Triangles	Reach slotted areas and reach into corners
Cones	More effective on concave and convex surfaces
Pyramids	Large, flat surface contact; works holes, doesn't pass through
Stars	Deburrs inside diameters, blind holes, reduces lodging
Tetrahedrons	Sharper points provide better penetration into remote areas
Wedges	Reduces lodging. Large, flat surface maximizes contact
Angle-cut cylinders	Best on concave surfaces, round areas, and holes
Tri-Cylinders	Excellent for concave and convex; corners, slots, angles
Spheres	Smooth rolling. Good for concave. Rolls around and through
Angle-cut triangle	Better penetration into remote areas
Ellipses	Good on concave surfaces

Deburring and rough cuts require ratios from 6:1 down to 1:1. Burnishing and high luster require 10-12:1 or up to 20:1.

The solutions are acidic, typically composed of the following inorganic acids: chromic, fluoboric, hydrochloric, phosphoric, and sulfuric, in varying combinations and strengths. Organic additives, such as glycols, help to condition the surface during electropolishing.

Spray Cleaning

A wide variety of ferrous and nonferrous metals are cleaned in this optional procedure. Spray cleaning can be accomplished off line, as a precleaning step, or in the process line operation. It provides the following benefits:

- Low foaming cleaning action with displacement of soils
- Mechanical action facilitates cleaning
- Lower temperature ranges for energy savings

The alkalinity level of the spray cleaner may range from near neutral (approximately 8) to high pH (14). This accommodates cleaning many metals (aluminum, brass, copper alloys, steel, stainless steel, and zinc). A desired or effective chemistry lifts soils. The concentration of surfactants and wetting agents can be low since mechanical action of spraying helps to dislodge soils. Displacement of

Table XII. Aluminum Alloy Designations

Aluminum Alloy Type	*Number Group*
99% minimum and greater	1XXX
Copper	2XXX
Manganese	3XXX
Silicon	4XXX
Magnesium	5XXX
Magnesium and silicon	6XXX
Zinc	7XXX
Other elements	8XXX
Unused series	9XXX

First digit: alloy type. Second digit: alloy modification. Third and fourth digits: aluminum purity of alloy.

Table XIII. Aluminum Soak Cleaner Operating Parameters—Bath Chemistry (oz/gal)

Metal	*Caustic*	*Silicate*	*Gluconate*	*Phosphate*	*Borates*	*Wetters*
Aluminum	—	—	0.15-0.30	0.8-1.2	3.0-5.0	0.4-0.8

oils and grease allows them to be collected in a side tank and removed by skimming or other separation device. This extends service life of the cleaner. It's a real benefit considering the heavy oil loading some incoming parts have. Removing displaced soils also prevents them from being sprayed on to parts that are to be cleaned. Water hardness conditioners in the spray cleaner are invaluable to prevent nozzle pluggage. Typical operating conditions shown in Tables IX and X.

Mass Finishing

This method helps with off-line capabilities. Cleaning, deburring, descaling, and burnishing are surface improvements accomplished by mass finishing. The base metal is conditioned prior to additional surface finishing. Critical areas are rounded out and burnishing can result in low rms value or high luster. The process combines mechanical energy and chemical action. The mechanical contribution is by tumbling in horizontal or oblique barrels or by using vibratory bowls. Specially blended chemicals are added in dilute-liquid form or low-concentration powders. They wet and react with the surface of parts, allowing other parts or special media (e.g., plastic, ceramic, or stone) to work on the parts. (See Table XI.) Mass finishing is especially helpful to seal porosity of aluminum and zinc before transfer to the plating line. If parts are to be mass finished or if this is a feasible option, trial evaluations are recommended to determine best suited equipment, media, and optimum: media-to-parts ratio, flow rates, and cycle times.

SURFACE PREPARATION FOR SPECIFIC METALS & ALLOYS

The selection of specific working solutions should be determined by first evaluating candidate baths to meet or exceed requirements while adhering to cycle and handling limitations. Information is given for the more commonly encountered metals and alloys.

Table XIV. Alkaline Aluminum Etchant Operating Parameters—Bath Chemistry (oz/gal)

Caustic	*Complexor*	*Conditioner*	*Wetting Agent*	*Defoamer*
6-7	3-5	2-4	0.006-0.009	0.02-0.05

Table XV. Acidic Aluminum Etchant Operating Parameters Bath Chemistry (% v/v)

Sulfuric Acid	Phosphoric Acid	Complexor	Wetting Agent
5-7	2-5	2.5-4.5[a]	0.006-0.009

[a]oz/gal

Table XVI. Aluminum Desmutting Chemistry Depends on Alloying Elements

Alloy Type	*Sulfuric Acid*	*Nitric Acid*	*Fluorides*
High silicon	10-25% v/v	—	3.0-8.0 oz/gal
High copper	—	15-25% v/v	1-3 oz/gal
Low alloys	10-25% v/v	—	—

Note: Volume balance as water. Ammonium bifluoride suggested source of fluorides.

Table XVII. Die Cast Alloy Compositions

Element	*Series 380 Assay*	*Series 413 Assay*
Magnesium	0.10 max.	0.10 max.
Zinc	3.0 max.	0.50 max.
Manganese	0.50 max.	0.35 max.
Silicon	7.5-9.5	11.0-13.0
Copper	3.0-4.0	0.60 max.
Iron	1.0 max.	0.80-1.1
Nickel	0.50 max.	0.50 max.
Titanium	—	—
Chromium	0.35 max.	0.35 max.
Tin	—	0.15 max.
Lead	—	—
Cadmium	—	—
Other	0.50 max.	0.20 max.

ALUMINUM

Aluminum is in a class by itself. It requires special handling, using some unique steps and considerations. Because of its light weight, heat capacity, durability, and corrosion resistance, aluminum is the metal of choice for many applications. A surface preparation cycle for electroplating or electroless plating generally consists of soak clean, etch, desmut, zincate, optional double zincate, strike plate, and plate.

It may seem easy but aluminum demands we invest in a quality effort to obtain a quality finish. Knowing the alloy designation is critical to selecting the optimum bath chemistries for each step in the surface preparation cycle. (See Table XII.)

Soak cleaning denotes no etching or attack of the base metal. (See Table XIII.) The cleaner bath pH ranges from 8 to 9.5. Ultrasonic soak cleaners also have a similar chemistry profile. They differ in containing higher detergency levels along with selected solvents.

Etching is accomplished using acidic or highly alkaline solutions. (See Tables XIV and XV.) This is the primary method of removing the outer, passive aluminum oxide skin. Etching also cleans the surface by undercutting soils and lifting them off.

Etchants and preferences:

- Alkaline—aluminum alloy extrusions, and stampings.
- Acidic—castings, polished parts, and prior to electroless nickel.

When etched, some alloys (in the 5000, 6000 series, and castings) tend to generate heavy smuts. This can lead to incomplete desmutting, detrimentally affecting the zincate treatment. Acidic etchants, being less aggressive, raise less smut. Typical desmutters are given in Table XVI.

Other desmutter baths for consideration:

- 50-100% v/v nitric acid
- 15-25% v/v nitric acid + 10-20% v/v sulfuric acid
- Iron salts (ferric sulfate 3-4 oz/gal + 5-10% v/v sulfuric acid

Table XVIII. Suggested Copper Strike Formulations

Component	*Concentration (oz/gal)*
Copper cyanide	3.50
Sodium cyanide	4.25
Sodium carbonate	4.00
Rochelle salts	4.00
Copper cyanide	1.5-3.0
Free sodium cyanide	0.2-0.4 Copper cyanide conc.
Potassium hydroxide	0.1-0.5

- Universal tri-acid. Mixture of 50% v/v nitric acid + 20-25% v/v sulfuric acid + 1-2 lb/gal ammonium bifluoride, balance water to 100%.

Aluminum die cast alloys (see Table XVII) are based on six major elements: silicon, copper, magnesium, iron, manganese, and zinc. An example of applying the preferred desmutting bath can be illustrated by the following casting comparisons.

Tips:

- The universal tri-acid is best suited to desmut both of these castings; however, the formula containing 2 lb/gal of ammonium bifluoride is recommended for the series 413 casting. That's because of its greater silicon content (41% more).
- Usually, the aluminum part will exit the desmut bath white and smut free. Close inspection may also indicate a very fine surface etch, which is actually beneficial for zincating or chromating. If the part fails a white paper towel wipe (smutty) chances are slim that subsequent processing will be successful.
- If the part gasses while immersed in the zincate there is a good possibility it hasn't been properly desmutted.
- If the desmut bath contains nitric acid be certain that good operating, compliant exhaust is in use to safely vent off nitric oxide fumes.

Zincating

This is an immersion treatment where a coating of zinc or zinc alloy is deposited over cleaned and activated aluminum. It is over this tightly surface-adherent film that plating can occur. There are three common zincating solutions:

1. Conventional zincate. This solution contains one metal, zinc, which is immersion deposited over aluminum. It also contains an oxidizer, such as sodium nitrate, conditioning the aluminum surface by mildly etching it. Tartrates are included as complexors. The viscous working solution is concentrated in sodium hydroxide (forming the chemical zincate). Baths prepared from powdered concentrates must be cooled for several hours before they can be used. 11-13 oz/gal sodium hydroxide, 2-3 oz/gal zinc oxide, 0.6-0.8 oz/gal sodium nitrate, 75-85°F (24-29°C), 0.5-2 minutes.
2. Conventional alloy zincate. Similar to the conventional zincate but differs as follows: contains iron, which forms an Fe-Zn alloy

Table XIX. Suggested Watts Nickel Strike Formulation

Component	*Concentration (oz/gal)*
Nickel metal	10-12
Nickel chloride	8-10
Nickel sulfate	32-37
Boric acid	5-6

immersion deposit. Chemistry and operation as previous plus 0.2-0.4 oz/gal ferric chloride

3. Modified alloy zincate. Similar to conventional alloy zincate but differing as follows: contains several metals (commonly from among copper, iron, nickel and zinc, forming a unique alloy immersion deposit. Copper and nickel control rate of zincate formation and enhance its tight, cross-linked structure. Gluconate complexors (small amounts of cyanide are optional) used in place of tartrates, and much less sodium hydroxide. The working solution is much less viscous, providing improved rinsing characteristics.

In each zincate described, the type and concentration of complexors are critical to maintain solubility of the alloying metals.

Which zincate to use? The conventional zincate is a good process when applied to high-purity aluminum alloys. But, it doesn't provide as strong adhesion over 5000 and 6000 series alloys as do conventional alloy and modified alloy zincates. The latter provide a far stronger bonding to a wider range of aluminum alloys. This is due to formation of less porous, denser, uniform films. They also protect sharpened corners and edges of zincated parts from being worn and abraded in barrel plating.

Tips on zincating include:

- Rinse well before the zincate bath to prevent drag in of desmut acid solution. For example, fluorides will detrimentally affect the zincate film.
- The zincate should be an even gray or blue-gray color. Splotchiness may indicate zincate solution components are out of balance.
- Poor adhesion of zincate to basis aluminum may be due to bath temperature out of range or poor cleaning and surface preparation.
- Spongy zincate (thickened) is usually a result of excess immersion time or too high bath temperature.
- A good, adherent zincate film will pass a Scotch tape pull.

Strikes

Copper

This bath is designed to coat the zincated surface with a strong bond, while not attacking it in the process. (See Table XVIII.) The deposit serves as an active site for reception of subsequent electrodeposits, some of which might be highly aggressive toward the unprotected zincate.

Both formulas operate at 4 A/ft^2 for 5 minutes or at 25 A/ft^2 for 10 seconds,

Table XX. Wood's Nickel Strike Bath Composition

Component	*Concentration*
Nickel chloride	30-34 oz/gal (225-255 g/L)
Hydrochloric acid, 22[deg]Be	10-12% v/v
Nickel anodes	Sulfur free

110-125°F (43-52°C). pH of first bath at 10-10.5. pH of second bath at 11.5-12.0. A proprietary grain refiner and anode corroder may also be added.

Electrolytic Nickel

The purpose is the same as the copper strike, protect and seal the zincate film, preparing the part for reception of additional deposits. (See Table XIX.)

The bath is operated at the same current density as Watts nickel barrel and rack plating solutions. Time is just sufficient to cover the zincate. Bath pH should be maintained at 4.4 to 4.6 to minimize attack of solution on the zincate. Proprietary wetting agent and zinc tolerant Class I brightener (carrier) are normally added. Routine low current density (LCD) dummying at 5 to 10 A/ft² is recommended to plate out zinc contaminant.

Where possible, live entry into any of the described strike baths is recommended. This can be accomplished by using an auxiliary cable, while parts are in transit "live" to the strike bath. Plating begins as soon as the parts contact the solution, significantly minimizing attack on the zincate.

Alkaline Electroless Nickel

The benefit of this bath is total, even nickel thickness of all exposed surfaces since this is an immersion process. The zincate itself is catalytic toward the electroless nickel solution. For a 10-min immersion the deposit thickness may range from 20 to 30 millionths of an inch, at 110°F (43°C). Bath pH is 8.5 to 10.0.

Low Carbon Steels (e.g., stampings and extrusions)

Standard soak clean, electroclean, and acid dip, as described in process bath descriptions.

High Carbon Steels (e.g., springs, fasteners, lock parts)

Classified as above 0.35% carbon. Base metal has higher smutting tendency. Preferred acid dip consists of 25 to 40% v/v hydrochloric acid with additions of a pickle aid and wetting agent. The pickle aid minimizes attack on the base metal, greatly reducing tendency for hydrogen embrittlement. Stress due to hydrogen embrittlement can be relieved by baking at 350 to 400°F (177-204°C) for to 3 hours.

Cast Iron

Standard alkaline soak clean, followed by alternate hot and cold rinsing to push solutions out of pores. Anodically electroclean in alkaline descaler. Parts exiting the electrocleaner should have a uniform light yellow cast. Dip in 15 to 20% v/v

Table XXI. Wood's Nickel Strike Operating Parameters

Operating Parameter	*Range*
Temperature	75-90°F (24-32°C)
Anodic Treatment	10-20 A/ft², 1-2 min (optional)
Cathodic Treatment	40-120 A/ft², 2-3 min

hydrochloric acid or 5 to 10% v/v sulfuric acid, to dissolve oxides, desmut, and form an active surface for plating.

High Strength Alloy Steels

These materials retain a Rockwell C hardness of 38 or higher. Hydrogen embrittlement can be avoided by using the acid dip as mentioned previously. Baking at 50 to 75°F (10-24°C) below the tempering temperature, 800°F maximum (427°C) is recommended.

Stainless Steel

Standard soak and electrocleaning followed by acid dip or pickle is not sufficient if the material is to be plated. Surface passivity must be overcome. This is accomplished by a treatment in the Wood's nickel strike solution. (See Tables XX and XXI.)

Beryllium Copper

This copper alloy typically contains 2% beryllium with 0.25% cobalt and 0.36% nickel.

Surface preparation cycle:

1. **ALKALINE SOAK CLEAN TO REMOVE ORGANIC SOILS. MILD TARNISH IS ACCEPTABLE.**
2. Electroclean in a specially buffered blend (refer to suggested formula for copper), having moderate caustic at 20-40 A/ft^2, anodic.
3. Activate in a mildly etching solution composed of peroxy derivatives, persulfates, or sulfuric acid with fluoride. Ex. 2% v/v of sulfuric acid and 4 oz/gal ammonium persulfate.
4. Rinse well,. proceed to plating bath.

Cobalt

Surface preparation similar to stainless steel. The Wood's nickel strike is very important to develop a sufficiently active surface to accept subsequent plated deposits.

LEADED BRASS (0.35-4.00% LEAD)

Red and Yellow Brasses Commercial Bronzes

Surface preparation cycle:

1. Soak or ultrasonically clean to remove buffing and polishing compounds. 20-40 KHz/gal. Highly wetted, with solvents, soap optional.
2. Secondary soak clean. Moderate alkalinity, containing surfactants, some inhibition preferred.
3. Electroclean at 10-30 A/ft^2, anodic. Buffered blend similar to application on copper alloys.
4. Activate. Sulfuric acid type containing fluorides, essential to dissolve lead smuts.
5. Rinse well, proceed to plating bath.

Bright Dipping Brass

Table XXII. Zinc Alloy Compositions

Alloy	*% Zinc*	*% Aluminum*	*% Magnesium*	*% Copper*	*% Lead*
Pure	99.9+	—	—	—	—
Zamak 3	Balance	4.0	0.04	—	—
Zamak 5	Balance	4.0	0.04	1.0	—
Zamak 2	Balance	4.0	0.03	3.0	—
Slush	Balance	4.75	—	0.25	—
Slush	Balance	5.5	—	—	—
Drawn	Balance	—	—	—	0.08

1. Mild to moderately alkaline soak cleaner.
2. 5% v/v sulfuric acid dip. Neutralizes and conditions the surface.
3. Chemically polish in either a peroxide-type or sulfuric acid/iron salts blend. Both solutions are wetted and specially inhibited.
4. Tarnish inhibit in dip application using either a soap (mechanical tarnish inhibit film) or a benzotriazole (active surface antioxidant).
5. Optionally lacquer (dip or electrolytic) or apply electrolytic chromate.

Inconel

This alloy constituent typically contains 13.5% nickel and 6.0% chromium. (Note: one alloy type may contain 2% silicon.)

Surface preparation cycle:

1. Alkaline soak clean. Mild to moderate alkalinity with sufficient detergency.
2. Acid dip. 20-30% v/v hydrochloric acid for primary oxide removal.
3. Anodically etch. Wood's nickel strike, 100-120°F (38-49°C), 50 A/ft^2, 20-30 sec.
4. Strike plate cathodic. Woods' nickel strike, 100-120°F (38-49°C), 50 A/ft^2, 2-3 min.
5. Rinse well, proceed to plating bath.

The above cycle is sufficient for Inconel X and Hastelloy C.

Nickel and Nickel Alloys

Require similar treatment as stainless steels. Anodically etch at 15 to 25 A/ft^2 for 1 to 3 minutes in a 25% v/v sulfuric acid solution. Next, cathodically condition at 150 to 225 A/ft^2 in the Woods' strike, or at 40 to 60 A/ft^2 in a sulfuric acid/fluoride/chloride solution. Parts not long aged may also be activated in an immersion dip consisting of 5 tp 10% v/v sulfuric acid and 2 to 4 oz/gal of potassium iodide at 75 to 90°F (24-32°C). These treatments also apply for replating aged nickel plated parts and rejects.

Powdered Metal

Same recommended surface preparation steps as for cast iron. Rinsing is very important, to facilitate drainage and removal of previous contaminating solutions.

Silver

The metal and its alloys tarnish readily, forming a blackish oxide film. After soak cleaning in an appropriate caustic containing cleaner, dip in 5 to 10% v/v sulfuric acid to neutralize surface. Next, chemically polish in a solution consisting of 20 to 25% v/v hydrogen peroxide, at 85 to 100°F (29-38°C).

Titanium

Activation is the critical factor. The following cycle may be appropriate with sufficient testing beforehand.

Surface preparation cycle:

1. Alkaline soak clean.
2. Activate and pickle in a solution consisting of 20-25% v/v hydrofluoric acid 75-80% v/v nitric acid.
3. Etch in solution of sodium dichromate at 30-35 oz/gal (225-263 g/L) and 4-5% v/v hydrofluoric acid for 15-30 minutes.

Thorough rinsing between each step.

Zinc and Zinc Alloy Die Castings

Zinc is molten and cast into many shapes and forms, comprising a wide variety of consumer and industry relegated parts. Just like aluminum, zinc is available in different alloys. (See Table XXII.) The casting operation does result in surface defects, which must be corrected in an appropriate manner either before shipment to the plater or in the surface preparation cycle. Pores, cracks, "cold shut," and roughness are some of these common problems. Mechanical operations, such as buffing and polishing, refine, and smooth the surface but leave accumulated buildup of related soils, grease, compounds, and rouges. The exceptionally high temperature of these mechanical finishing techniques will burn, harden, and drive contaminants into the metal surface. The sooner parts are cleaned the easier the surface preparation cycle becomes.

Surface preparation: (refer to specific cleaner baths and operating parameters, as previously given)

1. Soak or ultrasonically clean. Removing buffing and polishing compounds. The cleaner may be wetted with glycol and cyclic pyrollidone type solvents. A combination of high HLB and low HLB surfactants are helpful. Soaps are also an option. The cleaner should be buffered to prevent tarnish and etching of the zinc surface. Many buffing and polishing compounds are effectively softened in the soak cleaner at 175-190°F (79-88°C). Ultrasonic conditioning uses 25-43 KHz/gal of power in the solution to maintain effective standing waves, resulting in bubbles imploding on the surface for cleaning action. Temperature of the ultrasonic cleaner should be in the range of 160-180°F (71-82°C). Somewhat cooler to avoid higher temperatures, which distort the standing waves.
2. Secondary soak clean. Removes residual organic contaminants and any inhibiting films that may have formed on the surface during the step #1 soak cleaning.
3. Electroclean. Moderate alkalinity, inhibited.
4. Acid dip.

Zinc die castings may be treated in a specially blended acid solution, commonly referred to as immersion chemical polishing. This process facilitates surface preparation by deburring, smoothening, leveling, and brightening. Common base metal defects, such as nodules and pores, are effectively worked out. A typical solution consists of: 42° Be` nitric acid (20-30%), 66° Be` sulfuric acid (20-25%), ammonium bifluoride (20-40%), and nonionic or amphoteric surfactant (>0.5%).

Application: 65-115°F (18-46°C). Maintaining temperature is critical to avoid etching or dulling the surface. Immersion time depends on particular surface requirements. Organic soils (grease, oils, buffing compound, mold release, etc.) should be removed in a suitable soak or ultrasonic cleaner before the chemical polishing step.

Thorough rinsing is understood between steps.

Copper strike as per formulas given for zincated aluminum. Castings should be sealed with at least 0.03 to 0.05 mil. Additional copper as plated to 0.08 to 0.14 mil before application of nickel plating.

HIGH-SOLIDS, LOW-VOC, SOLVENT-BASED COATINGS

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This article focuses on the most common high-solids, solvent-based coating technologies. Each of the resin systems discussed is available to meet the Reasonable Available Control Technology (RACT) limits of most state volatile organic compounds (VOCs) regulations. Most systems are also available to satisfy the more stringent regulations of California and the Best Available Control Technology (BACT) requirements of other states.

The discussions and tables presented in this article provide sufficient detail to enable a company that is out of compliance with state regulations to make an initial selection of potential coatings that may satisfy the company's performance and production requirements; however, it will still be necessary to ask vendors for samples and to conduct comprehensive production-type tests before implementing the technology of choice.

AIR AND FORCE-DRIED ALKYDS

These alkyds are air- or force-dried at temperatures less than 90°C (194°F). Alkyd resins are essentially oil-modified polyesters and are made by reacting an alcohol with an acid. [Eq. (1)}

$$\text{Acid} + \text{Alcohol} = \text{Oil-free polyester} \qquad (1)$$

Typical acids used are phthalic anhydride and maleic anhydride. Typical alcohols used are pentaerythratol, glycerine, ethylene glycol, trimethylol ethane and trimethylol propane. These acids and alcohols can be combined in various combinations under very precise and controlled conditions. They form a wide range of alkyd resins, each of which, either alone or in combination, has its own distinctive chemical and physical properties. The coating formulator chooses the appropriate resin, or combination of resins according to customer requirements (see Table I).

Alkyds can also be modified with other resins to change or improve their fi-

Dark industrial air-drying enamels
Maintenance enamel
Automovtive refinishing top coats
Industrial air-dry primers and top coats
Chemical resistant coatings
Metal primers
Industrial maintenance enamels
Toy Enamels
Implement enamels
Exterior metal finishes
Exterior maintenance enamels where color and gloss retention are desired

Table I. Typical End-Uses of Solvent-borne Modified Alkyds

nal properties, such as hardness, gloss retention, color retention and sunlight resistance. [Eq. (2)]

Acid + Resin, phenol formaldehyde, vinyl toluene, styrene, acrylic, or silicone= Modified alkyd (2)

Typical modifying resins include styrene, vinyl toluene, acrylics, silicone and others. The modified resins are more commonly known as modified alkyds. Alkyd and modified alkyd enamels are available in VOC-compliant formulations as high-solids coatings with VOCs of 340–420 g/L (2.8–3.5 lb/gal).

The most important advantages of high-solids alkyds and modified alkyd [air- or force-dried, with VOCs less than 420 g/L (3.5 lb/gal)] are the following: (1) They are single-component coatings with performance properties similar to those of conventional solids alkyds. (2) They are available at VOC levels of 3.5 lb/gal, with a few at 2.8 lb/gal. (3) They can be formulated as primers and top coats and can be air-dried at ambient (room) temperature, although they should preferably be force-dried below 90°C (194°F). (4) They can be spray applied with conventional air-atomizing spray, airless, air-assisted airless and HVLP and the full range of electrostatic spray guns. (5) They are available in a wide range of colors and all gloss levels and are easy to self-touch-up. (6) They can be applied to most substrates, although they are not recommended for application directly to zinc or zinc-coated surfaces; a nonalkyd primer should be used instead. (7) They are less sensitive to the surface cleanliness of substrates than most other coatings. (8) They are the preferred choice of coating for many low-to-medium cost items or for large machinery that cannot be subjected to high-temperature ovens.

Disadvantages are the following: (1) High-solids formulations generally have long *ambient* air-drying times (approximately 6 to 8 hours). (2) It is often difficult to maintain film thicknesses less than 1.5 mils. This is particularly evident on complex geometries, such as weldments and assemblies. Therefore, by default more coating is applied than is actually required. (3) They tend to exhibit higher viscosities than high-solids polyurethanes of similar VOC content. (4) Some formulations require the coatings to be heated during spray application to adequately lower the viscosity for application. (5) Gloss and color variations can occur from one surface to the next, owing to uneven film thicknesses. (6) Long recoating times, sometimes several hours or overnight, are not uncommon. This is aggravated if the film thickness is too high. (7) Some modified alkyds have a "critical" recoating period. The coating cannot be recoated during a certain window, sometimes 2–10 hours. (8) They are not generally used for texture finishing. (9) They tend to be relatively soft coatings initially. Hardness improves over a period of days to a final pencil hardness value of approximately HB (compare this with a pencil hardness of 3H–6H for epoxies and polyurethanes). (10) They tend to have limited resistance to long-term ultraviolet (UV) (sunlight) exposure; chalking and color fading are prevalent. (11) They exhibit poor resistance to alkalinity, chemicals, solvents, and immersion in water.

Alkyds and modified alkyds are commonly used as general-purpose shop primers for steel and other substrates; however, they are not recommended for direct application to zinc or zinc-coated substrates.

Because alkyd resins can be modified in so many ways, they are still among

the most popular systems recommended for general-purpose topcoats. When high-performance properties are required, such as resistance to strong chemicals or solvents or color and gloss retention when the coating is exposed to sunlight over the long term, other resin systems are usually more appropriate. Alkyds and modified alkyds are also among the least expensive of the VOC-compliant coating systems.

BAKED ALKYDS

Baked alkyds include melamine formaldehyde, urea formaldehyde or phenolic modifications as well as polyester, oil-free and acrylic coatings. The primary difference between air- and force-dried alkyds and baked alkyds is that they do not dry at ambient (room) temperatures but must be cured at elevated temperatures, usually in the range110–176°C (230–350°F) for 45–10 minutes, respectively. Although the coatings may feel touch dry after air-drying, they can only achieve their optimum chemical and physical resistance properties after they have been fully cured at their specified baking schedules.

Non-air-dried (baked) alkyds are cross-linked with stabilized "aminoplast" resins because the cross-linking is initiated when the high temperatures are attained. The most frequently used aminoplast resins are urea formaldehyde and melamine formaldehyde.

In the white baking enamels that are used for metal shelving, metal furni-

$$\frac{\text{Polytester}}{\text{Polyhydric alcohol}} + \text{Coconut oil} = \text{Alkyd} \qquad (3)$$

$$+$$

$$\text{Polybasic acid}$$

$$\text{Alkyd} + \begin{matrix}\text{Urea formaldehyde}\\ \text{or}\\ \text{melamine formaldehyde}\end{matrix} = \text{Modified alkyd} \qquad (4)$$

ture, computer cabinets, etc., urea formaldehyde provides excellent initial color, color retention and resistance to heat, soap,water and fatty acids. Alkyd baking enamels based on melamine formaldehyde are harder, more chemically resistant and faster drying. They are used to coat refrigerators, washing machines, high-quality fluorescent light fixtures, and automotive components.

A typical sequence of reactions for these types of coatings is shown in Eqs. (3) and (4):

These coatings are available at 360 g/L (3.0 lb/gal), as required in most states. Some formulations are as low as 275 g/L (2.3 lb/gal).

The advantages of the baked alkyds are the following: (1) They are available at VOC levels [275 g/L (2.3 lb/gal)] to meet most regulations and offer excellent high performance properties. (2) They are single-component coatings, available in wide range of colors and gloss levels, and can be applied directly to metal substrates. (3) They are excellent for appliances, such as washing machines, driers, dishwashers, refrigerators, metal shelving and cabinets and lighting fixtures. (4) With proper controls, they can achieve uniform, thin film thick-

ness of approximately 1 mil. (5) They have excellent pencil hardness greater than 2H. (6) In many cases, they do not need special application equipment and have good adaptability to high-speed lines. (7) They offer film properties better than the air- and force-dried alkyds. (8) Some energy savings is possible because of lower solvent concentrations.

Disadvantages are the following: (1) High-energy usage. They must be baked at elevated temperatures with schedules such as 45 minutes at 110°C (230°F) or 10 minutes at 176°C (350°F). (2) Some formulations remain tacky at ambient temperatures and leave walls and floors of spray booths tacky. (3) High viscosities of some compliant formulations require special spray application equipment. Alternatively, apply at fluid temperatures of 100–110°F. (4) They are not for plastic or other heat-sensitive substrates because of the high baking temperatures. (5) Stains caused by the spray washer cleaning process are often "photographed" through the coating finish. (6) As with many high-solids coatings, smooth finishes, free of orange peel, may be difficult to achieve. (7) They may require close application controls. (8) An operator learning curve required. (9) Applied costs are greater than for conventional-solids baked enamels.

EPOXY ESTERS

Epoxy esters are coatings that in many ways resemble alkyds in that they are single component and require no mixing of multicomponents prior to application; however, they are harder and more chemically resistant. In addition, they are available in solvent- or waterborne formulations. Epoxy esters are air- or force-dried at temperatures less than 90°C (194°F).

The similarity between epoxy esters and alkyds lies in the fact that they are the products of reactions between moderate equivalent weight (800–1,500) epoxy resins and fatty acids. The properties of the resulting epoxy ester polymer resins are related to the actual equivalent weight of the original epoxy resin and the type of fatty acid with which it was esterified.

Consequently, some epoxy esters are softer, more flexible and slower drying than other formulations that may be harder and faster drying. They also tend to have better chemical resistance and are harder than alkyds.

These resins require metallic driers, as do alkyds, to start and maintain the drying sequence. These coatings are used in situations where alkyds would normally be selected but where a harder and more chemically resistant finish is required.

The advantages of epoxy esters are the following: (1) Coatings are single-component materials and therefore maintain a constant viscosity, provided that temperature remains constant. (2) They are available in high-solids formulations. (3) They can be formulated into VOC-compliant water-reducible formulations at very low VOC contents. (4) Storage stability is excellent for the solvent-solution types, with long-term stability for water-thinnable systems. (5) They can be easily pigmented with normally available mixing equipment. (6) The solvent-borne types are very similar to medium- oil-length alkyds in most characteristics. (7) The water-reducible coatings resemble their alkyd counterparts. (8) They can be applied using the full spectrum of available spray equipment. (9) Some are FDA approved and are used for applications in which such approval is important.

Disadvantages of epoxy esters are the following: (1) The major disadvantage for nearly all epoxy derivatives is their very poor resistance to chalking on exterior exposure. They chalk so heavily and so soon after exposure that they

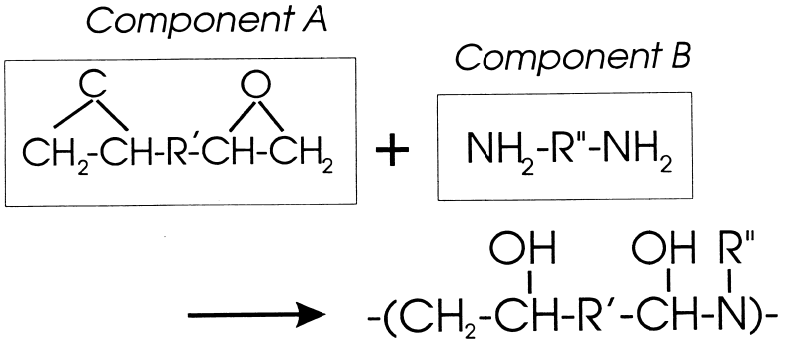


Fig. 1. Reaction for typical 2-component epoxy. R′ = bisphenol A derivative; R″ = polyamide chain. Component A = epoxy resin, which is the product of reaction of epichlorhydrin and bisphenol A; component B = solution of multifunctional polyamide.

have poor color retention. (2) For *exterior* service, they can be successfully used only as primers and must be top-coated as soon as possible after being applied on an exterior exposed surface. (3) Because of their poor exterior durability they should only be used as top coats for interior exposure. (4) Yellowing can be a problem depending on the epoxy and fatty acid from which the epoxy ester polymer was reacted.

CATALYZED EPOXY

Epoxy resins are the reaction products that result when epichlorohydrin is reacted with bisphenol A. For the coating to form a cured, useful film, the epoxy resin must be further reacted with yet another resin.

The unique features of an epoxy resin are due to the epoxy groups in the molecule as well as reactive hydroxyl (OH) groups. A typical reaction is shown in Fig. 1.

Typical Properties

In general, epoxy coatings are known for their toughness, flexibility and excellent adhesion to a wide range of substrates, including most metals, plastics, wood, ceramics, masonry, and glass. It is understandable therefore that epoxies are a popular choice as primers.

They are commonly used where resistance to many chemicals, solvents and alkalies, such as soaps and detergents, is required. In addition, they have excellent resistance to fresh water, salt (sea) water, and hot water. For these reasons, they are a popular choice for protecting structures, such as offshore drilling platforms, ships, and bridges, where resistance to marine environments is critical. They are also used to coat industrial and potable water tanks and pipelines.

One of the most notable weaknesses of epoxy coatings is their relatively poor resistance to UV light. For instance, when exposed to sunlight, many epoxy coatings tend to chalk readily, causing them to lose gloss and color. Although chalking takes place primarily at the surface of the film, it does not significantly affect the chemical properties of the coating.

When a decorative, corrosion-resistant or chemically resistant coating system is desired, such as on bridges, in chemical refineries, or on offshore drilling

equipment, it is customary to use epoxy coatings as the primer and undercoat and then apply a more UV-resistant top coat, such as an acrylic or polyurethane.

Epoxies should not be applied at low ambient temperatures, usually less than 50–60°F (10–15°C), because they will not cure properly. The common air- or force-dried, two-component epoxies that are used in the general metals, plastics ,and industrial maintenance industries comprise two separate packages, of which component A consists of the epoxy resin and component B can be a polyamine (for example, diethylene triamine, triethylene tetramine, tetraethylene pentamine), polyamide, polysulfide, or some other resin.

In the case of baked epoxy coatings that cure during a high-temperature bake, usually above 60–204°C (140–400°F), the two resins are preblended by the coating manufacturer and are supplied as a single-component package. Examples include blends of epoxy resin with amine, urea formaldehyde, or melamine formaldehyde resins. Only when the applied coating attains an elevated temperature do the two resin systems react to form the cured finish.

When clear coatings are required, neither component A nor component B is colored; however, for colored finishes, component A will usually contain the pigments and other additives, and component B will be clear.

Industrial Maintenance Coatings

If maximum chemical resistance is required, such as in industrial maintenance coatings that are used in chemical plants and refineries, component B is usually a polyfunctional amine. Unfortunately, these coatings tend to be very hard and sacrifice flexibility.

If the painting operators do not wear proper protective clothing and appropriate respirators during the mixing and application of the coating, and if the unreacted amine comes into contact with their skin or is inhaled, the operators can experience severe dermatitis; therefore, stringent safety procedures must be followed.

Epoxy-polyamine coatings have a relatively short pot life and must be used within a short time after the two components have been mixed. The manufacturers' technical data sheets will provide further details.

General-Purpose Industrial Epoxy Coatings

Improved toughness and flexibility are obtained when epoxy resins are reacted with polyamide resins. Unlike the polyamines, they do not cause severe dermatitis, and their pot life tends to be longer.

Availability as VOC-Compliant Coatings

For the general metals and plastics industries, several coating vendors supply VOC-compliant primers and top coats. Depending on the application, VOC contents are available as 168–420 g/L (1.4–3.5 lb/gal). Compliant epoxies are available that meet military specifications, such as MIL-P-23377 (primer), MIL-P-53022 (primer), MIL-C-22750 (top coat), and MIL- P-24441 (primer and top coat systems).

High-solids epoxies, with very low VOC contents, often well below the regulated limits, are also available for the industrial maintenance industry.

The advantages of high solids, solvent-based catalyzed epoxies, with VOCs less than 420 g/L (3.5 lb/gal), are the following: (1) They are used primarily as a primer because of excellent adhesion properties to metals, plastics, composites, wood, masonry, ceramics, glass, paper and other substrates. (2) They are available

to meet many military primer and top coat specifications (MIL-P-23377, MIL-P-53022, MIL-C-22750, MIL-P-24441). (3) They can be formulated into a wide range of colors and gloss levels. (4) Depending on the choice of curing agent (component B) they can achieve excellent hardness and chemical resistance, particularly alkali resistance. (5) They exhibit excellent resistance to many solvents, fresh water, sea water, and hot water. (6) Some formulations are more flexible than others, depending on the choice of curing agent. (7) They can be air-dried at ambient temperatures within 3 to 5 hours and force-dried at 150°F within 30 minutes. (8) They are primarily used in military, marine, offshore, and chemical plant applications. (9) Some high-build formulations allow for thick films in excess of 5 mils in one application.

Disadvantages are the following: (1) Usually they are two-component systems comprising component A (clear or colored epoxy resin) and component B (curing agent); therefore, they must be accurately mixed. (2) Any unused, mixed coating must be disposed of as hazardous waste. (3) They offer poor resistance when exposed directly to UV light (sunlight). (4) High-solids materials are difficult to apply to achieve dry films less than 1.5 mils, particularly when coating complex shapes. (5) They are generally not available in small quantities of custom colors. (6) Some formulations require an induction period of 20–30 minutes after

$$\text{Component A: Polyester (clear or pigmented)} + \text{Component B; polyiscoyanate} = \text{Cured coating: Polyurethane} \quad (5)$$

$$\text{Component A: Acrylic (clear or pigmented)} + \text{Component B; polyiscoyanate} = \text{Cured coating: Polyurethane} \quad (5)$$

the two components have been mixed before coating can be applied. (7) Pot-life limitations of 4 to 6 hours or less at ambient temperatures are common. (8) Application equipment must be cleaned before coating starts to set. (9) They are sensitive to cleanliness of the substrate. (10) It is difficult to strip coating from damaged, coated parts. (11) Some formulations, particularly those based on the more chemically resistant polyamine resins, can cause severe dermatitis and other health effects. They must be used with caution.

CATALYZED POLYURETHANES

Polyurethanes are a type of coating formed by the reaction of a polyisocyanate with a polymer that contains hydroxyl functionality. Two-component polyurethanes are supplied in two separate containers, of which the first is usually labeled component A and the second component B.

Component A can either be clear or pigmented, offering a wide range of colors and gloss levels. The primary resin (polyol) is usually an acrylic, polyester or polyether, each of which contains more than one hydroxyl group.

The second container, component B, contains a multifunctional, prepolymerized isocyanate. When components A and B are mixed according to the manufacturers' prescribed ratios, the polymers react to form a highly cross-linked polyurethane.

Figure 2 shows the simplified chemistry of the two components; Eqs. (5) and (6) depict the results of mixing the two components:

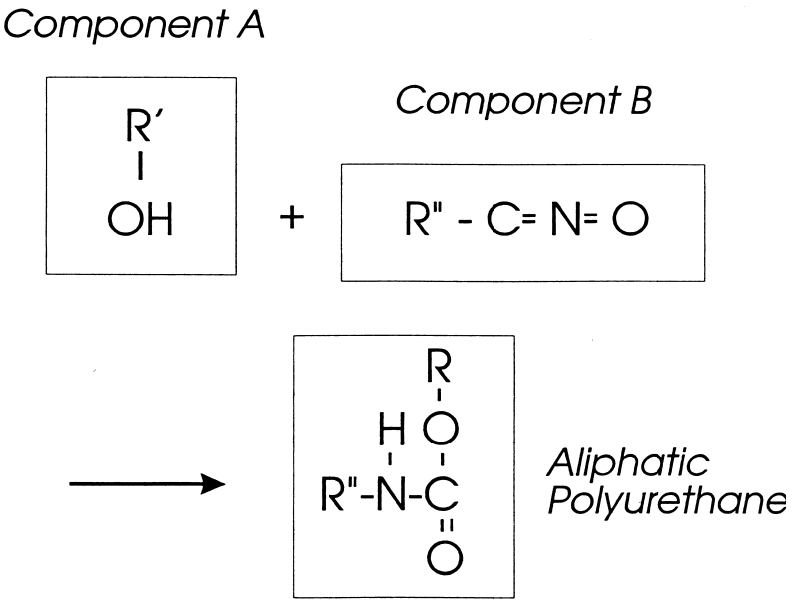


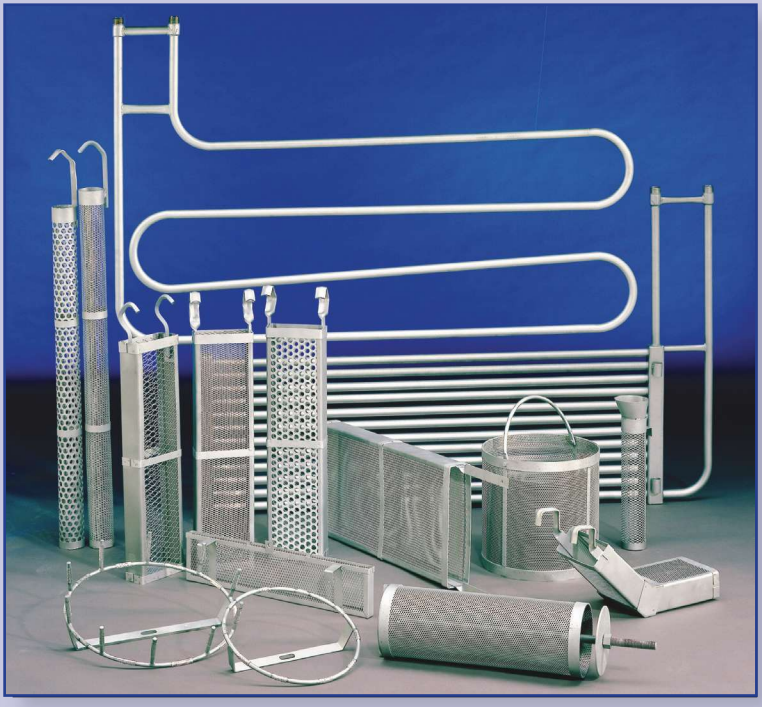
Fig. 2. Reaction for typical 2-component polyester-polyurethane, R' = aliphatic hydrocarbon chain; R" = aliphatic polyester chain. Component A = polyester polyol (clear or pigmented); component B = aliphatic polyisocyanate (clear).

Typically, polyfunctional polyisocyanates used in two-component polyurethanes are homopolymers or copolymers of toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), dicyclomethane diisocyanate (HMDI).

Components A and B can be batch mixed by manually mixing immediately before the coating is applied. Alternatively, special proportioning equipment can be set to automatically measure out each component according to its prescribed ratio. Each component is then pumped separately to a manifold, where they both come together in the fluid hose leading to the spray gun. Downstream of the manifold is a short static mixer that comprises a short plastic or stainless steel tube located in the fluid hose only a few inches or feet from the spray gun. Small baffles in the tube cause the components to be thoroughly mixed immediately before entering the spray gun. In-line mixing allows components A and B to be mixed on a continuous basis. The primary advantage is that the viscosity of the coating remains constant throughout the day and is used before it can outlive its pot life.

The most important advantages of two-component, high-solids polyurethanes [polyester urethanes with VOCs less than 340 g/L (2.8 lb/gal); acrylic urethanes with VOCs less than 420 g/L (3.5 lb/gal)] are the following: (1) They offer excellent physical film performance — abrasion resistance, toughness, hardness up to pencil hardness of 6H. (2) They have excellent resistance to most solvents and chemicals and excellent outdoor durability (primarily the aliphatic polyurethanes). (3) They can cure at ambient (room) temperatures, elevated temperatures or even under subzero conditions. (4) They can be used for application to steel,

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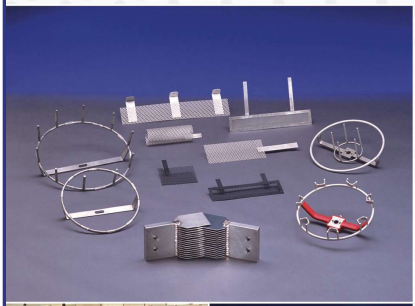
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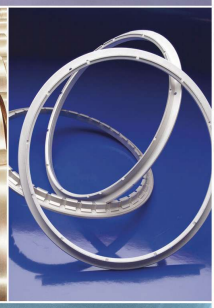
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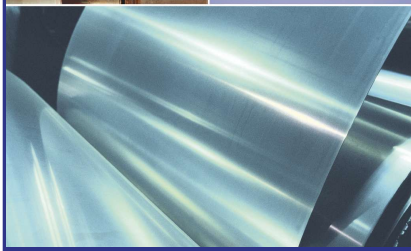
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aluminum, plastics, composites, wood, and masonry. (5) They can be spray applied with standard equipment-conventional air atomizing, airless, air-assisted airless, HVLP, electrostatic. (6) They are available in a wide range of solid and metallic colors, with quick turnaround. (7) On-site intermixing of colors, predominantly automotive, is available from several manufacturers. (8) They are available in a complete range of gloss and texture levels, and self-touch-up is possible. (9) They meet performance standards for top-of-the-line products, such as computers, business machines, aircraft and truck cabs, and meet various military top-coat and camouflage specifications. (10) For *polyester urethanes*, formulations are available with VOCs lower than 2.8 lb/gal. Coatings often have better chemical resistance; therefore, they are more commonly used on laboratory instruments, machine tools, computers, business machines, aircraft (where resistance to hydraulic fluids is important), industrial maintenance coatings for chemical plants, refineries, etc. (11) *For acrylic urethanes*, formulations are available with VOCs under 3.5 lb/gal and in some cases, under 2.8 lb/gal. Coatings are often reported to exhibit better exterior UV (sunlight) resistance; therefore, they are usually used on transportation equipment, such as automobiles, trucks, buses, and some private and commercial aircraft.

Disadvantages are the following: (1) The two-component system requires mixing in prescribed proportions. (2) They have a limited pot life, sometimes less than four hours, particularly in high-solids formulations. (3) Like many high-solids coatings, it can be difficult to achieve a uniform film thickness on complex-shaped parts. (4) Equipment must be cleaned before coating begins to set. (5) They are relatively expensive (usually $30/gal). Aliphatic polyurethanes for exterior exposure are more expensive than aromatic polyurethanes for interior exposure. (6) They must be handled with care, and paint operators must use appropriate respirators. (Consult coating vendor for appropriate recommendation). (7) Polyurethanes can have allergic sensitization in some people, particularly if they do not wear appropriate respirators. (8) They may need to be applied over epoxy primer, and like most other coatings, they must be applied over clean, pretreated surfaces. (9) At the present time, low-VOC, high-gloss *acrylic polyurethanes* are not readily available in small quantities of "automotive" colors, but are available in "fleet" colors.

New formulation polyurethane technologies are emerging. They will have very low VOC contents, while retaining manageable viscosities.

MOISTURE-CURED POLYURETHANES

In the previous section on two-component polyurethanes, we discussed the reaction of the polyhydroxy resin, such as the polyester, acrylic or polyether, with the polyisocyanate. It was explained that the chemical reaction commences as soon as the two components, A and B, are mixed; however, if the polyhydroxy resin is prereacted with a polyisocyanate but the reaction is not taken to completion, leaving some unreacted isocyanate groups, the coating then cures in the presence of moisture from the air. Such materials are called *moisture cured* polyurethanes. The coating is supplied in one package (the second component being atmospheric moisture) [Eq. (7)]:

Prereacted polyhydroxylisocyanate (clear or pigmented) + Atmospheric moisture = Polyurethane **(7)**

Table II. Comparison Between Methyl and Phenyl Groups

Methyl Groups	Phenyl Groups
Hardness while hot Flexibilty Water repellency Low temperature properties Chemical resistance Rate of cure Thermal shock Heat and oxidation resistance	Heat and oxidation resistance Better shelf life Less thermoplastic

In preparing moisture-cured polyurethanes it is critical that all of the coating pigments and solvents are totally free of water, because traces of moisture in the package can cause the coating to cure before application. In addition, the fluid hose leading to the spray gun and the head space above the coating in the pressure pot or reservoir must be free of moisture. A nitrogen blanket or a desiccant can be used to keep the head space dry.

The advantages of high-solids polyurethane, moisture-cured industrial coatings with less than 420 g/L (3.5 lb/gal) VOCs are the following: (1) This is a single-component system, hence no pot-life limitations. (2) It has all of the advantages of two-component polyurethane coatings. (3) It achieves chemically resistant properties more quickly than some two-component polyurethanes. (4) It is readily available in military camouflage coatings complying with MIL-C-53039.

Disadvantages are the following: (1) This is a technology with less field history than two-component polyurethanes. (2) Currently only a few companies supply military-specification-approved camouflage coatings. (3) They are not yet available in wide range of colors or in small quantities and may have a limited shelf life (less than 1 year). (4) They are very sensitive to moisture contamination, therefore requiring a special effort to keep moist air from the packaged or stored coating. (5) Drying time is affected by moisture in air. In very dry climates, the drying time may be longer than usual. (6) Currently they may be more expensive than two-component polyurethanes, with an average cost greater than $25/gal. (7) They have other disadvantages of two-component polyurethanes.

Typical polyurethane end uses are the following:

Aircraft skins
Missiles and other aerospace products
Over-the-road trucks
Buses
Rail cars
Automotive refinishing
Automotive (original equipment manufacturer): newly introduced high-gloss clear coat over metallic base coat; chip-resistant primer surfacers; flexible coatings for plastic facias bumpers
Military ground support equipment, such as tanks personnel carriers,vehicles, with resistance to live chemical agents (chemical agents-resistant coatings)
Architectural and Maintenance
Structures and vessels in chemical plants

Offshore drilling rigs
Roofs
Antigraffiti
Pipelines
Product finishing
Machine tools
Garden lawn mowers, snow blowers, tractors
Plastic housings, keyboards, computer monitors, etc.
Computer and business machines
Medical and laboratory equipment

SILICONE COATINGS

Silicone resins may be considered hybrids of glass and organic resins. Because of their inertness they can be used beneficially in conjunction with many other organic resins. Silicone resins with methyl and phenyl groups have been found to confer the most desirable properties; Table II lists their most important advantages.

Most silicone resins used in the coatings industry comprise combinations of methyl and phenyl groups, and the resulting properties are dependent on the ratio of one to the other.

High-Temperature Coatings

High-temperature-resistant coatings cure only when exposed to high temperatures, such as 260°C (500°F), but formulations are available in which coatings can cure at lower temperatures. In addition, inorganic pigments are commonly used.

Colored high-temperature coatings are available, but to retain their color, the exposure temperature should not exceed 204°C (400°F).

Weatherability

Although temperature resistance is one of the major benefits of silicone resins, they also exhibit excellent weatherability. This implies that they have improved color and gloss retention and exhibit less chalking. They may be incorporated into coatings, such as alkyds, phenolics, epoxies, polyesters, and other oleoresinous materials containing hydroxyl groups. Generally, the organic resins that are modified with silicone resins provide better properties than if the unmodified resins were to be exposed to the same environments.

Typical Applications

Unmodified silicone resin coatings are used on steel and aluminum substrates that will be subjected to high temperatures. These include such items as exhaust manifolds, mufflers, heat stacks, furnaces, boilers, ovens, heat exchangers, and aerospace and engine components.

Colored silicone coatings generally withstand lower temperatures but are used on items such as space heaters, clothes driers, stoves, and similar applications.

Copolymers, such as silicone-alkyds, are popular as industrial maintenance coatings where excellent exterior durability and chemical resistance are required. Applications include outdoor storage tanks, highway guard rails, railway tank cars, bridges, and aluminum siding.

Unlike the unmodified silicone coatings, the silicone-organic copolymers, such as silicone-alkyds, -acrylics, -phenolics, -melamines, can be cured at ambient temperatures or typical baking temperatures. They are also commonly used as coil coatings.

The silicone-modified alkyds and other organic copolymers are available in low-VOC formulations, typically with VOC contents of approximately 420 g/L (3.5 lb/gal).

Advantages of silicone-based coatings are as follows: (1) They are generally available as single-component coatings. (2) They can be air-dried or baked, depending on formulation. (3) Depending on the formulation and pigmentation, silicone resins can withstand temperatures 260–360°C (500–600°F) up to 540–650°C (1,000–1,200°F). Although their temperature resistance is excellent, color stability will depend on the choice of pigments and their resistance to high temperatures. (4) Copolymers, such as silicone-alkyds exhibit excellent resistance to exterior weathering .(5) Nonchalking coatings are available. (6) They have excellent resistance to thermal shock and corrosion and excellent water repellency. (Clear, thin coatings are commonly used as water sealers on the exterior of buildings.) (7) They can be formulated as copolymers with organic resins to obtain the advantages of each resin. (8) They have excellent electrical insulating properties; therefore they are used in resistors, capacitors, rectifiers, etc. (9) They have good adhesion, but require excellent surface preparation of substrate.

Disadvantages are as follows: (1) High-temperature-resistant coatings must usually be cured at temperatures above 260°C (500°F). This can be a problem when coating large furnaces, stacks, etc. (2) If high-temperature-resistant coatings are not fully cured before being placed in service, corrosion of the substrate may take place. (3) Silicone resin-based coatings are sensitive to surface preparation and must be applied to properly prepared substrates. (4) They exhibit generally poor hardness and poor abrasion resistance. (5) Low-VOC, high-temperature coatings are not readily available.

LOW-VOC WATERBORNE COATINGS

BY RON JOSEPH (1944 - 2011)
RON JOSEPH & ASSOCIATES INC., SAN JOSE, CALIF.

This article focuses on a comprehensive range of waterborne coating technologies, which include water-reducible, dispersion, and latex formulations. Advantages and disadvantages of each of the resin systems are listed to serve as a guide to assist in the selection of a VOC-compliant coating.

Metal fabricators and coating users located in areas that are considered to be in nonattainment with the ozone standard have already addressed the problems of selecting VOC compliant coatings. However, the New Clean Air Act amendments of 1990 have more clearly defined when an area is in attainment with the standard. In fact, the implementation of VOC regulations for surface coatings will depend on whether an area has been designated extreme (only Los Angeles-Anaheim-Riverside), severe, serious, moderate, or marginal. Consequently, thousands of fabricators and other coating users who have not previously been affected by the VOC regulations, will soon be searching for low-VOC coatings. The predominant question people will need to resolve is whether to convert to low-VOC, solvent-based coatings or waterborne coating systems.

Numerous papers have been published extolling both types of systems. Indeed, since the mid 1980s, high-quality compliant coatings have been available to meet even the stringent requirements of California and other state rules.

This paper is devoted solely to compliant waterborne coatings, which are applied by dip, flow, or one of the many types of spray equipment commonly used in coating facilities. The paper does not claim that waterborne coatings are better than their solvent-based cousins, or vice versa. On the contrary, both types of systems should be carefully considered before making the final selection.

Before discussing the various waterborne resin systems, it must be pointed out that most VOC regulations limit the VOC content of a coating in terms of pounds per gallon or grams per liter, *less water*, and less exempt solvent. Exempt solvent-containing coatings are not discussed in this paper; therefore, only the less-water terminology will be explained.

One gallon of a waterborne coating (water reducible, water dispersible, or latex) contains many ingredients, specifically, the resin or binder pigments, extender pigments, coalescing agents, a small quantity of co-solvents, and usually a fairly substantial amount of water. The volatile portion of the coating comprises the co-solvents and water. In a one-gallon can, the co-solvents, which are considered to be the VOCs, may account for less than 1.0 lb. In other words, the VOC content of the coating may only be 1.0 lb/gal. The VOC regulations, however, require that the VOC content of the coating be calculated as if no water were in the coating. Depending on the coating formulation, the VOC content, less water, may be considerably higher, such as 2.0 lb/gal or more.

In this section all references to VOC content automatically assume the less-water values; therefore, when it is stated that a coating technology is commercially available with a VOC content of, say, 2.3 lb/gal, it can be assumed that implies less water.

For those who are not familiar with the EPA's differentiation between air- or force-dried coatings and those that cure by baking, a few words of clarification

are in order. The EPA has defined air- or force-dried coatings as those that dry or cure below these temperatures, and many rules establish special VOC limits for this category. In contrast, coatings that cure above 194°F are often regulated as "baked" coatings for which other VOC limits are established. Mostly the limits for air- or force-dry category are higher than for the baked.

Probably the most common waterborne coatings used for application to metals are air- or force-dried at temperatures below 90°C (194°F).A wide range of coating formulations fall into this broad category. The most commonly available technologies are water-reducible alkyds and modified alkyds, acrylic latexes, and acrylic epoxy hybrids. Often consumers are unaware of which of these technologies they are purchasing, as the coatings are frequently sold as generic "waterborne" products. A brief descriptive overview of the basic differences follows, and the most notable advantages and disadvantages of each resin system are specifically highlighted.

As a generic group, water reducible formulations, dispersions, and latexes are ideal for companies that need to get into compliance with VOC regulations, yet do not require the coatings to have sophisticated properties.

As a group, the waterbornes tend to have VOC contents well below 2.0 lb/gal, less water and some are even below 1.0 lb/gal (120 g/L). Moreover they are readily available in a wide range of colors and gloss levels. Generally they exhibit good performance properties, but are probably not as durable or chemical- and solvent-resistant as two-component polyurethanes, epoxies, or baked finishes. They should be considered for applications such as dipping primers and topcoats,general-purpose shop primers, and spray applied enamels. Typical end uses include steel roof trusses, steel building support structures,farm implements (not combines or tractors), electrical cabinets, boxes,frames, fence posts, and similar products.

When applying the coatings in humid and/or cold environments they should be force dried at a low oven temperature of approximately 120 to 150°F. If an oven is not available, consider blowing air over the parts to promote the evaporation of water from the coating film. Failure to do so can lead to a poor quality film that is easily damaged by handling and susceptible to the early onset of corrosion and other premature failures.

Water-reducible, or *water-thinnable alkyds and modified alkyds* are similar to the solvent-based alkyds. Like the solvent-based coatings, they are modified polyesters, but have high acid values and employ special chemical blocking agents, such as carboxylic acid functionalities. When the alkyds are neutralized with ammonia or volatile amines, it is possible to use water as the reducing liquid.

Although they may take longer to dry, the resulting coatings have similar gloss, flow, and leveling properties compared with their solvent-borne counterparts.

The *acrylic latexes* include other polymers such as vinyl acrylic and styrene acrylic. The resins are characterized as high-molecular-weight polymers dispersed as discreet particles in water. Those formed by polymerizing a single monomer are called *homopolymers*, whereas those polymerized from a blend of two or more different monomers are called *co-polymers*.

Because desired film characteristics can be built into the resin by the choice of the monomers used, most of the latexes used for coating miscellaneous metal parts are co-polymers.

Latex coatings, like lacquers, do not go through a chemical change as they

dry. The characteristics of hardness, flexibility, chemical resistance, abrasion resistance, physical, and chemical attributes are derived from the basic latex polymer and specific modifications.

Acrylic latexes are known for their good exterior durability and excellent resistance to ultraviolet (UV) degradation. When used for outdoor exposure they retain their original gloss and color over longer periods. In this regard they are superior to unmodified alkyds, which tend to have poorer gloss and color retention.

*Acrylic epoxy hybrid*s are less commonly specified. They comprise two- or three-package systems in which emulsified epoxies are used to cross-link aqueous acrylics. Properly formulated coatings are corrosion resistant and can produce finishes that have very good gloss, hardness, alkali, and abrasion resistance. Unlike conventional solvent-based epoxies, some mixed waterborne coatings have pot lives up to 36 hours at reasonable ambient temperatures.

Acrylic epoxy hybrids are used in applications where the hardness, flexibility, and chemical resistance of an epoxy is desired. These coatings will be used for general metal finishing where high performance in terms of physical and chemical properties are not required, but improvements over the acrylic latex is preferred.

Epoxy water reducible coatings that can be air- or force-dried below 90°C (194°F) with VOC levels at or below 340 g/L (2.8 lb/gal) are available from a few vendors. Generally, they are supplied as two- or three-package systems. In the later case, neither components A nor B contain water. However, after they have been mixed in prescribed proportions water is added in fairly large quantities to adjust viscosity to sprayable levels, usually in the range of 20 seconds on a Zahn #2 cup.

The most commonly available water reducible epoxies are formulated as primers complying with military specifications MIL-P-53030 (lead- and chromate-free) and MIL-P-85582 (containing chromates). They can be top-coated with most other coatings systems, in particular ,polyurethanes, and are used when good corrosion resistance is required. As with all high-performance coatings, properly prepared surfaces are mandatory. You might consider specifying the water-reducible epoxies when you require better corrosion resistance than can generally be obtained from alkyd and alkyd-modified primers.

Because epoxies tend to chalk when exposed to weather and sunlight (whether water or solvent borne), they are usually not used as topcoats. However, vendors do formulate these epoxies as topcoats where high performance is a requirement.

As primers, they are commonly specified for military hardware, steel and aluminum frames and weldments, cold-rolled steel panels and cabinets, aerospace, and electronic components. As with all other resin systems, particularly waterbornes, proper pretreatment of the substrate is essential.

Polyurethane dispersions are waterborne systems that can air/force dry at temperatures below 194°F (90°C). Essentially, they are polyurethane lacquers dispersed in water, which implies that as the water evaporates, the coating film is formed. No other curing mechanisms take place. In fact, they are completely reacted products with no free isocyanate groups, and after the water has evaporated, the film is as hard as it ever will be.

Apparently, very low VOC contents are achievable; however, the technology is relatively new and is still in the process of being tested by various companies. While the polyurethane dispersions can be used on metal parts, much like the con-

ventional two-component polyurethanes, the primary focus at the present time is in the wood-finishing industry.

All coating systems discussed so far can be dried and cured either at room temperature, or force dried in low-temperature ovens, less than 90°C (194°F). As was pointed out earlier, the alkyds, modified alkyds, acrylic latexes, and acrylic epoxy hybrids are excellent choices for applications in which superior physical and chemical properties may not be required. However, there is a wide range of waterborne resin technologies that perform extremely well when exposed to chemical environments. Among them are the alkyd, alkyd-modified, polyester, and acrylic water-reducible coatings, which cure at temperatures of 121°C (250°F) and above. The upper temperature limit is usually in the 162 to 204°C (350–400°F) range.

This group of coating formulations are water reducible or water thinnable and are similar to their solvent-based counterparts in chemical structure. Like their solvent-based counterparts, these resins are modified with aminoplast resins to allow for cross-linking at elevated temperatures.

Typically these coatings are used where any of the following properties may be required; hardness, mar and abrasion resistance, excellent color and gloss retention, particularly when the coating is exposed to sunlight, chemical, detergents, and solvents.

End uses include metal office furniture, large appliances, supermarket shelving, computer mainframes and metal hardware for the computer and business machines industry, metal laboratory equipment, bicycle frames, lighting fixtures, automotive, and transportation applications where the components can withstand the relatively high baking temperatures.

As regards compliance with VOC regulations, formulations are readily available with 360 g/L (3.0 lb/gal) VOCs, less water, and some are even below 275 g/L (2.3 lb/gal) levels.

AIR AND FORCE-DRIED ALKYDS

Both water-reducible alkyds and modified alkyds are either air-cured, or forced-air dried at temperatures less than 90°C (194°F).

Advantages

1. VOCs are generally below 2.0 lb/gal (240 g/L), less water.
2. The coatings are made for use on steel, aluminum, and plastics.
3. The coatings are composed if a one-component material with no pot life limitations and can be touched up and repaired.
4. Cleanup is relatively easy, being comprised of flushing hoses with water, then solvent, then water.
5. The coatings have low curing temperatures and air-dry at ambient temperatures in less than an hour, or force dry at 65°C (150°F) for 10–20 minutes.
6. The coatings can be spray-applied with standard equipment, but may not be compatible with airless and air-assisted airless spray guns. New formulation and spray application technologies are overcoming these limitations.
7. The coatings are ideal as dipping primers and enamels and excel lent for general purpose primers and topcoats.
8. Available in a wide range of color and gloss levels, the coatings can also be tex-

tured.

9. The coatings pose little fire hazard; toxicity is less than solvent-based counterparts.
10. The costs for reducing solvents and cleanup are lower for these coatings than for solvent-based counterparts.
11. Exterior durability is very good.
12. Chemical and solvent resistance are fair to good, but cannot compete with baked or two-component coatings.

Disadvantages

1. Generally, these coatings have poorer chemical resistances compared with two-part polyurethanes or baked water-reducible coatings.
2. A three-step equipment cleanup is required: water, solvent,water.
3. The coatings do not meet standards for "high" performance in industry, such as heavy-duty maintenance, aerospace, appliance, automotive.
4. The coatings are more sensitive to substrate cleanliness than most solvent systems.
5. The coatings require a greater reaming curve with regard to viscosi ty management than other compliant coatings.
6. Generally, primers do not have as good a salt spray resistance as con ventional solvent-based counterparts.
7. In high humidity areas, the coating must be force dried, or high velocity air must be blown over the part to quickly evaporate the water from the film. It is imperative that the water evaporate before the coalesc ing solvent evaporates.

AIR AND FORCE-DRIED ACRYLIC LATEXES

Acrylic latex coatings are air- or forced-air dried at temperatures less than 90°C (194°F).

Advantages

1. These coatings have very low VOC contents, often less than 240 g/L (1.5 lb/gal), less water. New technologies currently being developed will all but eliminate VOCs.
2. The single package coatings have unlimited pot life as long as they are in covered containers.
3. The coatings air dry rapidly when relative humidity is low.
4. The coatings exhibit excellent resistance to sunlight, demonstrated by retention of gloss, color, and flexibility over long periods of exposure.
5. Generally, the coatings are available in a wide range of colors and all but very high gloss levels.
6. The coatings adhere to most clean surfaces and to most industrial primers.
7. Since water is used for thinning and cleanup, costs are minimized.
8. The coating's low flammability, offers potentially reduced insurance costs and improved working conditions.
9. The coatings may be applied with most conventional spray equipment, but

may not be compatible with airless or air-assisted airless spray guns.

Disadvantages

1. If coatings are dried in low-temperature and/or high-humidity environments, poor films may form leading to degraded physical and chemical properties.
2. The coatings must be applied over exceptionally clean, oil- and grease-free surfaces.
3. Typical problems of improper surface preparation or mixing can include edge pull, substrate wetting, and cratering.
4. Unprimed or poorly primed ferrous metals will produce severe flash rusting with most latex paints.
5. The film remains thermoplastic and soluble in any solvent that would dissolve the basic polymer.
6. Latex paints contain appreciable quantities of water-soluble, non volatile materials, such as thickeners, surfactants, and other addi tives that remain in the dried film. On exposure, these leach out and leave the film less continuous and more permeable.
7. Splashes and spills must quickly be cleaned up with water before the coating dries. Once the coating is dry, solvents are required for cleanup.
8. Equipment cleanup often requires three steps: water, solvent, water.
9. Storage areas should be protected.
10. Storage areas should be protected from excessively low temperatures to prevent freezing and from excessively high temperatures to prevent degradation of the coating.
11. General housekeeping must be rigorous to prevent bacterial or fungal growth.

AIR AND FORCE-DRIED ACRYLIC-EPOXY HYBRIDS

Acrylic-epoxy hybrid coatings should be air- or forced-air dried at temperatures less than 90°C (194°F).

Advantages

1. Coatings cross-link to form insoluble, thermoset films.
2. The acrylic portion provides ultraviolet (UV) resistance, which appreciably improves chalk resistance, gloss, and color retention on exterior exposure.
3. The epoxy portion improves adhesion and alkali resistance.
4. The very long pot life (36 hours at normal ambient temperature) of the mixed and catalyzed coatings greatly adds to their utility.
5. The low precure molecular weight helps gloss development so that high gloss finishes are possible.
6. Water is used for thinning and cleanup reducing costs of cleanup.
7. Increased safety due to low flammability may result in lower insurance costs and better working conditions.
8. The coatings may be applied by most conventional spray equipment, but may not be compatible with airless and air-assisted airless spray guns.

Disadvantages

1. Preparation requires mixing of two or three components.
2. If coatings are dried in low-temperature and/or high-humidity environments, poor films may form, leading to degraded physical and chemical properties.
3. Surfaces to be coated must be free of traces of oil and grease.
4. Improper surface preparation or mixing can cause edge pull, poor substrate wetting, and cratering.
5. Material handling and application equipment must be of corrosion-resistant materials due to the corrosive nature of the liquid coating.
6. Storage areas should be protected from excessively low temperatures to prevent freezing of the coating.
7. Storage areas should be protected from excessively high temperatures to prevent degradation of the coating.
8. General housekeeping must be rigorous to prevent any bacterial or fungal growth that can interfere with product quality. Plant personnel must be trained in this preventive maintenance.
9. The paint operator may need to go through some form of training to learn how to establish the correct spraying viscosity.

AIR AND FORCE-DRIED EPOXIES

Water-reducible epoxy coatings are air- or forced-air dried at temperatures less than 90°C (194°F).

Advantages

1. VOC levels are at or below 340 g/L (2.8 lb/gal), less water.
2. Primers are available with chromates, or lead and chromate-free.
3. Primers comply with military specifications MIL-P-85582 and MIL-P-53030.
4. The coatings dry to recoat quickly, even in highly humid environments provided that there is good ventilation.
5. Compatible with many types of topcoats, especially polyurethanes.
6. Can be applied with most types of spray equipment, but may not be compatible with airless and air-assisted airless spray guns.
7. Primer is available in only a small range of colors.
8. Topcoats can be made in a range of colors and gloss levels.

Disadvantages

1. The coatings are two- or three-component systems comprising a base, a catalyst (curing agent) and, water.
2. The coatings must be applied to properly prepared surfaces.
3. Depending on formulation, it can be difficult to mix the base and catalyst components due to their high viscosity. After adding water, the viscosity drops to manageable levels.
4. The coatings must be mixed using prescribed procedures.

5. The coatings are relatively expensive as packaged, but competitive with solvent-based epoxies.
6. Pot life can vary from about 6 hours to more than 8 hours.
7. Sometimes the coatings can be difficult to clean up when stuck to equipment and skin.

POLYURETHANE DISPERSIONS

Advantages

1. Coatings made from polyurethane dispersions dry to tough films of dependable hardness and flexibility.
2. Coatings for metals, textiles, leather, wood, glass, paper, and rigid plastics are made from these versatile products.
3. Application can be done with most commonly used equipment with water thinning and water cleanup.
4. Very little, if any, solvent and only very small quantities of coalescing aids are used.
5. Films dry to predetermined gloss and color and, because they do not chalk, both gloss and color retention are excellent.
6. Like all lacquers, no chemical change occurs during drying and exposure; the dry films retain their original properties for long periods.

Disadvantages

1. These coatings have the typical problems of waterborne finishes: drying time is dependent on temperature and relative humidity.
2. Like most lacquers, total nonvolatiles are quite low (35–40% by weight), so multiple coats are necessary for good film buildup.
3. Unlike solvent-borne lacquers, care must be taken to ensure good intercoat adhesion because the topcoat does not tend to dissolve any previous coats.
4. Surface cleanliness and freedom from any oil or grease, both on the surface and in application equipment, is essential for good film quality and adhesion.

BAKED ALKYDS, MODIFIED ALKYDS AND ACRYLICS

Alkyds, modified alkyds and acrylics should be cured using a water-reducible bake at temperatures less than 90°C (194°F).

Advantages

1. Coatings are available at VOCs less than 360 g/L (3.0 lb/gal), less water; and some even below 275 g/L (2.3 lb/gal), less water.
2. The coatings have excellent film performance, often equivalent to polyurethanes.
3. The coatings are made for use on metal substrates only due to high temperature of bake, except perhaps for high-temperature plastics.
4. There are no pot life limitations; the coatings are a one-component materi-

al.

5. Water is the primary solvent.
6. The coatings can be spray applied with standard application equipment.
7. Touch-up and repair is possible, although this should first be con firmed by experimentation.
8. The coatings are available in a wide range of colors and gloss levels, and can be used for texture finishing.
9. The coatings meet industry standards for many top-of-the-line ap plications, such as computers, business machines, lighting fixtures, ap pliances, automotive, coil, etc.
10. The coatings are available as primers and topcoats, although the coating can sometimes be applied directly to metal without the need for a primer.
11. The coatings have a lower fire hazard and lower toxicity than solvent-based systems.
12. Costs are lower for reducing solvents and cleanup.

Disadvantages

1. The coatings require a high-temperature oven, 121–204°C (240–400°F), for more than 10 minutes.
2. A larger energy supply (and cost) is required.
3. The coatings are not for use on plastics, and other heat-sensitive sub strates, except perhaps some high-temperature plastics.
4. Performance on porous castings is unreliable due to outgassing, un less special precautions are taken to minimize the problem.
5. Touch-up may require a second bake or use of another air-dry coating.
6. The coatings are not applicable where parts such as machined surfaces have tight dimensional tolerances and cannot tolerate warpage.
7. Surface cleanliness is more critical than for solvent systems.
8. As with most resin systems, which cure at elevated temperatures, color changes can occur if the coating is overbaked.

CONCLUSIONS

Discussed here is a comprehensive selection of waterborne coating technologies that can be used in a wide range of industries. Waterborne coatings can be applied to most types of substrates — metal, plastic,wood, glass, and masonry surfaces.

These coatings are commercially available at low VOC levels and satisfy even the most stringent regulations.

Depending on the resin system and coating formulation, a full spectrum of physical and chemical performance properties can be expected; therefore, companies that now need to get into compliance with the air-quality regulations can and should consider waterborne coatings as possible candidates.

INTRODUCTION TO PAINT APPLICATION SYSTEMS

BY RON JOSEPH (1944-2011)
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A typical line for organic finishing of metals includes the following steps: precleaning, pretreatment, dry-off, primer application, flash-off and/or cure, and final cure. In some cases a primer or intermediate coating may not be used, and multiple applications of topcoat are not unusual. The combination of a pigmented basecoat, often containing metallic flakes, and a final clear, lustrous topcoat is common today.

PRECLEANING

Procedures for preparation of metal parts for painting often include a precleaning step. Removal of gross soils such as oil, grease, scale, weld spatter, lubricants, and other materials can be accomplished by mechanical means, with solvents, acids, or alkaline cleaning agents. Blasting, polishing, pickling, and solvent degreasing are described in the *Metal Finishing Guidebook and Directory Issue*. While the purpose of precleaning is to remove the contaminants from the surface, this process in and of itself does not provide any protection to the metals.

PRETREATMENT

The term pretreatment refers to a combination of chemical cleaning and conversion coating. The purpose of a conversion coating is twofold. It improves corrosion resistance and provides a surface more accepting of the organic coating, subsequently enhancing adhesion. Further details will be found in the pretreatment section of this *Guidebook*.

DRY-OFF

After pretreatment the wet parts are immediately transferred into a high-temperature dry-off oven. For lightweight metal parts the oven temperature can be as low as 250°F; however, if the parts are heavy and bulky, the oven temperature may be as high as 204°C (400°F). The sole purpose of this oven is to evaporate off the water as quickly as possible to prevent flash rusting. In coating operations in which the parts are immersed into a dip tank containing a waterborne coating, the dry-off oven may sometimes be eliminated.

COATING APPLICATION METHODS

There is a wide choice of application methods available for both primers and topcoats. In addition, consideration must be given as to whether manual or automatic techniques should be used. Local regulations may also limit the choice of equipment.

Some states, notably California, regulate a minimum transfer efficiency of

coating application. (Transfer efficiency refers to the percentage of solids applied to the part.) In California the minimum acceptable transfer efficiency is 65%. Conventional air atomized, airless, and in some cases air-assisted airless spray equipment are not approved for use in some parts of California. High volume low pressure (HVLP), electrostatic, dip, flow, brush, and roller applications are considered to be "approved." This does not imply that these methods necessarily meet the 65% minimum; rather, they are considered to be more efficient than the nonapproved devices.

The most extensively used coating techniques include spray, dip, electrodeposition or electrocoating, coil coating, and powder coating. Each of these techniques is described in one of the following sections of this *Guidebook*. Other methods are described briefly below.

Brush

Brush techniques are well known to the homeowner and the public at large. This is a versatile method with high transfer efficiency, but is slow, labor intensive, and not readily automated. It is commonly used for application of maintenance coatings, for touch-up, and in masking for a variety of finishing operations.

Flow Coating

In flow coating, the part is suspended and the coating is poured over it. The excess is collected for subsequent reuse. This technique is useful for large or oddly shaped parts, which may be difficult or impossible to dip.

Nozzles may be directed over the part, but they are not of the atomizing type used for spray application. This technique is also useful for paints without long-term stability, which could not be used for dipping. The same control factors noted under dipping also apply in this case. Similarly, as with dipping, there is minimal control of film thickness, appearance, and film properties. Both dip and flow coating generally require little space, are low in cost, and require minimal operator skill.

Curtain Coating

Curtain coating consists of the rapid horizontal movement of flat or slightly curved parts through a curtain of falling paint. Since the volume of paint can be carefully controlled by the slot width, it is possible to apply either thin or heavy build films. The process is readily automated.

Direct Roll Coating

In this method the coating is applied by roller. It is limited to fixed shapes such as sheets and is used for continuous coating of steel or aluminum in the container industry. The coatings can be patterned or embossed to add decorative effects.

CURING PROCESSES

Drying is the process by which the solvents and/or water in the coating evaporate to allow the film to achieve a "dry-to-touch" or "dry-to-recoat" state. Curing, on the other hand, implies that the coating resin undergoes a chemical reaction, rendering the cured film hard, abrasion resistant, and relatively inert to the environment (chemicals, solvents, sunlight, etc.). Each resin type (alkyd, epoxy, polyurethane, etc.) undergoes its own type of curing mechanism. Some coatings, such as nitrocellulose lacquers, need only dry by solvent evaporation in or-

Table 1. Common Automated Coating Processes

Process	Primers	Top Coats
Dip coating	Yes	No[a]
Flow coating	Yes	No[a]
Electrodeposition	Yes	Yes
Spray coating	Yes	Yes

[a]Unless quality and appearance of finish are not critical

der to achieve their final finish. Most other coatings require both drying and curing before they achieve their optimum properties.

Plural-component paints include the curing agent as one of the components. These include two-part epoxies and polyurethanes. Some coatings cure when they are exposed to special high-energy ultraviolet light or electron beam sources. These coatings cure very quickly (1–5 sec) when exposed to the light of an ultraviolet lamp. Screen inks for printed circuit boards are a typical application, as are other substrates, which are heat sensitive.

Coatings can also be classified as air dry or bake. Air dry coatings will cure at room temperature. When heat is applied, usually less than194°F, they are termed force air dried. Baked coatings require the use of an oven, and are usually cured at temperatures in excess of 250°F. There are three major types of ovens.

1. *Impingement ovens* are used for forced-air drying of flat surfaces, or parts. Coated parts are passed along a conveyor belt and hot air is blown over them.

2. *Forced convection ovens* are versatile devices, which consist of an enclosure with means to circulate heated air. They can handle a wide variety of shapes and sizes. The desired temperature for curing can be selected and a uniform temperature maintained. Batch or continuous systems can be devised. These ovens are described in a separate section of this *Guidebook*.

3. *Radiant heat ovens* use infrared lamps with reflectors arranged around the pieces. The primary feature of these lamps is that they provide rapid heating. Their main disadvantage is line of sight limitations. In other words, only coated surfaces that are exposed to the infrared rays benefit from the process. Coated areas, such as in recesses shaded from the light, do not cure as rapidly. A separate section of this *Guidebook* provides details on infrared ovens.

CONSIDERATION FOR AUTOMATION

In facilities that coat large volumes of metal, automated coating application is common. The application methods can vary depending on the size and shape of the parts, the number of parts being coated per hour, whether or not there are long runs of one part geometry, and other factors. When conditions favor automation, or when the primer does not need to have a high appearance finish, any of the methods listed in Table I can be used for pri mer application. Automated spray guns can be in the fixed position or can be mounted on reciprocators or robots.

Topcoat application is usually fairly demanding, particularly when the final finish is expected to have a high-quality appearance. Under such circumstances dip and flow coating are less likely to be used, although electrodeposition, which produces a superior finish, remains a viable option. For the most part topcoats are applied by spray.

The decision to use manual or automated spray application depends largely on the length of the runs and the consistency of part geometry .For instance, if the runs are short and part sizes vary significantly between runs, manual spray application may be chosen. On the other hand, if the runs are long and the part geometries are relatively simple, automated application may be preferred.

POWDER COATING WITH ROBOTS AND DENSE PHASE TECHNOLOGY—A CRITICAL BLEND OF ADVANCED TECHNOLOGIES

BY JOHN BINDER, MARKETING MANAGER, NORDSON POWDER COATING SYSTEMS, NORDSON CORP., AMHERST, OHIO

The efficiencies of robotics designed specifically for painting—coupled with advances in powder coating application and delivery technology through the use of dense phase technology guns, pumps and controls—provides greater productivity, higher repeatability and savings in daily powder coating operations.

There was a time when powder coaters would adapt large welding robots to powder coating applications. The result was costly over-sized machines that did not lend themselves well to powder booths or precise powder paint applications. Often the window or opening for the robot would need to be sized to accommodate the robot's painting motion. This caused higher than desired open booth area and up-sized collectors to allow for the necessary booth airflows to contain powder.

Since then, robot technologies have progressed at a rapid pace. Today, there are robots designed specifically for powder painting that are smaller, more cost effective and more precise with advanced part identification and controls that communicate between the powder application equipment and the robot. As a result, powder coaters achieve higher productivity, greater repeatability – and savings!

Robotics and powder coating—for greater process control and efficiency.

Because of their virtually unlimited range of motion, robots are more flexible than fixed axis machines–be they single, dual or even triple axis machines. Since robots can maintain a gun-to-part distance that is more precise and flexible than fixed axis machine, they are able to contour a part as well as reach into hard-to-reach areas. This allows for more uniform coverage of the powder coating on all coated surfaces. Additionally, a robot makes the same motion every time for each and every part, translating into less variability of the coating than if coated with a manual powder gun.

Some might ask, then–what if the part is not hung correctly or the same way every time? Fortunately, there are robots available with sophisticated part identification that can sense if a part to be coated is misaligned.

In fact, robot controls when combined with powder system controls cannot only sense part orientation but can also sense part type and shape. This makes it possible for both the robot to know what motions to make and the powder gun to know what application parameters to use. In other words, part identification information can be sent to the powder gun controller such that the correct presets for powder flow and electrostatic control match the part to be powder coated. This same sophisticated part identification technology allows the robot to then powder coat the same parts with precise robot arm speed, repeatable motion and consistent gun-to-part distance parameters that are both optimized and harmonized with the powder coating equipment application settings. This trans-

lates into consistent and repeatable part quality that eliminates powder waste, minimizes rejects and rework, and reduces cycle time when compared to manual powder coating operations. The greater repeatability that is achieved through robotics—when coupled with dense phase powder coating delivery and application equipment—delivers even greater levels of productivity and more savings than would otherwise be achieved with conventional methods of moving guns (fixed axis or manual operator) and venturi pump powder delivery and application equipment.

Dense phase technology and robotics—for greater application control and efficiency.

So, what is dense phase technology? It is essentially dense phase powder pumps, guns and controls that are superior to venturi powder coating equipment and all other dense phase powder equipment on the market. Previously, automatic powder guns with conventional venturi pumps could not paint fast enough, or effectively enough, to take full advantage of robotic technology. However, the advent of dense phase powder pumps and spray guns has created a perfect match for the speed, accuracy and repeatability of today's painting robots.

Dense phase technology was born of the need for 20-second color changes, hundreds of colors on a powder coater's color palette, and same day shipments–therefore, the need for many color changes not only within a single 8-hour shift, but within a single hour. Dense phase technology was initially developed for North American office furniture manufacturers that were spraying hundreds of different colors and needed to ship complete office sets (desk, chair, file, drawers, etc.) the same day they received an order. They eventually determined that it was less costly to throw powder away than to have any amount of significant downtime for color changes. These same customers were also running line speeds as fast as their conventional powder equipment would allow them—in order to coat as much product as possible. This was initially achieved by manually switching air and powder lines between multiple hoppers with different colors, equipped with venturi pumps and manual powder spray guns. However, venturi pumps did not lend themselves well to powder coating at high line speeds because so much air was required to propel the powder—propelling much of it past the part when the air flows were turned up to achieve greater powder flow in order to accommodate higher line speeds.

It was here that a "dense phase" delivery pump was developed (Figure 1). This pump was designed to deliver more powder at lower velocities because it was more of a metering pump with two chambers. The first chamber with two valves would pull the powder in with vacuum and push the powder out with pressure. The second chamber would operate similarly but its timing would be opposite that of the first chamber, such that when the second chamber applied pressue, for example, to push powder out—the first chamber would apply vacuum to pull powder in.

Alternating cycles resulted in smooth dense powder flow with no pulsing and very little air to propel the powder. This was a quantum leap for powder delivery and application equipment—providing higher transfer efficiency with less overspray—allowing powder coaters to increase line speeds and, in some cases, even eliminate manual gun stations.

Not visible to the naked eye is the ability of dense phase technology to charge powder better due to the lower powder velocity and the increased relaxation

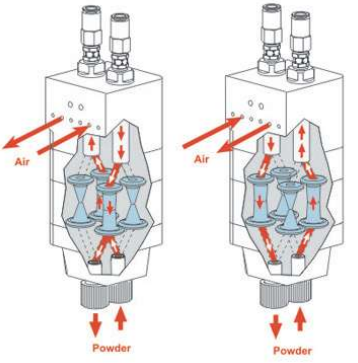


Figure 1. In this schematic, a dense phase technology pump illustrates alternating cycles of the two chambers, each containing two valves.

time of the corona charge. In other words, more powder at a lower velocity means that more powder has a greater time to attract a charge as it passes through the corona field in front of the powder gun. When compared head-to-head with a manual spray gun and a venturi pump, the dense phase technology gun and pump will apply more powder, with fewer strokes, in a shorter amount of time.

The ability of dense phase powder application to reduce gun-to-part distance stands out as being more transferable to robot painting than all other benefits. Due to the lower velocity and relatively shorter "throw" of the powder as compared to conventional venturi pump technology, the gun-to-part distance for dense phase powder coating guns becomes shorter.

Please note: this does not mean that the effective fan pattern width is reduced as there is a wide range of nozzle configurations for dense phase guns that allow them to match, and in some case, exceed the maximum fan pattern width of powder guns using conventional venturi pumps. Similarly, the same features and benefits of dense phase delivery pumps that make them useful with robots also makes them perfect for use with automatic guns.

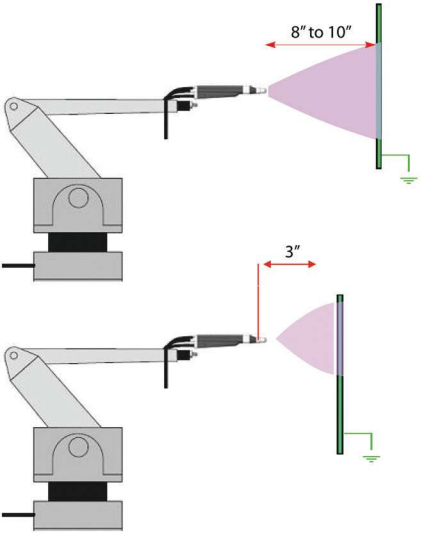


Figure 2. The gun-to-part distance of a dense phase gun is much closer to the part, making it the perfect powder coating tool for use with robotics.

Dense phase technology and robotics—a perfect marriage of advanced technologies.

As more and more powder coaters adopted dense phase technology for use with manual guns and fast 20 second color changes, it was a natural evolution to adapt this same technology to automatic guns. This was done not only for use in spray-to-waste systems, but also for use in reclaim systems that recovered the over-spray and reused it. It was determined during this evolution that the decreased gun-to-part distance that applied to the manual guns, not only applied to the automatic gun as well, but also lent itself very well to the combination of an dense phase gun on a robot.

Because of the almost infinite movement and longer reach of a robot (as compared to a manual oper-

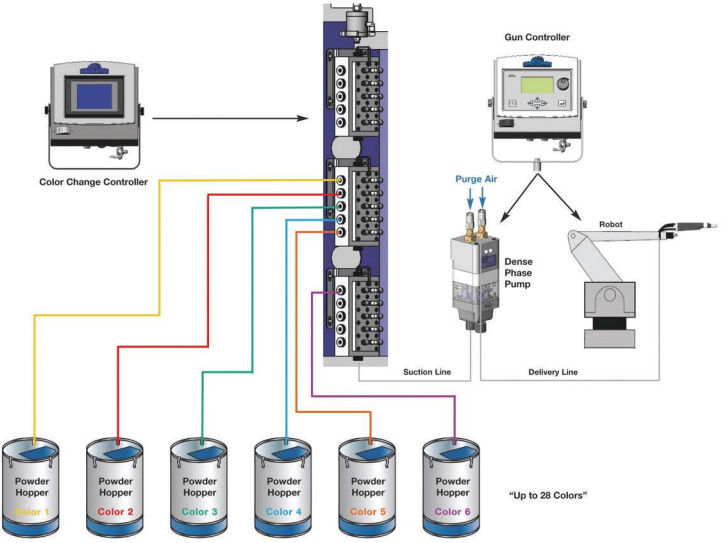


Figure 3. When combined with color-on-demand technology, dense phase application equipment can provide color changes in 20 seconds or less.

ator), the dense phase gun could track very close to the part at a high speed, resulting in exceptional powder uniformity, better standard deviation of film build, reduced over-spray, and reduced cycle time. Coupled with AFC (automatic feedback control) current limiting technology, this allowed the robot to not only contour the part quickly, but to reach back into cavities and coat them uniformly without bounce-back due to the low velocity of powder and without defects caused by too high of a current.

When a powder gun is at its optimum distance from the part–the effective charging voltage of the powder is optimized and current draw is low. When the gun-to-part distance decreases, effective voltage also decreases and the current increases. This causes a defect on the powder coated surface of the part commonly known as back ionization. In the case of cavities, this can result in what is known as the Faraday Cage Effect, resulting in poor powder coverage of the surface of the cavity. Dense phase with its low powder velocity and the resulting reduced bounce back—coupled with AFC current control—makes it the perfect match for use with robots for all powder coating applications. This is especially true for those that require frequent color changes.

Because dense phase pump is purge-able in both directions, the powder delivery line can be cleaned quickly and effectively. When coupled with "color-on-demand" technology, dense phase technology provides automatic color changes in less than 20 seconds. When combined with automatic gun presets that control application parameters—such as powder flow and electrostatics (KV and AFC) for each and every part as well as each and every powder—powder coaters now have the ultimate tool for productivity and flexibility in their powder coating operations.

Office furniture manufacturers in Japan have been using dense phase tech-

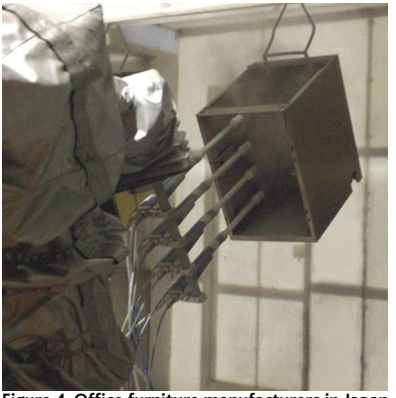


Figure 4. Office furniture manufacturers in Japan have successfully used dense phase, robotics and color-on-demand technology for several years now.

nology, robotics and color-on-demand technology for several years now to powder coat effectively and change colors quickly using multiple dense phase guns on a single robot—and sometimes using multiple robots on the same booth. Additionally, dense phase technology is not limited to organic powders. It can also be used to pump and spray PE (porcelain enamel) powders. An appliance manufacturer in North America is currently using dense phase guns on robots to apply porcelain enamel powder to oven cavities. In the end, these manufacturers are a testimony to the superior process control of robotics and the unparalleled application control of dense phase technology when married together.

SUMMARY

The benefits of dense phase powder coating equipment, when coupled with robotics, deliver advanced application and process technology. As a result, it provides increased productivity, greater repeatability–and savings!

Increased **Productivity**
- Faster cycle times
- Higher line speeds
- Increased up-time and reduced downtime
- Higher first pass yields

Greater **Repeatability**
- Reduced process variations with robotics
- Reduced powder application variations with presets (part recipes)
- Elimination of human interaction variables

Savings
- Higher first pass transfer efficiency—more powder on the part and less over-spray
- Reduced compressed air usage with dense phase technology as compared to conventional venturi pumps
- Decrease in required number of manual gun operators
- Less rework and fewer rejects

DIP COATING

BY THOMAS C. JONES
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Dip application of a protective coating involves simply immersing a workpiece into a suitable tank containing the coating material, allowing the part to drain after withdrawal, and force drying or baking the wet coating to achieve the finish. Dip coatings are used in many industries for both primer and one-coat finishes.

Thorough cleaning of parts is essential prior to dipping. For optimum quality, a phosphate conversion coating is also recommended.

BENEFITS

Simplicity: Manpower and equipment requirements are minimal. The process is easily automated.

Low Cost: Paint utilization should be relatively high (e.g., greater than 90% transfer efficiency) on properly operated systems, since nonused paint (drainage) is mostly recovered and returned to the system.

Ease of Control: Minimally skilled operators can maintain solids, viscosity, and other factors for acceptable application properties.

Good Coverage: Except for air bubbles or pockets, all contact areas are coated. Close racking of parts is possible.

Consistency: Similar parts receive coatings similar in appearance and film thickness (i.e., the process is independent of the operator).

LIMITATIONS

Nonuniform Coatings: "Wedges" (thin films on upper surfaces, thicker on lower surfaces) tend to form on vertical surfaces. Flow lines around holes or openings can also occur. "Beads" on bottom edges are inherent defects, although proper viscosity control can minimize this effect.

Part Design and Hanging: Improperly racked parts can bucket paint, leading to waste and potential blistering in the puddled areas. Entrapped air pockets can prevent access of paint, with resultant bare areas. It may be necessary to design drain/access holes into some workpieces to allow for immersion application. An attempt should be made to rack a part so that drainage occurs from a single point. Oscillation during immersion can sometimes remove air pockets.

Solvent Washing: Entrapped solvent during the curing process can resolubilize an already dried film, resulting in bare areas.

Product Change: A change from one formulation to another requires either extensive cleaning and recharging of a single tank or the availability of multiple dip tanks. Thoroughness of clean-out is especially important when switching incompatible materials (e.g., replacing a solvent-borne system with a waterborne system).

Flammability: The potential for fire is always present when solvent-borne dip primers are used. With waterborne systems, this problem is greatly reduced.

Foam: Undesirable foam, which usually originates in the paint recirculation system, can produce voids or craters in the final finish.This problem is more preva-

lent with waterborne paints.

Sticking: Small objects, such as fasteners processed in baskets or trays, can fuse together during cure. Processes, such as autodeposition or electrodeposition, that utilize water rinsing following the coating tank generally do not produce this effect.

Viscosity: Control is critical. High viscosity gives thick films and excessive consumption. Low viscosity produces thin films.

TYPICAL COATINGS USED

Selection of a coating system (i.e., resin type, pigment color) is directly related to the performance intended for the finished parts. Although any formulation with the appropriate viscosity for acceptable transfer efficiency (i.e., greater than 90%) can be used, properties of appearance, quality, cost, and other factors must be taken into account.

There is a trend toward the use of waterborne formulations because these are both fire resistant and ecologically desirable. Defoamers are often required to control foam in waterborne systems; however, silicone-containing materials must be avoided. Waterborne paints are often more aggressive toward equipment than solvent-borne formulations.

EQUIPMENT REQUIREMENTS

If high-volume throughputs are desired, a continuous conveyor for work transfer is usually employed in contrast to a manual or programmed hoist. Circulating pumps are required to maintain uniform viscosity and constant paint composition. The "bead" that characteristically forms on the lower most edge of a draining part is sometimes removed by ultrasound, by electrostatic detearing, or by air jets; the latter is generally the least expensive technique.

A controlled withdrawal rate is useful in controlling coating thickness. This is more readily varied with a hoist system.

Tank/Agitation System

A tank lining chemically resistant to the coating employed is required. Epoxy-type coatings with a 15-mil minimum thickness are commonly employed. The tank and piping for circulation can be mild steel for solvent-borne coatings but should be stainless steel for waterborne systems.

Tank volume is dependent on work package size and the transport system in use, with conveyorized systems requiring longer tanks than a hoist system. The work package should be submerged at least 3 in. below the surface and at least 6 in. above any circulation piping at the bottom of the tank. Overflow weirs, to remove floating debris, are usually located at the entrance end of the tank and/or along the sides.

Agitation can be either from an eductor positioned on the bottom of the tank bisecting the longest dimension, which tends to minimize parts falling from the rack, or by eductors directing flow along the bottom of the tank, which results in a circular motion. Centrifugal- or turbine-type pumps are normally used for solvent systems; however, where shear sensitivity and/or foam are potential problems (as with waterborne paints), double-diaphragm pumps, with an accompanying surge suppressor, are recommended. As with other metal components, stainless steel is recommended for wetted pump surfaces when waterborne systems are used.

Pump wear can be reduced by a filter on the suction side. Self-cleaning filters reduce maintenance times.

In some installations, the dip tank is complemented by an additional collection tank (for return of the drippings) and a circulation tank (for isolated additions of paint, solvent/water, and other additives). Paint flows from the collection tank to the circulation tank (for adjustment) and then to the dip tank. Care must be taken not to introduce foam along the way. Covers (removable) on the collection and circulating tanks elevate humidity and help to reduce foam.

Drip/Flash-Off Zone

The area following the dip paint tank allows the recovery of paint by means of a pan that returns drippings to the tank. Depending on formulation, air-flow regulation and temperature control may be required. Some waterborne paints require humidity control.

Too rapid solvent loss will result in a rapid increase in coating viscosity on the surface that tends to "fix" runs or sags, with a resultant decrease in the quality of appearance.

A minimum of 3 min is recommended for dwell time to allow 90% plus paint recovery and enable optimum flow/leveling. In general, high air velocities should be avoided.

Some installations provide a controlled heat input, either from the cure zone or from some other related source (e.g., pretreatment) to prepare the film for the final cure.

Curing Zone

The time and temperature parameters for cure are dependent on the polymer and cross-linking polymer used. Although a forced-air convection oven is used most often, infrared technology has also been employed.

Energy can be consumed by bottom entry and exit from the oven.

The exhaust system should result in an oven under negative pressure compared to the shop.

Forced air can be used following the oven to facilitate cooling.

MAINTENANCE

Floating residues must be removed from the paint tank to prevent clinging of the material on withdrawn workpieces. This is usually accomplished by periodic skimming.

Overhead conveyor systems require lubrication for maximum life. However, any lubricants used should be pretested as potential contaminants in the paint because some materials can cause cratering and other defects in the final product.

Racks must be periodically stripped of dried paint. Either thermal stripping (molten salt bath or high-temperature oven), cryogenic stripping (exposure to liquid nitrogen, followed by physical removal of the embrittled paint), or media blasting (sand, steel shot) can be used.

Cleaning of the drain-off area must occur on a regular basis. Care must be taken to avoid getting dried paint into the circulation system, with resultant damage to filters, pumps, and nozzles.

SPRAY APPLICATION PROCESSES

BY JERRY P. HUND
JPH FINISHING CONSULTANTS, WEST CHICAGO, ILL.

The spray application of coatings to protect and decorate products has undergone considerable change since its inception some hundred years ago. The Industrial Revolution has given us an unlimited supply of new products to finish, along with an ever-increasing variety of coating materials to use on those parts to provide them with protection and decoration.

Presently, we have four major processes of spray applications: (1) air atomization-conventional air spray and high-volume, low-pressure (HVLP) atomization, (2) airless atomization, (3) air-assisted airless atomization, and (4) electrostatic atomization, which can be combined with any of the three previously mentioned forms, or used with rotational atomizers. Regardless of the finishing system, all have their advantages as well as their limitations. What may be suitable for one situation may not be suitable in another.

To select properly which system is best suited for your needs, a review of the advantages and limitations of each process is in order. Table I lists advantages and limitations for each process (see also Figs.1–3).

CONVENTIONAL AIR SPRAY

Conventional air spray (siphon/gravity/pressure feed) is the oldest system, coming into prominence during the 1920s with the growth of the automobile and furniture industries. It remains today as the finishing system most widely used by industry.

Advantages

Conventional air spray lays claim to two basic advantages over the other methods as follows.

Control. This is the most controllable process available. The spray operator, when properly trained, can control the spray pattern from a fine dot to a large production-type spray pattern. This permits the spraying of small or large areas without changing guns or nozzles.

Also, the degree of atomization can be controlled. This process provides the finest degree of atomization available in a hand-held system. Needless to say, it is the choice for those who want the best quality finish possible.

Versatility. This process affords the operator the ability to spray the widest range of coating materials. It is also the easiest system to operate and maintain. Just the fact that the process has been around so long has resulted in a huge inventory of equipment, plus volumes of knowledge regarding application techniques.

Disadvantages

On the other hand, conventional air spray has a low level of transfer efficiency. Often, more material is wasted than is actually deposited on the part. This condition is usually aggravated by excessive pressure and poor operator technique. Air spray also consumes large amounts of compressed air (7–35 cfm at 100 psi).

How the System Works

The material to be sprayed is supplied to the spray gun by either a siphon or

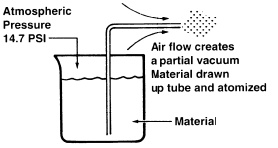
Table I. Spray Application Processes

Figure No.	Process	Advantages	Limitations
1.	Air-atomization–most commonly used for industrial finishing.	Complete pattern control. Finest atomization.	Uses more air. Creates most fog. Low transfer efficiency.
1.1	Siphon fed–uses vacuum created at nozzle to draw material from cup, external atomization.	Lowest cost. Less maintenance. Changes color quickly.	Operator carries weight of material at gun. Sprays light materials only. One quart maximum. Spray position limited.
1.2	Gravity fed–material is fed to gun via attached cup.	Ideal for most refinishing. Easy to clean. Improved atomization versus siphon fed.	Same as 1.1 Unfanmiliar technology to some.
1.3	Pressure fed (external atomization)–uses external pressure source, tank, or pump to force material from nozzle; material and air mix outside of nozzle.	Delivers more material than 1.1. Wide viscosity range. Sprays most materials. No air nozzle wear. Spray in any position. Independent control over air and fluid pressures.	Consumes most air. Creates most fog. More controls to learn.
1.4	Pressure fed (internal atomization)–material and air mix inside nozzle.	Less fog than 1.3. Larger patterns. Less air consumption.	Coarse atomization. Fixed patterns. Nozzles wear. Fast drying coatings not recommended.
1.5	Pressure fed (external atomization) with heated material–same as 1.3 except material is heated to reduce viscosity.	Better control. Reduced air and fluid pressures. Limits overspray and rebound. Finer atomization for a better finish. Better adhesion. More film build per coat. Reduced blushing. Reduced solvent use.	Not all materials can be heated. Special paint formulations are required. Additional equipment to maintain. Equipment must be explosion proof (electrical). High electrical demand. Reduces pot life for catalyzed coatings.
1.6	High-volume, low-pressure atomization (HVLP)–available in systems as discussed in 1.1, 1.2, 1.3, 2.2, and 2.4	High transfer efficiency, Sprays well into recesses and cavities. Complies with most air quality regulations.	Atomization not as fine as that of air spray. Not recommended for some heavy materials or where high production is required. Some systems for generating HVLP air may be expensive.
2.	Airless (hydraulic) atomization–atomization caused by release of high fluid pressure through small orifice. Most widely used by painting contractors and maintenance painters.	High fluid capability. Large patterns. Fastest spray application process. Low air consumption. Limited fog and "bounce-back". Permits spraying into cavities.	Potentially hazardous hydraulic injection. Higher rate of overspray. Sharp patterns; difficult to blend. Expensive nozzles may flood surface. Equipment requires top maintenance.
2.1	Airless atomization (heated)–same as 2 except with heat to reduce viscosity. Used by furniture manufacturers and industrial finishers.	Better flow of material. Higher solids per pass of gun. Viscosity control. Finer atomization than 2.	Strict maintenance. Same limitations as 2.

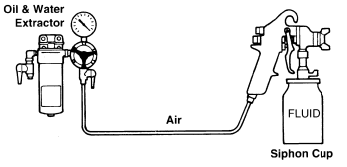
Table I. Spray Application Processes

Figure No.	Process	Advantages	Limitations
2.2	Air-assisted airless–lower fluid pressures than airless (normally below 1,000 psi); low pressure is added via the air nozzle to further atomize the ready preatomized spray. Used by furniture and industrial finishers.	Material savings 50% better than air spray plus lower overspray and fog. Less tip wear; longer pump life than airless. Higher film build per pass than air spray.	Atomization not as fine as air spray. Hydraulic injection may occur. Tip plugging. Strict maintenance is required.
2.3	Air-assisted airless (heated)–uses same principle as 2.2 with the addition of heat to reduce viscosity and improve flow.	Better flow of material. Higher solids per pass of gun. Viscosity control. Finer atomization than 2.2.	Strict maintenance. Same limitations as 2.2.
3.	Electrostatic atomization–voltage difference between paint dispenser (low-speed rotating disc or bell) and work causes paint to be attracted to the grounded work. Used by most appliance manufacturers. High production of uniformly shaped parts.	High transfer efficiency at 65–95%. "Wrap around" effect, coating other surfaces. Minimum overspray.	Parts must be conductive. Limit to shapes that may be coated. High production rate required. High voltage and spinning cup or disc may be hazardous.
3.1	Electrostatic attraction–material is atomized using convention air, airless, or air-assisted airless principles; particles are electrically charged and attracted to the work. Electricity may be turned off to permit normal spraying.	"Wrap around" effect. Material savings through minimized overspray. Use with or without electrical charge.	Some conductive materials will require special equipment. Parts must be conductive. Difficult to penetrate cavities or recesses with power supply on.
3.2	Electrostatic attraction (heated materials)–same as 3.1 except materials are heated.	Ability to use the systems coupled together to get all the advantages as in 1.5, 2.1, 2.3, and 3.1	Same limitations as in 1.5, 2.1, and 3.1.
3.3	High speed rotation atomizers–high speed (10,000–70,000 rpm) rotating disc or bell gives exiting paint particles velocity and direction. Voltage differential then takes over and allows electrically charged paint particles to attract themselves to a grounded part.	High transfer efficiency. "Wrap around" effect, coating other surfaces. Works well with high solids coatings. Minimum overspray.	Parts must be conductive. Limit to shapes that may be coated. High production rate required. High voltage and spinning cup or disc may be hazardous.

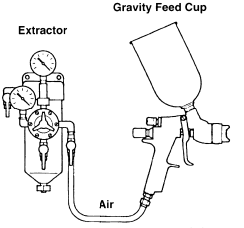
1. AIR ATOMIZATION



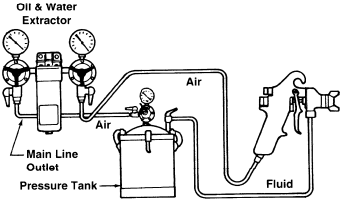
1.1 SIPHON FEED HOOKUP
(External atomization)



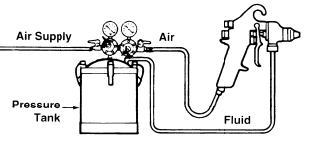
1.2 GRAVITY FEED



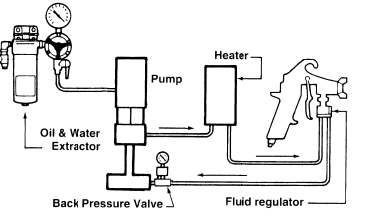
1.3 PRESSURE FEED TANK HOOKUP
(External atomization)



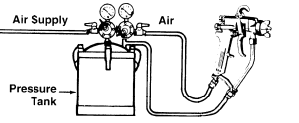
1.4 PRESSURE FEED TANK HOOKUP
(Internal atomization)



1.5 PRESSURE FEED HEATED MATERIAL



1.6 LOW PRESSURE LOW VOLUME
ATOMIZATION (LPLV)



1.7 HIGH VOLUMN LOW PRESSURE
ATOMIZATION (HVLP)

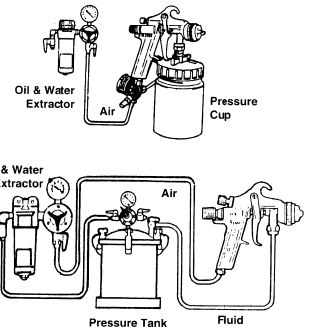
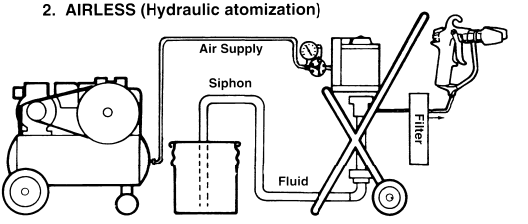
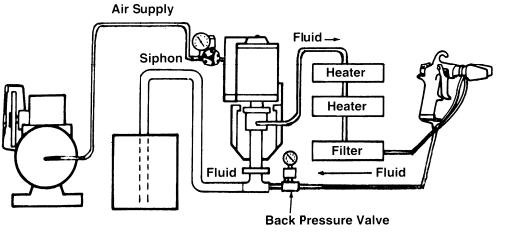


Fig. 1. Typical air atomization spray systems.

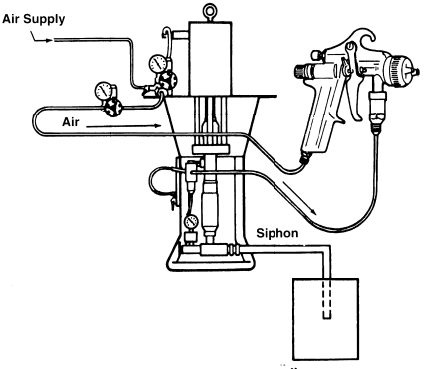
2. AIRLESS (Hydraulic atomization)



2.1 AIRLESS ATOMIZATION (Heated)



2.2 AIR ASSISTED AIRLESS ATOMIZATION



2.3 AIR ASSISTED AIRLESS (Heated)

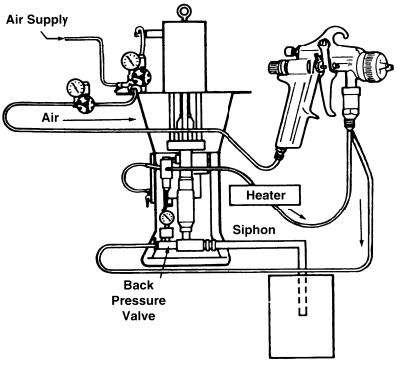


Fig. 2. Typical airless atomization spray systems.

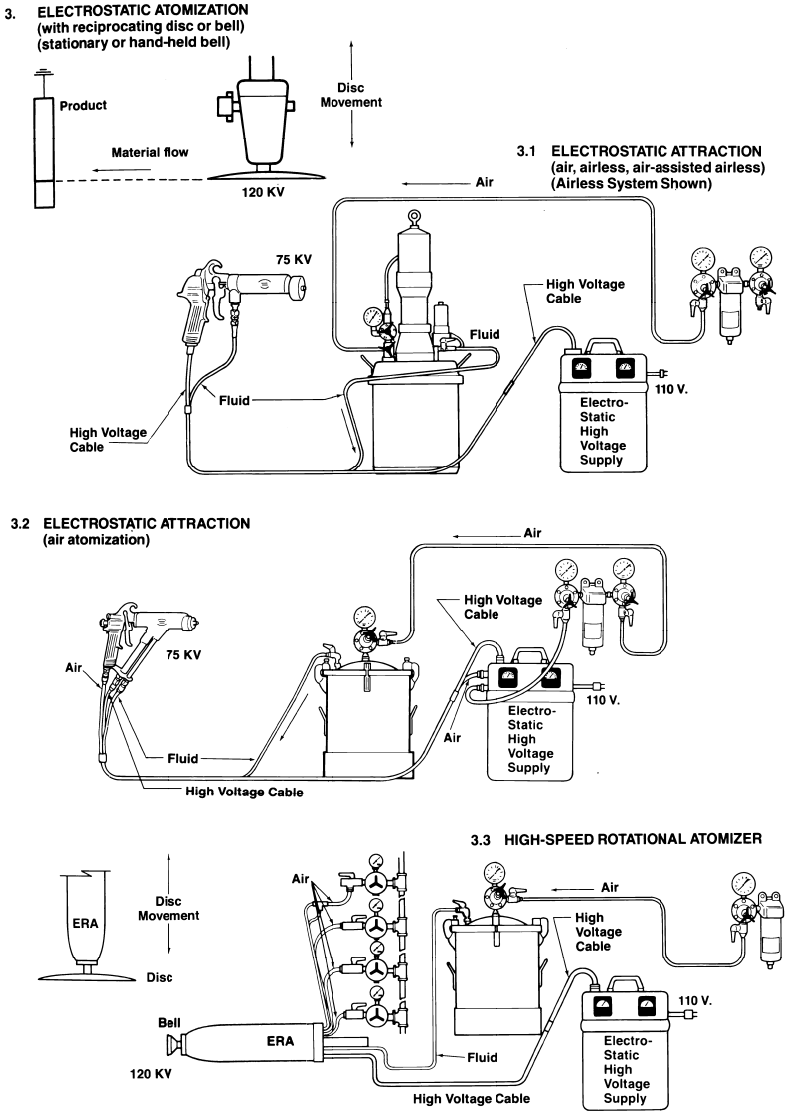


Fig. 3. Typical electrostatic atomization spray systems. (Note: High voltage power supplies shown here. Electrostatic spray guns may also receive current from low voltage power supplies where it is converted to high voltage inside the electrostatic spray gun. High voltage may also be created from air-driven cascade generators located inside the spray gun. Consult electrostatic spray gun manufacturer for further details.)

gravity cup mounted to the gun or by a pressure feed device such as a pressure tank or pump. When the gun is triggered, the material is discharged through the fluid nozzle of the gun in the form of a liquid stream. Upon exiting the gun, this stream is immediately surrounded by a hollow column of compressed air, usually under high pressure, emitted from the center of the air nozzle of the gun. The action of this column of air on the fluid stream converts it into small droplets and imparts forward velocity to them. Additional jets of high-pressure compressed air from the face and horns of the air nozzle are directed into the droplets, forming even smaller droplets and an elliptical or fan spray pattern.

The ability to control these forces at work at the head of an air spray gun is the key to a successful spray application. The proof that you have this control is in the quality of the spray pattern produced.

HIGH-VOLUME LOW-PRESSURE ATOMIZATION

Worldwide concern over increased air pollution has necessitated numerous changes, including in how we finish our products. HVLP air atomization and electrostatics are now the only accepted methods of production spraying in certain parts of the country.

Although all HVLP spray guns operate with the same objective in mind, how they accomplish this goal may differ. First, air used in the atomization process reaches the HVLP spray gun's nozzle in one of four ways: (1) standard high-pressure compressed air, which has its pressure restricted within the gun body; (2) standard high-pressure compressed air, which is assisted with a venturi feed and then filtered ambient air prior to its pressure restriction within the gun's body; (3) standard externally fed HVLP turbine air; and (4) compressor-assisted externally fed turbine air. Items 1 and 3 have seen the most growth and ultimate acceptance in recent years.

All HVLP spray guns should operate at air pressures between 0.1 and 10 psi (at the air nozzle) and consume air volumes of 15–30 cfm to be considered true HVLP spray guns. Although some HVLP guns with internal restrictors can exceed 10 psi air pressure, it is up to the operator to follow local regulations when necessary.

Advantages

The benefits of HVLP atomization are improved transfer efficiency, often approaching 65–75%, compliance with local finishing regulations, a softer spray that penetrates easily into recesses or cavities, reduced material (costs) consumption as well as reduced spray booth maintenance and reduced hazardous waste. Turbine-operated HVLP systems enjoy great portability and ease of operation where compressed air is not available. HVLP spray guns with internal restrictors use existing air supplies, are easy to operate, and are low in cost.

Disadvantages

The most notable limitation to the HVLP process is that the finish quality from some HVLP spray guns is not as fine as conventional air spray. This may not pose a problem to some finishers, but to others it may mean additional polishing, a change in the material formulation, or switching to electrostatics. Turbine-generated HVLP systems may be expensive to purchase and to operate. HVLP guns using internal restrictors must have an adequate supply of clean and dry air to operate efficiently. Turbine guns use a larger air hose, which may be difficult to work with. Some high-volume production lines may find HVLP to

be too slow. Fluid deliveries that exceed 20 oz/min. may sacrifice finish quality for speed.

AIRLESS ATOMIZATION

In the 1960s, attention turned to another process of atomization known today as airless spraying. Airless spraying is a method of spray application that does not directly use compressed air to atomize the coating material. Hydraulic pressure is used to atomize the fluid by pumping it at high pressure (500–4,500 psi) through a small orifice (0.007–0.072 in.) spray nozzle tip located at the front of the airless gun. As the fluid is released at these high pressures, it is separated into small droplets, resulting in a finely atomized spray. The fluid is discharged at such a high velocity that it tears itself apart and sufficient momentum remains to carry the minute particles to the surface. The spray pattern size, or fan angle (3–21 in.) and orifice are usually preselected, but different spray angles deposit the same amount of paint over a different area. A good rule is to determine the largest fan angle and the smallest orifice that is practical for your needs.

Advantages

The main benefit of airless atomization is speed of application. It is the fastest method of spray atomization. This process can deliver twice the amount of material as a compressed air system. Other advantages include improve transfer efficiency due to a reduction in fog and overspray, the ability to spray into recesses and cavities with a minimum of material bounce-back, and reduced spray booth maintenance.

Disadvantages

The airless process has had to cope with several limitations over the years and one is coarse atomization. Although some users, such as maintenance painters, ship builders, and highway stripers, find airless atomization acceptable, others may not. Automotive finishers and refinishers, for example, would not select airless atomization. Other limitations include less control of spray pattern when compared to air spray or HVLP.

An airless gun is either on or off; there is no "feathering" capability. The tendency is to flood the surface, causing runs or sags if the spray gun movement is momentarily delayed. Also, one must provide strict maintenance with this system. Any foreign object in the fluid supply that is larger than the spray-tip orifice will cause the system to block or shut off. Equipment maintenance on pumps is also high because of the high pressures used. Nozzle tips will wear and may prove costly to replace. Finally, the high velocity of the fluid stream and spray pattern, as it immediately exits the gun or hose, is a potential hazard. Never allow any part of your body to come into close contact with this high-pressure material. Failure to keep several inches away from the coating as it exits the gun or hose will cause serious injury.

AIR-ASSISTED AIRLESS ATOMIZATION

In the 1970s, various combinations of spraying systems emerged. Air-assisted airless was one that developed to fill a need that resulted from escalated material costs and newly enacted Environmental Protection Agency (EPA) regulations. Air-assisted airless, under ideal conditions, combines the best features of air spray along with the best of airless.

Air-assisted airless spray guns first partially atomize the fluid with a special fluid nozzle tip similar to a standard airless tip. Second, they complete the atom-

ization with small amounts of compressed air from the face and/or the horns of the air nozzle that they use. The result is a finely atomized spray pattern closely resembling that of a compressed air system. Newly designed low-pressure, air-assisted airless systems are also available. Some systems restrict the atomizing air pressure to comply with various EPA guidelines; as a result, these systems can be considered HVLP air-assisted airless.

Advantages

The primary advantage of air-assisted airless is its "soft" spray atomization. Atomization air pressures are usually low, and as a result, this system provides a fine finish with most coatings approaching that of compressed-air atomization. With air-assisted airless we can see an approximate 30% improvement in transfer efficiency over compressed air. This system allows us to increase flow rates, while also spraying into recesses and cavities, without excessive bounce-back of material. This means less booth maintenance and cleanup time. We also can expect a reduction in compressed-air supply requirements. Since fluid pressures generally range from 200 to 800 psi, less wear on the pump and tip is to be expected.

Disadvantages

Tip plugging may still be a problem with air-assisted airless. Many operators feel that air-assisted airless is too slow when compared to airless and that the finish is still not as good as compressed-air atomization. Many operators tend to use excessive fluid and air pressures with this process. There are more controls to learn to use it correctly.

ELECTROSTATIC ATOMIZATION

During World War II, paints and solvents were in short supply or very expensive when available. Thus, to fill that need and to maximize the use of these materials, electrostatic atomization was developed.

The coating is first atomized using either the compressed air, airless, or air-assisted airless methods previously discussed. Although these systems require equipment designed for electrostatic use, the atomization principles are the same as those for nonelectrostatic applications. The atomized paint particles, at this point, are provided with forward velocity and direction.

The particles are made to pass through a cloud of free-floating electrons (negative charges) produced by a high-voltage source such as an independent power supply, cable, and electrode at the gun, or a turbine-operated generator located inside the spray gun. The basic principle of electrostatics is that "like" electrical charges repel one another and "unlike" electrical charges attract.

Since each particle of material is negatively charged from 30–140 kV and 0–200 mA, it will want to seek the closest grounded object (positive) to complete the electrical circuit. If the product is sufficiently grounded, particles that would have missed that part will now be drawn back or attracted to it. This is commonly referred to as the "wrap effect."

Rotational Atomizers

The first low-speed rotational atomizers premiered in the early 1950s. This type is sometimes referred to as a "true electrostatic" system. The atomization is created by the high voltage itself. The rotation of the electrically driven disk or bell evenly disperses the paint to the edge of the spinning disk or bell.

When the unit is charged to approximately 120 kV DC, a current flow devel-

ops between it and the grounded object. This current flow pulls the particles of coating off the spinning disk or bell and carries them to the product.

With the introduction of paints high in solids these atomizers had to use higher speeds. Thus, electric motors were replaced with high-speed air-driven turbines. These high-speed rotational atomizers (10,000–60,000 rpm) use centrifugal force to atomize the coating and carefully directed compressed air to give the atomized paint particles forward velocity and direction. A voltage differential (120 kV DC) then takes over and allows the charged particles to migrate to the grounded part.

Disk versus Bell

The spray pattern needed for the kind of parts being finished, the shape of the product, and racking, or the existing facility, determine whether a disk or bell is used. For long, thin parts and flat stock, the reciprocating disk directs the horizontal spray in the thin, narrow plane that is needed to provide a fine even coat in conjunction with the omega-style conveyor and booth. For shorter, wider parts, the donut-shaped cloud produced by a bell directs a fine even coat and is mounted horizontally or used with a vertical short-stroke oscillator in a standard overhead conveyor system and booth.

Advantages

The principal advantage of electrostatic spraying is the savings in material and labor. This process can provide transfer efficiency ratings from 65 to 95% if all conditions are favorable. Air velocity in the spray booth where electrostatic spraying is performed may be reduced from 100 to 60 ft/min. This means a 40% reduction in air makeup costs as well as reduced emissions.

Disadvantages

The old saying "Where the current goes, so goes the paint" applies here. The Faraday cage effect will make painting in some corners and recesses difficult, thus manual nonelectrostatic touch up will be necessary. Contrary to some beliefs, electrostatics will not improve adhesion or provide superior gloss, nor will it always provide a complete wrap effect. Also, some users may find excessive buildup on corners and edges unacceptable. The parts you want to spray electrostatically must always be conductive, either by virtue of the material

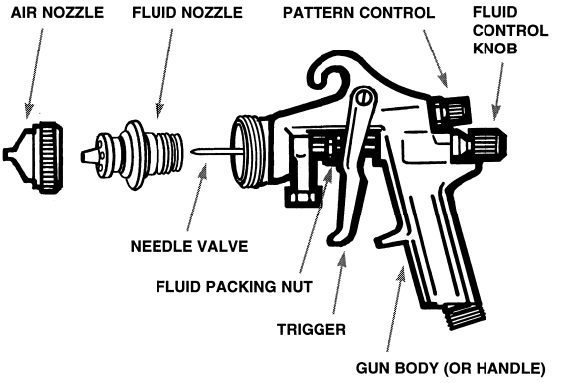


Fig. 4. Typical air spray guns.

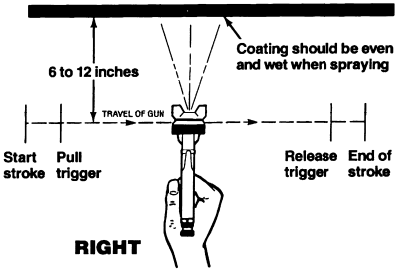


Fig. 5. Gun should be moved parallel to surface being sprayed.

from which it is made or through the application of a conductive pretreatment.

Recent equipment developments now make it relatively simple to apply water-reducible coatings with electrostatic equipment. Both hand-held and automatic systems are available. Since the material is highly conductive, it is necessary to isolate the material supply. The fluid supply will be highly charged, and it is, therefore, necessary to erect barricades to prevent physical contact with this portion of the system.

Sometimes the added expense to apply this coating may not justify the material savings. Also, added maintenance — cleaning the hangers, supports, or conveyors — to assure conductivity to ground is necessary. All electrically conductive items, such as containers and spray equipment, within 10 ft of the spray area should be grounded to prevent static buildup. Operators grounding out any static buildup may experience a severe shock.

COMPONENTS OF A SPRAY SYSTEM

A spray finishing system consists of the following components: a spray gun, a compressed air supply, a fluid supply, and other necessary items such as hoses, fittings, regulators, and proper respiratory equipment

Spray Gun

Spray guns (see Fig. 4) are available in a wide variety of performance capabilities and costs. The three factors in order of importance are function, service, and price. As with anything, you pay for quality. Cheap spray guns, which may look like the expensive guns they imitate, have no place in a production finishing shop. Consult your spray gun supplier for correct air and fluid nozzle recommendations. After all, this is the part of the spray gun that develops the atomization desired.

Compressed Air Supply

The compressor you use does not make air, it only compresses it. The condition of your air supply usually tells a lot about the compressor and the air-supply lines. A compressor is rated for its volume, measured in cubic feet per minute (cfm), and its pressure, measured in pounds per square inch (psi). To assure maximum performance of any spray finishing system, the compressed air supply should always exceed the required psi and cfm requirements of its components. This is especially true when using HVLP spray guns. The rule of thumb is to expect about 4 cfm for every 1 horsepower at 100 psi with an electric compressor. Gas compressors are some-

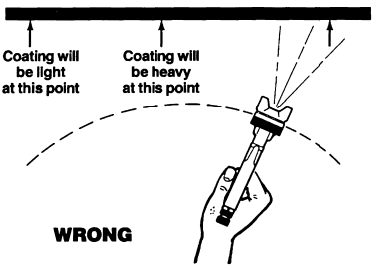


Fig. 6. Fanning will result in an uneven coating.

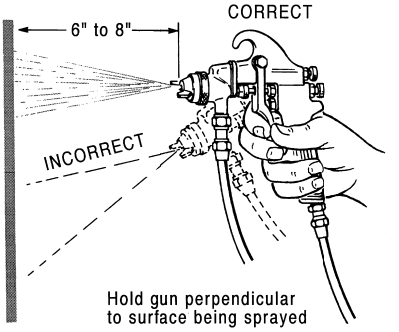


Fig. 7. Hold gun perpendicular to surface being sprayed.

what lower in performance.

Do not ignore the necessity of properly selected, cleaned, and operating air-supply components such as extractors, regulators, ball valves, and hoses. Failure to do so only adds to finishing-room difficulties.

Pulling back slightly on the trigger opens the air valve to allow use of the gun as a blow gun. In this position the trigger does not actuate the fluid needle and no fluid flows. As the trigger is further retracted, it unseats the needle in the fluid nozzle, and the gun begins to spray. The amount of paint leaving the gun is controlled by the pressure on the container, the viscosity of the paint, the size of the fluid orifice, and the fluid needle adjustment. In industrial finishing where pressure tanks or pumps are used, the fluid needle adjustment should normally be fully opened. In a siphon cup operation, the needle valve controls the flow of paint.

Fluid Supply

The fluid supply can range from siphon cups, to pressure tanks, to material handling pumps for dead-end or circulating systems. Siphon and gravity cups remain popular with refinishers, and those on touch-up lines. Pressure tanks remain popular with those on low- to medium-production lines, using compressed air or HVLP atomization. Pumps are generally used on medium- to high-volume production lines, circulating systems, and airless and air-assisted airless production lines. Pumps may be powered by compressed air, hydraulics, or electricity.

Paint Heaters

Paint heaters, when used correctly, provide viscosity control, reduced solvent use, sprays of higher solids, reduced flash time, reduced air and fluid pressures, and improved flow. Heaters may be used with pumps on compressed air, HVLP, airless, air-assisted airless, and all types of electrostatic systems. Paint heaters are becoming more prominent in the finishing industry as solvent use is restricted to meet compliance standards.

OPERATOR TECHNIQUES

More often than not, spray painters are usually improperly trained (if trained at all), allowed to develop many bad habits, and, in many cases, frequently change positions or employers, taking their knowledge and skills with them.

On the other hand, management sometimes fails to recognize the importance of training until problems exist. The organization may have the best coating materials and spray equipment mon-

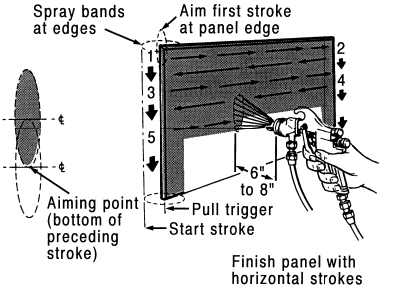


Fig. 8. Proper pattern overlap produces an even coating.

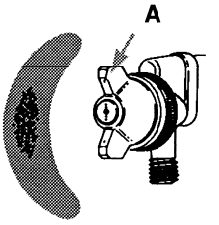


Fig. 9. "C" spray pattern caused by dried material clogging the side port (A). To correct the problem, dissolve the dired material w ith thinner. Do not use metal devices to probe into the air nozzle opening.

ey can buy, but without skilled operators the entire system will fail.

Examine the following variables that can lead to problems in the finishing room. Failure to observe these rules may result in finishing problems. These are the five operator variables that must be controlled to improve application efficiency.

1. Distance of gun to work.
2. Stroking speed.
3. Pattern overlap.
4. Spray gun attitude (heeling, toeing, fanning).
5. Triggering.

Figures 5 through 8 illustrate proper versus improper spraying technique.

SPRAY PATTERNS AND PRESSURES

The general rule of thumb for setting pressures is to always use the lowest pressure that will give a satisfactory pattern. This rule applies to all spraying processes. Failure to observe this rule, or using faulty or dirty nozzles, will usually result in faulty spray patterns. Typical patterns with suggested corrections are shown in Figures 9–13.

Keeping the spray gun too far from the substrate will increase the likelihood of fallout. Fan patterns that are excessive in width will increase overspray. Excessive pressures will contribute to off-spray and rebound (see Fig.14).

MAINTENANCE

The spray gun is a precision tool and will perform best if kept clean and lubricated.

Siphon Spraying: Wipe off the siphon tube with a solvent rag. Dip the siphon tube into a container of clean solvent and spray. Trigger repeatedly to thoroughly flush the passageway and clean the fluid nozzle and needle. (Consult local codes for restrictions on spraying solvent.)

Gravity Spraying: Turn off atomization air to spray gun. Remove material from cup. Wipe interior of cup clean with solvent rag. Pour solvent into cup. Pull trigger allowing gravity to flush all fluid passages. Repeat until clean.

Pressure Spraying: Substitute clean solvent under pressure for the paint being sprayed, using low fluid pressure (no atomizing air is necessary) trigger the gun repeatedly to permit the solvent to flush out the passageway. Do this until clean.

Wipe off the gun body with a cloth wet with solvent and lubricate the spray gun with a drop of light machine oil each day.

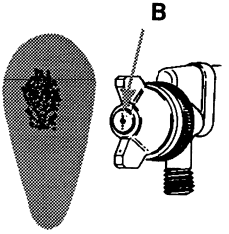


Fig. 10. Inverted tear-drop spray pattern caused by dried material stuck to the outside of the fluid nozzles tip (B), or by a loose air nozzle or a bent fluid nozzle or needle tip. If dried material is the problem, remove air nozzle and wipe off fluid tip, using a rag wetted with thinner. Tightewn the air nozzle and replace the needle, if bent.

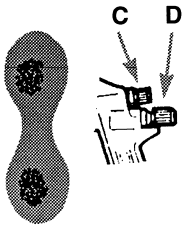


Fig. 11. Split spray pattern caused by too much atomizing air pressure and/or trying to widen the spray pattern too much. Remedy the problem by opening the fluid control knob (D) to the full position and turning the spray control knob (C) down to narrow the spray pattern width.

TROUBLESHOOTING SPRAY GUNS

If fluid is leaking from the needle packing nut, check for a loose packing nut or dried-out packing. Tighten the nut until leaking stops, or replace packing, if required.

If air is leaking from the front of the gun, check for foreign matter on the air valve stem or seat, a broken air-valve spring, or a bent air-valve stem; check the air valve packing nut to see if it is too tight, the air-valve assembly to see if is tight enough, and the air valve assembly gasket for leaks; and check to see if the gun is a bleeder-type spray gun.

If fluid is leaking from the front of gun, check for a worn or damaged needle or fluid nozzle, dirt in the fluid needle seat, and a broken fluid control spring; check to see if the fluid packing nut is too tight, and if the wrong size needle is being used.

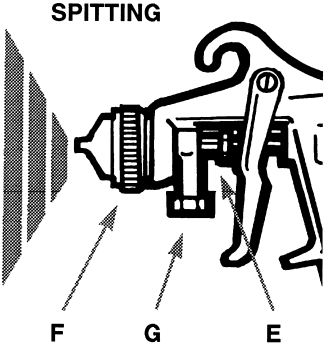


Fig. 12. Spitting, caused by air bubbles in the fluid supply, can be remedied by securing all fittings and connections. Loosen nut (E) and place two drops of machine oil on the packing. Replace the nut and finger-tighten. In aggravated cases, replace the packing. Remove the air and fluid nozzles (F) and clean the back of the fluid nozzle and nozzle seat in the gun body using a rag soaked with thinner. Replace and tighten fluid nozzle with the wrench supplied with the gun. Replace the air nozzle. Tighten or replace swivel nut (G).

FAULTY PATTERNS AND HOW TO CORRECT THEM

Dried material in a side port of a spray nozzle restricts passage of air through the port on one side resulting in full air pressure coming from the clean side of the part in a "C" or fan pattern in the direction of the clogged side (see Fig. 9). This situation can be remedied by dissolving the material with thinner. Do not use metal devices to probe into the air nozzle openings.

Dried material also gets stuck around the outside of the fluid nozzle tip restricting passage of atomized air to a point at the center of the air nozzle opening causing an inverted tear-drop-shaped spray pattern (see Fig. 10). This faulty pattern can also be caused by a loose air nozzle, or a bent fluid nozzle or needle tip. If dried material is causing the trouble, remove the air nozzle and wipe off the fluid tip using a rag soaked with thinner. Tighten the air nozzle and replace the fluid nozzle and/or the needle, if it is bent.

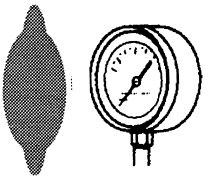


Fig. 13. Fan spray pattern caused by low atomizing air pressure or too much spray material being fed through the gun. To correct the problem, increase air pressure from air supply.

A split spray pattern — heavy on each end of a fan pattern and weak in the middle — is usually caused by (1) too much atomizing air pressure; (2) attempt-

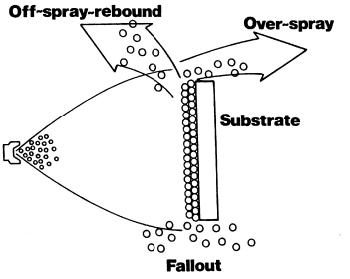


Fig. 14. Improper spraying creates paint losses in the form of overspray, rebound, and fallout.

ing to get too wide a spray with thin material; or (3) too little spray material available to pump through the spray apparatus. This situation can be remedied by (1) reducing the air pressure; (2) opening the fluid control knob to the full position; and (3) turning the spray pattern control down to narrow the spray pattern width. This reduces the width of spray but will correct the split pattern (see Fig. 11). Spitting is caused by air entering the fluid supply, and by dried or missing packing around the material needle valve that permits air to get into the fluid passageway. Dirt between the fluid nozzle seat and body, or a loosely installed fluid nozzle, can also contribute to the problem, as well as a loose or defective swivel nut, siphon cup, or material hose. To stop the spitting, be sure all fittings and connections are tight.

A fan spray pattern that is heavy in the middle, or a pattern that has an unatomized (salt-and-pepper) effect, indicates that the atomizing air pressure is not sufficiently high or that there is too much material being fed to the gun. This problem can be solved by increasing the pressure from the air supply. Correct air pressures are discussed elsewhere in this article.

ELECTROSTATIC SPRAY PROCESSES

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PRINCIPLES OF ELECTROSTATICS

Electrostatic Theory

Electrostatic finishing got its start in the early 1950s. Coatings engineers needed an application method that would significantly increase transfer efficiency and reduce finishing costs. They reasoned that particles and objects with like charges repel each other, and objects with unlike charges attract each other. The same would apply to charged spray coatings and a part to be painted. They discovered that by negatively charging the atomized paint particles and positively charging the workpiece to be coated (or making it a neutral ground), an electrostatic field would be created that would pull paint particles to the workpiece. (See Fig.1.)

With a typical electrostatic spray gun, a charging electrode is located at the tip of the atomizer. The electrode receives an electrical charge from a power supply. The paint is atomized as it exits past the electrode, and the paint particles become ionized (pick up additional electrons to become negatively charged)

An electrostatic field is created between the electrode and the grounded workpiece. The negatively charged paint particles are attracted to the neutral ground. As the particles deposit on the work piece, the charge dissipates and returns to the power supply through the ground, thus completing the electrical circuit. This process accounts for the high transfer efficiency. Most of the atomized coating will end up on the part.

The degree to which electrostatic force influences the path of paint particles depends on how big they are, how fast they move, and other forces within the spray booth such as gravity and air currents. Large particles sprayed at high speeds have great momentum, reducing the influence of the electrostatic force. A particle's directional force inertia can be greater than the electrostatic field. Increased particle momentum can be advantageous when painting a complicated surface, because the momentum can overcome the Faraday cage effect — the tendency for charged paint particles to deposit only around the entrance of a cavity. (See Fig. 2.)

On the other hand, small paint particles sprayed at low velocities have low momentum, allowing the electrostatic force to take over and attract the paint onto the workpiece. This condition is acceptable for simple surfaces but is highly susceptible to Faraday cage problems. An electrostatic system should balance paint particle velocity and electrostatic voltage to optimize coating transfer efficiency.

Electrostatic Advantages

The main benefit offered by an electrostatic painting system is transfer efficiency. In certain applications electrostatic bells can achieve a high transfer efficiency exceeding 90%. This high efficiency translates into significant cost savings due to reduced overspray. A phenomenon of electrostatic finishing known as "wrap" causes some paint particles that go past this workpiece to be attracted to the back of the piece, further increasing transfer efficiency.

Increased transfer efficiency also reduces VOC emissions and lowers hazardous waste disposal costs. Spray booth cleanup and maintenance are reduced.

Coating Application

Any material that can be atomized can accept an electrostatic charge. Low-, medium-

, and high-solids solvent borne coatings, enamels,lacquers, and two-component coatings can be applied electrostatically.

The various types of electrostatic systems can apply coatings regardless of their conductivity. Waterborne and metallic coatings can be highly conductive. Solvent-borne coatings tend to be nonconductive. Any metallic coatings can contain conductive metal particles. These metallic coatings must be kept in circulation to prevent a short circuit in the feed line. As high voltage is introduced into the system, the metal particles can line up to form a conductive path.System modifications may be required because of coating conductivity to prevent the charge from shorting to ground. (See Fig. 3.)

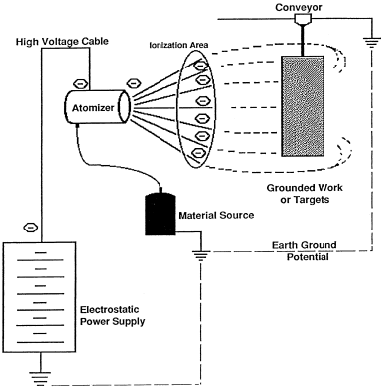


Fig. 1. Electrostatic application circuit for solvent-based coatings

Operating Electrostatics Safely

Electrostatic finishing is safe if the equipment is maintained properly and safety procedures are followed. All items in the work area must be grounded, including the spray booth, conveyor, parts hangers, application equipment (unless using conductive/waterborne coatings), and the spray operator.

As electrical charges come in contact with ungrounded components, the charges can be absorbed and stored. This is known as a capacitive charge buildup. Eventually, enough charge is built up so that when the ungrounded item comes within sparking distance of a ground, it cand is charge as a spark. Such a spark may have enough energy to ignite the flammable vapors and mists that are present in the spray area.

An ungrounded worker will not know that the capacitive charge has been absorbed until it is too late. Workers should never wear rubber- or cork-soled shoes, which can turn then into ungrounded capacitors. Special shoe-grounding devices are available. If workers are using hand-held guns, they should grasp them with bare hands or with gloves with cut-outs for fingertips and palms that allow adequate skin contact.

Proper grounding of all equipment that is not used for the high-voltage process is essential. Grounding straps should be attached to equipment and connected to a known ground. A quick inspection of all equipment, including conveyors and part hangers, can reveal improper grounding.

Good housekeeping can pay dividends. Removing paint buildup from parts hangers can help ensure that workpieces are grounded. Ungrounded objects, such as tools and containers, should be removed from the finishing area.

PAINT PARTICLE CHARGING

Electrostatic charging of paint particle got its start back in the early 1950s. Engineers were looking for methods to reduce the cost of finishing products. Harold Ransburg, the inventor of the electrostatic process, reasoned that since unlike electrical charges are attracted to each other, the same idea would apply to charged paint particles and a part to be painted.

Everyone's heard the saying that "opposites attract, and likes repel." This is true with both a magnetic field and with the electrostatic process of charging paint particles.

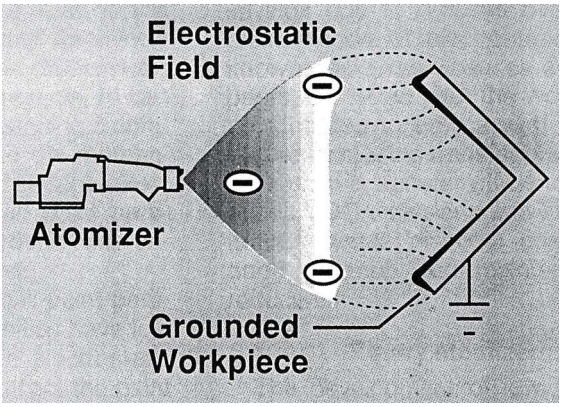


Fig. 2. Faraday cage effect

The electrostatic process is almost identical to the way a common magnet works. By creating an electrostatic field between a negatively charged paint particle and a positive grounded workpiece, the paint particles are attracted and deposit themselves onto the workpiece. The basic building block of electrical energy is the charged particle. All matter is made from electrically charged particles. These particles are either neutral, negative, or positive.

Back in the early days of particle charging, a process referred to as the Number One Process was developed by Harold Ransburg to charge paint particles. Paint particles were sprayed into an electrostatic field by conventional air spray guns. Two wire grids were aligned parallel to each other at a certain distance, then the parts were conveyed through these grids. At one end of the grids, atomized paint particles were sprayed into the electrostatic field. The paint particles would become negatively charged and would be attracted to the positively grounded parts.

These wire grids are now the wire electrode in an electrostatic spray gun. The three most common ways of charging paint particles are the electrostatic spray gun, a rotary bell, or a rotary disk.

All three of these methods work by the same common principle of the electrostatic field between the atomizer and the workpiece then introduce atomized paint particles into the field and they will be attracted to and deposit themselves on the positive grounded workpiece.

With an air spray or an HVLP electrostatic spray gun, a high voltage DC charge is supplied to the applicator's nozzle electrode, creating an electrostatic field between the gun and the grounded target object. (See Fig. 4.) The coating materials are charged at the point of atomization. The charged paint particles are attracted to and deposited on the grounded target object. This electrostatic charge allows a more efficient, uniform application of the coating material to the front, edges, sides, and back of the product. The electrostatic forces allow for a high percentage of the charged paint particles to be deposited on the workpiece.

The electrostatic process can also be used to charge paint particles using airless and air-assisted airless electrostatic spray guns. The only difference is the coating material is atomized by different methods. An air spray or HVLP electrostatic gun utilizes much lower air pressure to atomize the coating material, the airless and air-assisted airless methods use a much higher pressure. Coating material is delivered at high pressure to the atomizer. There, the material is atomized by passing through a very small orifice under high pressure. The resulting spray mist particles then become electrostatically charged and are attracted to the workpiece in the same manner as electrostatic air spray or electrostatic HVLP.

Today, rotary bells are generally about 1 to 3 in. in diameter and rotary disks are about 6 to 12 in. These atomizers operate on the same principle except they are po-

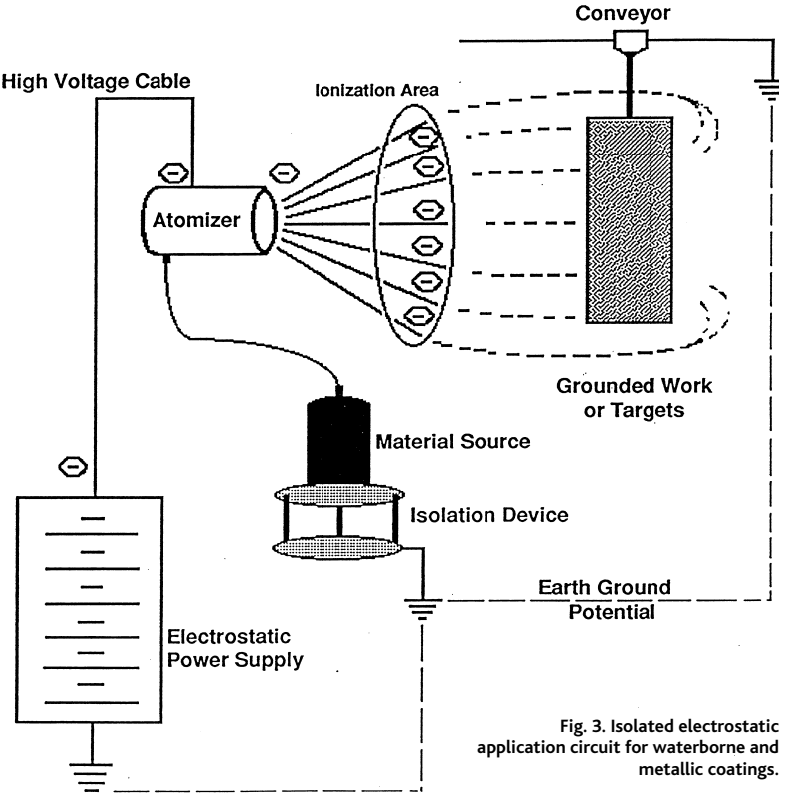


Fig. 3. Isolated electrostatic application circuit for waterborne and metallic coatings.

sitioned differently to the workpiece.Bells are positioned with their axis horizontal to the part, and disks are positioned vertically.

A rotating disk or bell distributes a thin, even coating to the edge of the atomizer. There the coating is atomized either by the electrostatic force or centrifugal force. A low speed rotary atomizer utilizes almost all electrostatic forces, a high speed rotary atomizer relies on the centrifugal force of the atomizer to atomize the coating material. A DC high voltage charge is then supplied to the rotating atomizer, creating an electrostatic field between it and the grounded target object. The negatively charged paint particles are attracted to and deposited on the positive grounded workpiece. The forces between the charged particles and the grounded target are sufficient to turn normal overspray around and deposit it on the back surface of the target; therefore, a very high percentage of the paint particles are deposited on the part.

Paint resistivity, often referred to as conductivity, is critical when spraying materials electrostatically. Waterborne materials are very conductive; therefore, measures such as voltage blocking devices,external charging probes, or completely isolating the fluid supply and fluid lines must be taken or the paint particles will not be able to maintain the electrostatic charge. Due to the low resistance of waterborne materials, all of the electrostatic voltage will drain off to ground and short out the system. If one of the three previous methods mentioned are not used, the paint particles can-

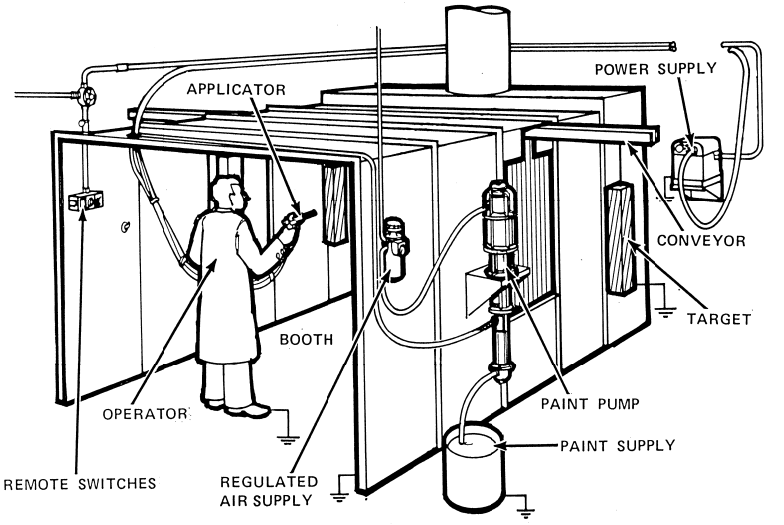


Fig. 4. Typical electrostatic hand gun application.

not be charged electrostatically.

Solvent-borne materials paint resistivity will vary from one material to another. When spraying solvent-borne coatings with electrostatics,it is critical to measure and monitor the resistivity of the paint being sprayed. Materials that are too conductive, (very low resistance,often referred as "hot") will also drain some or all of the electrostatic voltage off to ground. This will greatly reduce the electrostatic effects on the paint particle. On the other hand, when using materials with a very high resistance, often referred to as "dead," the paint particles will not readily accept the electrostatic charge and the transfer efficiency will be very poor.

Coating suppliers can easily formulate their solvent-borne materials tobe within a specific resistivity range. The optimum resistivity may differ depending on the tool used for application. For example, with an electrostatic disk or bell, the optimum resistivity range is between 0.05 and 1 megohms on a (Ransburg) paint resistivity meter. An electrostatic spray gun however, can effectively spray coating materials between 0.1 to 00 megohms of resistance.

Another example is the No. 2 Process on-site electrostatic spray gun.This gun requires a more precise paint resistivity because it relies solely on the electrostatic charge to atomize the coating materials. The paint used with this gun must read between 0.1 to 1 megohms on the (Ransburg) paint test meter to work properly.

Another key element in the electrostatic process or charging of paint particles is particle size. Large particles sprayed at high speed have greater momentum and reduce the influence of the electrostatic force.Increased particle size and momentum can be an advantage when coating complicated surfaces because the momentum can overcome the Faraday cage areas (where paint particles are attracted to the edges of a work piece while avoiding inside corners and recessed areas).

On the other hand, small paint particles sprayed at low velocities have low momentum, thus allowing the electrostatic force to take over and attract the coating material to the target object. This condition is acceptable for simple surfaces but is highly susceptible to Faraday cage problems.

ELECTROSTATIC PROCESSES/EQUIPMENT

The electrostatic application of atomized materials was developed to enhance finish quality and improve transfer efficiency. (See Fig.5.)

Presently, there are seven types of electrostatic processes for spray application:

Electrostatic air spray atomization

Electrostatic high-volume, low-pressure (HVLP) atomization

Electrostatic airless atomization

Electrostatic air-assisted airless atomization

Electrostatic electrical atomization

Electrostatic rotary-type bell atomization

Electrostatic rotary-type disk atomization

Regardless of the electrostatic finishing systems, each has its advantages and limitations. What may be suitable for one situation may not be suitable in another. (See Table I.)

Electrostatic Air Spray Atomization

Electrostatic air spray uses an air cap with small precision openings that allows compressed air to be directed into the paint for optimum atomization. Electrostatic air spray is the most widely used type of atomization in the industry today due to its control and versatility. Electrostatic air spray provides very high transfer efficiency by utilizing the electrostatic charge to wrap paint around edges and capture overspray that would have been unusable waste. Standard electrostatic air spray provides transfer efficiencies in the 40 to 90% range depending on the type of material and application.

Electrostatic HVLP Spray Atomization

Electrostatic HVLP spray utilizes the same atomization characteristics as electrostatic air spray technology with slight modifications. When using air HVLP, the pressure of the compressed air at the air cap must be reduced to a range of 0.1 to 10 psi. Transfer efficiency is greater when using HVLP spray to lower the particle velocity and atomize the material thus causing less waste and blow-by of material. Some electrostatic equipment can be easily converted or transformed between air spray and HVLP spray technology by simply changing four parts. HVLP spray technology helps meet stringent EPA codes requiring reduced VOCs and waste. Electrostatic HVLP spray provides transfer efficiencies in the 60 to 90% range depending on the type of material and application.

Electrostatic Airless Spray Atomization

Electrostatic airless spray technology utilizes the principle of fluid at high pressures (500-5,000 psi) atomizing through a very small fluid nozzle orifice. Size and shape of the spray pattern along with fluid quality is controlled by the nozzle orifice. Airless spray technology evolved after air spray to aid in faster application rates using higher delivery and heavier viscosities on larger parts.

Electrostatic Air-Assisted Airless Atomization

Electrostatic air-assisted airless spray technology uses the airless spray principle to atomize the fluid at reduced fluid pressure with assisted atomizing air to aid in reducing pattern tailing and affect pattern shape. Air-assisted airless spray technology offers some of the desirable characteristics of both airless spray and air spray. The desirable characteristics being medium to high delivery rates, ability to spray heavy viscosities at low velocities, and high transfer efficiency.

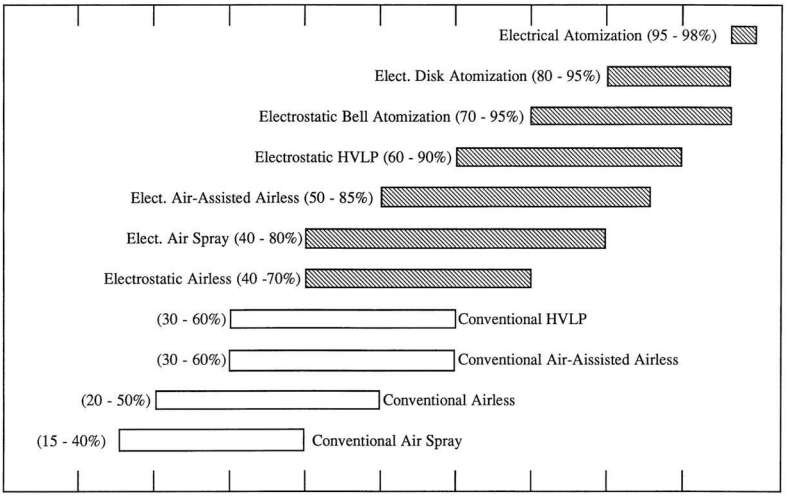


Fig. 5. Typical transefer efficiencies for various electrostatic and conventional spray processes.

Electrostatic Electrical Atomization

Electrostatic electrical atomization is accomplished by using a rotary bell on the end of a gun to evenly dispense paint to the edge of the bell. Once the coating material reaches the edge of the bell it is introduced to an electrical charge. The electrical charge at the sharp edge (approximately 100 kV) causes paint of a medium electrical resistance range (0.1 to 1 megohms) to disperse onto the product. The pure electrical application is a slightly slower process than an air spray or air-assisted airless technology and requires a rotational type spray paint technique, due to the bells spray pattern, but is the most transfer efficient spray gun process in the industry today. The ultrasoft forward velocity of the spray pattern achieves transfer efficiencies of nearly 100% on most products. This high transfer efficiency spawned the industry of painting and refurbishing machinery and furniture in place.

Electrostatic Rotary-Bell-Type Atomization

An electrostatic bell atomizer is a high-speed rotary bell that uses centrifugal force as well as electrical atomization to atomize material and efficiently transfer material from the bell edge to the target being painted. (See Fig. 6.) The bell is used on a turbine motor where the pattern is carefully directed by the use of compressed air,introduced to the pattern at the edge of the bell cup. The compressed air gives the material forward velocity to aid in penetrating recessed areas. The bells are usually mounted stationary or reciprocated to coat products on straight line conveyors. The bells may also be positioned on both sides of the conveyor. Rotary-bell-type atomization provides transfer efficiencies in the 70 to 95% range.

Electrostatic Rotary-Disk-Type Atomization

An electrostatic rotary-disk atomizer is a high-speed flat rotary atomizer that uses centrifugal force along with electrical atomization to atomize coating material and efficiently transfer the material from the disk edge to the target being painted. The disk is used in an enclosed omega shape loop (see Fig. 7) to coat the product. Disks may be mounted stationary and tilted (up to 45°) to coat small parts of 12 in. or

less, or mounted on reciprocating arms to coat parts up to 40 ft. in height but generally no wider than 4 ft.in width. The disk produces transfer efficiencies in the 80 to 95% range.

WATERBORNE ELECTROSTATICS

Over the last several years, government regulations on VOC emissions coming from paint application facilities, have fueled the need for coating manufacturers to reduce the amount of VOC from their coating materials. Waterborne coatings have been around for many years,but due to tougher government regulations they are rapidly gaining more and more momentum in today's finishing industry. Many of current users of solvent borne coatings will be forced to make the switch to a more compliant coating in the future. And many of these manufacturers, in an effort to utilize as much of their existing finishing equipment possible, will make the move to waterborne coatings.

Although the application of these waterborne coatings is basically the same as with solvent borne coatings, many factors must be taken into consideration. Are my system's components compatible with waterborne materials? Many alloys and metals will rust and corrode over time when coming in contact with waterborne materials; therefore, you must ensure that all components such as pumps, valves, piping and the atomizer itself are constructed of materials compatible with waterborne coatings such as 316 stainless steel or Teflon.

A decision must be made as to how the system will be isolated from high voltage grounding out back through the to waterborne fluid supply. Water is a good conductor of electricity, and all components that come in contact with the waterborne material will be at high voltage. This includes all atomizers, fluid supply hoses, pumps, regulators, valves,and the fluid supply itself.

In today's finishing environment waterborne materials must be safely isolated. This is accomplished by: (1) complete system isolation; (2) voltage blocking device; or (3) indirect charging of the coating material.

Complete System Isolation

Complete system isolation is the most commonly used method of isolating high voltage from the waterborne fluid supply. This low-tech approach has been around for decades. (See Fig. 3.)

In an isolated system, any components that come in contact with the waterborne material must be kept isolated from any possible grounds.The fluid supply must be enclosed in a caged area with the supply bucket, drum, or tote on an isolation stand. The gates to these cages must be equipped with safety interlocks. When an operator opens the gate to enter the cage, a pneumatically operated ground rod must shortt he systems' high voltage to ground. This ensures that the operator will not come in contact with a charged waterborne fluid supply. In addition, one of the isolation stand's legs should have a 1,050 megohm bleed resistor installed inside it and attached to earth ground so that when the high voltage is turned off the voltage can bleed off to ground in a timely manner.

Despite the fact that these properly confirmed waterborne systems may have safety interlocks and bleed resistors, *never assume* that all of the high voltage has been discharged to ground. Before approaching any of the wetted systems components, always take a secondary ground wire and touch it to all system components to make sure that the system is fully discharged. Failure to do so could result in a painful shock to the operator.

Failure to keep the entire system properly isolated from ground can result in a shorting condition. This can potentially short some or all of the high voltage to

Table I. Advantages and Characteristics of Electrostatic Spray Processes

Process	*Advantages & Characteristics*
Electrostatic Air Spray	Complete pattern control Finest atomization Higher TE than non-electrostatic Can be used with all materials (2k, waterborne, high solids) Fast application Excellent finish quality (Class A)
Electrostatic HVLP Spray	Complete pattern control Good atomization Higher TE than air spray Fast application Used with all materials (2k, waterborne, high solids)
Electrostatic Airless Spray	Good atomization Very high TE (due to electrostatic wrap) Very fast application Larger pattern/high delivery
Electrostatic Air-Assisted Airless Spray	Good atomization Very high TE Very fast application
Electrostatic Electrical Atomization	Excellent finishing quality Highest TE of any electrostatic gun (no overspray)
Electrostatic Rotary Bell Atomization	Excellent finish quality Excellent atomization Very high TE Used with all materials (2k, waterborne, high solids) Automatic application
Electrostatic Rotary Disk Atomization	Excellent finishing quality Excellent atomization Very high TE Used with all material (2k, water, high solids) Very fast application Automatic application

TE = transfer efficiency.

ground. This can greatly reduce the electrostatic affect which can lead to poor transfer efficiency. Example: A fluid supply hose, of a fluid supply container too close to ground, can short the system out completely or create a high load (high microamp reading) on the power supply which in turn lowers the actual voltage at your applicator. This can significantly reduce transfer efficiency.

In addition to keeping all the equipment isolated, the cages (fluid supply) must be kept relatively close to the application equipment.This can result in a significant amount of lost floor space. In many occasions, the amount of floor space it takes to enclose the fluid supply may not be available. In many installations, floor space is extremely valuable and cannot be afforded when lost.

External Charging (Indirect Charging of Material)

External charging of waterborne coatings allows the fluid supply to remain grounded. The fluid supply area can remain the same as it was configured for a solvent based coating. Since the paint particles are charged externally, or as some say "indirect," the high voltage does not follow the conductive path through the fluid lines back to ground.

The indirect charge of the material is accomplished by placing a probe, which is at high voltage, a few inches away from the gun electrode.This probe creates the electrostatic field to charge the paint particles without coming in direct contact with the waterborne material. Thus, the high voltage does not follow the conductive path back through the fluid lines.

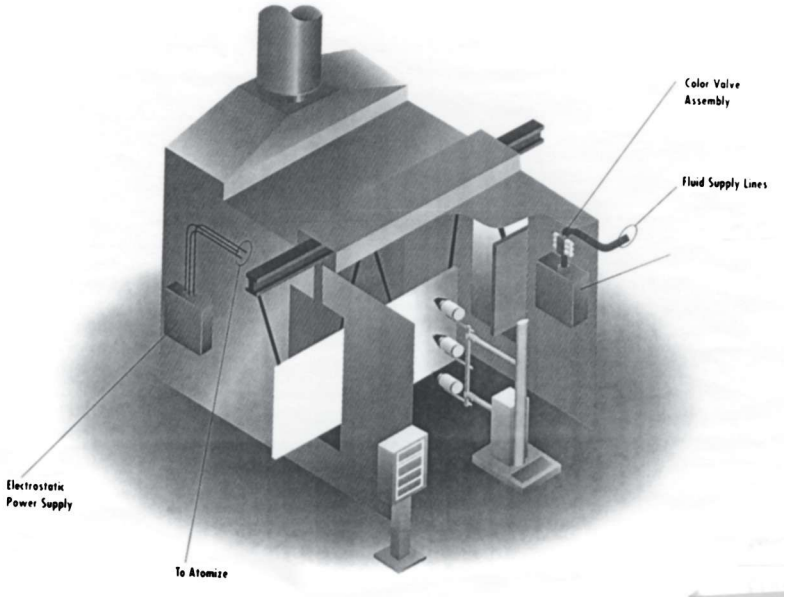


Fig. 7. Typical bell-type installation.

With automatic applicators such a rotary atomizers, a ring of probes (6-8) is placed around the applicator a few inches back and away from the rotary bell. This configuration is often referred to as a "Copes" ring. Many U.S. automotive assembly plants have switched to waterborne basecoats and the Copes bells have become widely accepted in the automotive market. Utilizing Copes technology, color changes in the ten-second range can still be achieved.

Unfortunately, of the three common methods of spraying waterbornes electrostatically, the external or indirect charging method is the least efficient. Voltage blocks and isolated systems have been proven to provide higher transfer efficiencies.

Voltage Blocks

In recent years, the application of waterborne coatings has become simpler and safer with the development of voltage blocking devices.

Voltage blocking devices isolate the spray applicators from the grounded fluid supply. This prevents the high voltage from following the conductive path through the fluid lines back to the ground fluid supply and grounding (shorting) out the system high voltage.

These devices can be used to feed both manual and automatic spray applicators. In a handgun situation, only one applicator can be fed from a single voltage blocking device. Where as with an automatic applicator the voltage blocking device can feed multiple applications.This is due to the fact that any and all applicators will be charged back through their fluid lines when connected to one blocking device.

Voltage blocking devices eliminate the need for safety cages and interlocks and protect the operator from coming in contact with a charged fluid supply. This eliminates the need for isolation stands and the isolation of the fluid supply from ground. It is now a grounded fluid supply. This can lead to a significant amount of savings in floor space.

Summary

Of the three methods discussed for spraying waterbornes electrostatically all have their advantages and disadvantages. The end user must decide as to which method is best suited for their application. Voltage blocks are the simplest and can be used with any type of fluid supply, but up front cash can sometimes be a factor in the mind of the decision maker.

Isolated systems can be cheaper on most occasions, but can also take up a lot of valuable floor space. Isolated systems are also the least safe and may be impractical when your fluid supply is a remote paint kitchen.

Although indirect charging may be the least efficient of the three methods discussed, it may be the most practical in some applications. For example, in automotive assembly plants where a large paint kitchen is involved or extremely fast color changes are necessary. Voltage blocks and isolated systems have been proven to provide higher transfer efficiencies.

ELECTROSTATIC PROCESS FOR PLASTICS & OTHER NONCONDUCTIVE SUBSTRATES

The ideal application for the use of electrostatics is metal because the only thing that needs to be done to spray electrostatically is to connect a ground wire to the product; however, when you try to electrostatically spray a nonconductive substrate, such as plastics, it must be made conductive. There are several ways of making the part being coated or the application conductive. The most common of these being:

1. Build a bracket of grounded metal and place the nonconductive part between the applicator and the conductive fixture.(The charged particles will see the ground and be drawn to the part being coated. Examples for utilizing this method of technology would be the coating of fabrics, paper or other thin structures.)

2. Certain materials become conductive with heat. Materials such as glass, rubber products, and some plastics may be heated until they are conductive and electrostatically sprayed while warm.

3. All nonconductors, such as wood, rubber, plastic and glass, may also be treated with chemical sensitizers. These are generally hydroscopic chemicals that attract moisture onto the surface of the product to create conductivity. Controlled concentrates of the sensitizer may be applied by dipping, wiping, spraying or a mist chamber. After treatment, the part becomes conductive when exposed to adequate humidity such as a humidity chamber or high ambient humidity (70% relative humidity). Sensitizers are non film-forming liquids.

4. Another method of making the part conductive is by using a conductive primer. The conductive primer can be applied to the substrate by conventional means, thus allowing the top coat to be applied electrostatically. Conductive primers may be sprayed, dip coated, flow coated, or molded in.

The reason for making nonconductive parts more acceptable to an electrostatic charge is to utilize the most efficient process with the highest quality finish at the most minimal cost. By utilizing the electrostatic process, you will achieve each of these benefits.

COST SAVINGS

Transfer Efficiency/Paint Savings

The cost savings associated with the use of electrostatic equipment can be realized in many different areas. The most obvious savings is in paint usage. With the increase of high-solids,plural-component, and base/clear finishes, it is not unrealistic to pay

Table II. Payback in Dollars per Year (225 Working Days)

Paint Usage (gal/day)	*Transfer Efficiency Improvement*				
	4.00%	*8.00%*	*12.00%*	*16.00%*	*20.00%*
5	675	1,350	2,025	2,700	3,375
10	1,350	2,700	4,050	5,400	6,750
15	2,025	4,050	6,075	8,100	10,125
20	2,700	5,400	8,100	10,800	13,500
25	3,375	6,750	10,125	13,500	16,875
30	4,050	8,100	12,150	16,200	20,250
35	4,725	9,450	14,175	18,900	23,625
40	5,400	10,800	16,200	21,600	27,000
45	6,075	12,150	18,225	24,300	30,375
50	6,750	13,500	20,250	27,000	33,750
100	13,500	27,000	40,500	54,000	67,500
150	20,250	40,500	60,750	81,000	101,250
200	27,000	54,000	81,000	108,000	135,000
250	33,750	67,500	101,250	135,000	168,750
300	40,500	81,000	121,500	162,000	202,500
350	47,250	94,500	141,750	189,000	236,250
400	54,000	108,000	162,000	216,000	270,000
450	60,750	121,500	182,250	243,000	303,750
500	67,500	135,000	202,500	270,000	337,500
550	74,250	148,500	222,750	297,000	371,250
600	81,000	162,000	243,000	324,000	405,000
650	87,750	175,500	263,500	351,000	438,750
700	94,500	189,000	283,500	378,000	472,500
750	101,250	202,500	303,750	405,000	506,250
800	108,000	216,000	324,000	432,000	540,000
850	114,750	229,500	344,250	459,000	573,750
900	121,500	243,000	364,500	486,000	607,500
950	128,250	256,500	384,750	513,000	641,250
1,000	135,000	270,000	405,000	540,000	675,000

Cost of paint: $15/gal.

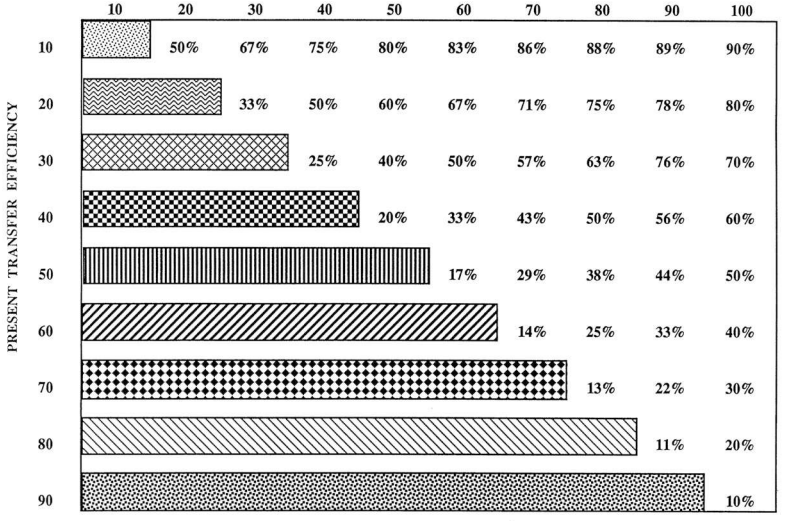


Fig. 8. Emission reduction from installation of new equipment.

Table III. Maintenance Costs Estimated in Dollars

Approximate Paint Usage		*Waterwash Chemical Usage*		*Waterwash Sludge Removal*		*Dry Filter Disposal Cost*		*Dry Filter Usage*	
Gal/ day	*Gal/ day*	*TE (65%)*	*TE (75%)*	*TE (65%)*	*TE (75%)*	*TE (65%)*	*TE (75%)*	*TE (65%)*	*TE (75%)*
5	1,250	104	64	295	183	1,023	632	307	190
10	2,500	208	129	591	366	2,045	1,265	614	380
15	3,750	312	193	886	548	3,068	1,897	920	570
20	5,000	416	257	1,181	731	4,091	2,530	1,227	760
25	6,250	521	322	1,477	914	5,113	3,162	1,534	950
30	7,500	625	386	1,772	1,097	6,136	3,795	1,841	1,140
35	8,750	729	450	2,067	1,280	7,159	4,427	2,148	1,330
40	10,000	833	515	2,362	1,463	8,181	5,060	2,454	1,519
45	11,250	937	579	2,658	1,645	9,204	5,692	2,761	1,709
50	12,500	1,041	644	2,953	1,828	10,227	6,325	3,068	1,899
55	13,750	1,145	708	3,248	2,011	11,249	6,957	3,375	2,089
60	15,000	1,249	772	3,544	2,194	12,272	7,590	3,682	2,279
65	16,250	1,353	837	3,839	2,377	13,294	8,222	3,988	2,469
70	17,500	1,457	901	4,134	2,559	14,317	8,855	4,295	2,659
75	18,750	1,562	965	4,430	2,742	15,340	9,487	4,602	2,849
80	20,000	1,666	1,030	4,725	2,925	16,362	10,120	4,909	3,039
85	21,250	1,770	1,094	5,020	3,108	17,385	10,752	5,216	3,229
90	22,500	1,874	1,158	5,315	3,291	18,408	11,385	5,522	3,419
95	23,750	1,978	1,223	5,611	3,473	19,430	12,017	5,829	3,609
100	25,000	2,082	1,287	5,906	3,656	20,453	12,650	6,136	3,799
	Note: 250 days/yr	Note: 1 oz/lb of overspray Estimated $1.41/lb of chemical		Note: 400 lb/drum $100.00/ disposal drum		Note: 60 filters/drum $200.00/ drum of filters		Note: $1.00/filter	

TE = transfer efficiency.

$100 per gallon for these coatings. Considering this cost, it is crucial that the coating is applied to the product as efficiently as possible. With a conventional air spray gun, roughly 15 to 40% of the paint sprayed from the gun is applied on the part. This is known as transfer efficiency. The remaining 60 to 85% is lost in the filters or left as overspray on the floor and walls. Conventional HVLP guns are more efficient than conventional air spray guns. HVLP guns will typically yield transfer efficiencies of 30-60%.

Electrostatic guns can obtain even greater transfer efficiency. An electrostatic air spray gun is normally in the 40 to 80% transfer efficiency range. This means you can coat twice as many parts with an electrostatic air spray gun, compared to a nonelectrostatic air spray gun given the same quantity of paint. As with nonelectrostatic guns, HVLP technology shows significant improvement in transfer efficiency.The same holds true with electrostatic HVLP technology as well. In some cases, electrostatic HVLP has obtained efficiencies as high as 90%.

Typically, cost justification is obtained from paint cost savings alone. Its typically enough to cost justify the purchase of the electrostatic applicator. Table II displays the dollar figure in paint savings that can be achieved by slightly increasing transfer efficiency.

VOC Reduction

Another savings area is emission reduction. With federal and local regulations becoming tougher by the day, VOC (volatile organic compound) emissions has become a major issue. We are constantly trying o reduce the amount of VOCs emitted into the atmosphere. By increasing transfer efficiency you lower VOC emission. (See Fig. 8.) This is a result of more paint being applied on the part and less paint being deposited into the booth filters or atmosphere.

Many states, such as California, now mandate that you use either HVL Por electrostatic technology to qualify for a permit to install a new spray booth. A manufacturing facility is permitted to emit a specified amount of VOCs (in tons) per year. If the tonnage limit is exceeded, strict fines are enforced. These fines can easily exceed thousands of dollars. As a result of these laws many companies have invested in electrostatic finishing equipment to comply with VOC regulation.

Decreased Maintenance Costs

As stated earlier, when transfer efficiency increases, the amount of overspray deposited into the spray booth decreases. This means spray booths that previously required weekly cleanings and filter changes may now require biweekly maintenance. Water-wash booths that previously consumed 55 gallons of chemicals in one month may now use only 30 gallons. Not only is the cost to purchase these materials reduced, but the cost to dispose of them is decreased as well. Dirty booth filters and contaminated booth water must typically be disposed of as hazardous waste.

In recent years, the cost associated with the disposal of hazardous waste has sky rocketed. Not only is there a direct cost reduction, such as filters, chemicals and disposal (see Table III), there is also an indirect savings in labor cost, due to the fact that booth maintenance can easily consume on an average up to 8 man-hours per week.

Better Coverage/Improved Quality

Electrostatic finishing has many other benefits in addition to cost savings. Application time may be reduced with the aid of electrostatic wrap. Electrically charged paint particles can change direction and be deposited on the top, bottom, and sides of the part when sprayed from one direction. Depending on part size and configuration this wrap-around may sufficiently coat all of the product at once, eliminating the need for additional passes.

When using a nonelectrostatic gun you must point the gun at every area that requires paint, if you miss a particular angle it will not be painted. With electrostatic applicators, the wrap-around may coat these areas producing a more uniform finished product. As a result of a more uniform finish, many manufacturing facilities have experienced a lower reject rate in their production.

In the case of on-site furniture refinishers or appliance refurbishers,it would be virtually impossible to paint without electrostatic finishing equipment.

CONVERTING TO WATERBORNES

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Just as government regulations concerning gasoline mileage in the '70s helped spur today's improved automobile engines, so government regulations concerning VOC emissions from coating lines have spurred the development of some remarkable waterborne and water-based coating materials. Now manufacturers need to know how to convert their operations to use these new materials efficiently. This means that they need to know what application equipment is suitable and how best to use it to apply waterbornes.

A likely first question is "What is the best way to apply a waterborne material?" The answer is "There is no best way." The process that works best in a particular application with a solvent-based coating will usually continue to be the best after converting the application to a waterborne coating. The dynamics of getting material from the applicator to the part are similar whether the material contains mostly solvents or mostly water.

ATOMIZER SELECTION

Most coating material applicators break the material up into fine droplets or particles, which are then carried through the air to the part being coated. The process of breaking up the material is called atomization, and the equipment that does the atomization is called an atomizer. Typical atomizers are air spray guns, rotary atomizers, and disks. None of these is "best" for all waterborne applications. Instead, the shape of the part being coated, the coverage required, and the production rate determine the best atomizer for a particular application using waterbornes, just as they do with solvent-based materials.

To illustrate the importance of part configuration on atomizer selection, consider a simple box-like part, open on one end, requiring paint on both the inside and outside surfaces. The outside of the box might best be painted with a soft spray using electrostatics to get good part coverage, high transfer efficiency (TE), and good wrap. A rotary atomizer with electrostatics would be a good choice for the outside of the box.

The rotary atomizer and electrostatics would be a poor choice, however, for the inside of the same box because the Faraday cage effect caused by the electrostatics and the walls of the box would actually keep most of the paint out of the box. A better choice for the inside of the box would be an airless spray atomizer. Airless spray uses the momentum of the paint particles to get the paint to the part, rather than electrostatic attraction.

The point is that a manufacturer who has spent a lot of time perfecting the coating application process for solvent-based material should stick with that process when converting to waterbornes, if the latest technology and good equipment are already in place and good TE is being obtained.

Sometimes a particular waterborne coating formulation may need to be modified slightly to accommodate the atomizer. For example, an emulsion may tend to separate when subjected to severe centrifugal force on a spinning rotary atomizer cup.

Does this mean that you don't have to change anything in order to convert to waterbornes? No, it doesn't. Even though the basic application process may not change, some of the specific pieces of equipment used for that process may not be suitable for waterborne materials. Metal parts may corrode. Seals may swell or leak.

CONSTRUCTION MATERIALS

Waterbornes rust plain steel and in some cases attack aluminum. Even stainless steel parts can be damaged by some formulations. For example, 400 series stainless steel can dissolve over time in contact with a highly acidic formulation. On the other hand, parts made from 316 stainless steel hold up well with most waterbornes.

This means that at least some of the application equipment will need to be replaced when a system is converted to waterbornes. Piston pumps made of plain or alloy steel have to be replaced with pumps made of stainless steel. Pipes and distribution systems need to be made of corrosion-resistant materials such as stainless steel. Atomizers should contain only stainless steel or plastic wetted parts. Parts made from aluminum will perform satisfactorily for some waterborne materials, but will corrode quickly in contact with others. Some waterborne formulations can even become "explosive" in contact with aluminum.

Seals in atomizers and pumps need to be changed if they are not compatible with the waterborne material. There is no single best seal material for waterbornes because the formulations vary so much. In some cases, the seals in equipment used for solvent-based coating materials are also suitable for waterbornes. For example, Buna-N is suitable for some solvent-based paints and is also a good choice for many waterbornes.

One caution about reusing equipment from a solvent-based coating operation for waterbornes, a surprising amount of "dirt" from the old coating material can turn up in the new coating material after the conversion to waterbornes. A few filters in the fluid lines can prevent a lot of downtime due to plugged nozzles and orifices.

As with the coating application process and most of the equipment, the physical plant does not necessarily need to change in order to convert to waterbornes. Often the formulation of the waterborne material can be tweaked a little to accommodate the facility. For example, the drying time for a waterborne primer may need to be adjusted for the time available before the color coat is applied. The TE can drop after converting to waterbornes even though the application process is the same and much of the equipment is unchanged. This is especially true if the application process includes atomizing the material.

ELECTROSTATICS

All spray guns and centrifugal applicators, like rotaries and disks, atomize the coating materials and propel the atomized particles toward the part being coated. With these devices, all the particles that are not aimed directly at the part will miss it and be wasted. The waste can be minimized and TE improved if the atomized coating material is given an electrical charge that is opposite in polarity to the charge on the part being coated. Opposite electrical charges attract and some of the material that would miss the part entirely instead gets drawn to it by the electrical forces. The technique is called electrostatics and has been used for years by painters and

coating applicators to improve the TE of their operations.

Until recently, most coating materials were solvent based and did not conduct electricity readily. This made it easy to use electrostatics with these materials by simply placing a high-voltage electrode in the coating material at the atomizer nozzle. The coating material picks up a static charge of electricity as it is atomized.

Waterborne coating materials conduct electricity much more readily than solvent-based materials, however, and the electrical charge drains off down the paint hoses. None of the charge gets into the particles of atomized coating material, so there is no electrostatic attraction between the particles and the part being coated. Without electrostatics, TE drops to unacceptably low levels.

The challenge in converting to waterbornes is getting comparable TE with these conductive materials as with the nonconductive solvent-based materials they replace. This means finding a way to get the electrostatic voltage into the atomized particles rather than letting it drain away through hoses and equipment made conductive by the waterborne coating material. Any equipment that contacts an electrical ground, such as a pipe or a damp concrete floor, provides an electrical pathway that drains off the electrostatics. This means that the electrostatics won't work in a waterborne system unless all the wetted equipment is isolated from potential grounds.

SYSTEM ISOLATION

Waterborne systems are commonly isolated in one of three ways. (1) Complete isolation of all equipment that contacts wet coating material. (2) Isolation of the charging electrode from the wet coating material. (3) Isolation of only the atomizer and its feed hose by using a voltage blocking device. Each method has advantages and disadvantages.

Complete Isolation

The advantage of completely isolating the entire application system is that the coating material can be directly charged with electrostatic voltage. If isolation is successful, the resulting TE will be the highest possible for the specific application. The exact TE that can be achieved in a specific application depends on the part geometry, line speed, application equipment, and other factors, the same as it would with a solvent-based coating material.

To isolate a complete waterborne system, every pump, tank, pipe, atomizer, or other piece of equipment that sees wet coating material must be set on a plastic table or hung from a plastic rod or stuffed in a plastic pipe sleeve. Suitable common and inexpensive plastic materials for this purpose include polyvinyl chloride (PVC), polyethylene, and polypropylene. Teflon, some nylons, and Delrin are also good isolation materials for high voltage, but are relatively expensive.

Dry air is one of the best isolation materials. A 12-in. air gap will isolate equipment charged with electrostatic voltage, except in cases of extreme humidity. Air has some advantages over plastic as an isolator for an electrostatic system. A paint spill down a plastic table leg can make it conductive. Humidity in a thick coating of dust on a plastic pipe can make it conductive. The disadvantage of air as an isolator is that it is an easily penetrated barrier between a charged part and a grounded part — too easily penetrated by personnel or by loose hoses or other equipment.

Unfortunately, it's almost impossible to design an isolated system that won't accidentally ground out, and a system that grounds out is less efficient. In one case, for example, an 18-in. long, hollow PVC table leg provided a direct path to

ground because it was set on a concrete floor and humidity from the concrete made the inside of the leg conductive. That particular short took a full week of troubleshooting to find and correct.

Besides being inefficient, isolated systems can be dangerous because they can store too much electrical energy. All the equipment that gets wetted with electrically charged coating material stores electrical energy, much like a giant capacitor. All that stored energy gets discharged if the system gets shorted out. If the system is big enough, and stores enough electrical energy, an operator can get injured by shorting it out accidentally by touching a charged hose or atomizer.

It is impossible to draw a definite line that says, "A system this small is safe, and a system that big is dangerous." Trying to define a safe electrical shock is like trying to define a safe height from which to fall. For example, a shock itself might only be annoying, but the victim might be so startled by it that it results in a bump on the head or an injury in some other way. Although a safe system, with regard to storage of electrical energy, may be a contradiction in terms, some guidance regarding the size of a "probably unsafe" system would be useful. Unfortunately, no regulations directly applicable to electrically charged waterborne systems are available.

By making some assumptions about the meager data that is published, extrapolating to the 70,000\100,000 V range used for electrostatics, and plugging the resulting voltage and capacitance values into the standard equation for storing electrical energy in a capacitor, the following can be developed:

$$\text{Maximum\Energy} = 3.5 \text{ Joules} = CV^2$$

where C=Capacitance (farads)

$$\text{Rearranging: } C_{MAX} = 7/V^2$$

where the voltage is the maximum available from the power pack.

This equation can be used as an indicator of the potential for a given isolated system to pose a serious shock hazard. The capacitance of the system, as measured with a capacitance bridge or a suitable capacitance meter, must be less than the value of C_{MAX} if there is a possibility of accidental human contact, which could result in an electrical shock. For example, if a 100,000-V electrostatic paint system has a capacitance G700 picofarads, caging and interlocks should be considered for operator protection.

For comparison purposes, a single 55-gal. drum and 200 ft of 3/8-in. inner diameter hose, all set 12 in. above a ground, can have between 450 and 900 picofarads of capacitance. This means that a typical paint system, which has much more hardware, would almost certainly exceed the maximum capacitance value and could store potentially dangerous levels of electrical energy.

The storage of electrical energy can be reduced by lowering the electrostatic voltage. The voltage term is squared in the equation for energy storage in a capacitor. This means that a given system at 100,000 V will store four times the energy that it would at 50,000 V. At the lower voltage, not only will the system be safer, but guns and cables will last much longer before breaking down electrically. Perhaps an even more compelling reason for lowering the voltage is to maximize TE. The maximum TE for most waterborne coating materials occurs between 40,000 and 60,000 V. By comparison, the maximum TE for a less conductive solvent-based material can be 90,000 V or more. Handguns present a special problem when a coating application system is converted from solvent-based materials to waterbornes.

An isolated electrostatic system for waterbornes can have multiple automatic atomizers or it can have a single handgun. It cannot have both, nor can it have more than one handgun. National Fire Prevention Association (NFPA) regulations dictate that the electrostatic voltage to any handgun must turn off when the trigger is released. Since all the atomizers in a waterborne system are connected electrically by their fluid hoses, the voltage remains "on" to an idle handgun as long as it is "on" to any atomizer in the system. This means that a handgun cannot be used with electrostatics if there are other atomizers in the system, and without electrostatics it is impossible to achieve the maximum TE.

To summarize, completely isolated systems have the potential to allow the maximum TE for a given application because they allow the coating material to be directly charged with electrostatics. In practice, that potential is rarely achieved unless the application system is very small because it is difficult to keep the electrostatic charge isolated.

Fully isolated systems can store too much electrical energy and become dangerous. To prevent operator injury, such systems need to be caged and equipped with interlocks to prevent access while the system is operating. Unfortunately, this means that even minor maintenance to the equipment is impossible while any part of the system is operating at high voltage because all the equipment is electrically connected by the fluid hoses. This is also why only one handgun can be permitted in a completely isolated system.

Indirect Charging

Indirect charging avoids many of the problems of completely isolated systems, but at a price. Indirect charging systems charge the coating material between the nozzle of the atomizer and the part, rather than at the atomizer. This is done by placing the high-voltage electrode in the air stream near the nozzle but not in direct contact.The coating material particles pick up a charge after they leave the atomizer.

Because the high voltage never directly contacts the application equipment, there is no opportunity for the charge to drain away down paint hoses. On the other hand, any charge inadvertently imparted to the application system drains away harmlessly to ground because the system is not isolated from ground. In fact these systems can, and should, be intentionally grounded to prevent storage of electrical energy.

There is little capacitive storage of electrical energy in an indirect charged electrostatic system so any electrical hazard is greatly reduced. This means that safety caging and interlocks can be less intrusive, or eliminated completely. With handguns no longer connected electrically by their hoses, there is no need to limit the number of handguns in a particular application system.

Several coating application equipment manufacturers offer atomizers specially designed for indirect charging. These devices position the electrostatic electrode away from the coating material stream so that there is no direct electrical contact between the application equipment and components charged with high voltage. Some conventional atomizers can also be retrofit with indirect charging apparatus, making the conversion to waterbornes easy and relatively inexpensive.

The downside of indirect charging is lower than optimum TE. Indirect charging does improve TE over comparable nonelectrostatic systems. Unfortunately, tests prove that the TE with indirect charging is less than the TE that can be

achieved by direct charging in any given application — that means using the same applicators, coating material, part shape, etc.

The difference can be considerable, up to 40% improvement in TE in extreme cases. Even the best indirect charged systems rarely achieve TEs within 10 percentage points of what is possible for the same application but using direct charging for the electrostatics.

To maximize TE, the coating material should be directly charged with electrostatic voltage, but to minimize shock hazards and operational problems, the size of the charged parts of the system should be minimized. This can be achieved by using a voltage block at each atomizer. Each atomizer then becomes a mini-isolated system with no electrical connection to any other atomizer in the system.

Voltage Blocks

Voltage blocks are devices that allow coating material to pass through to the atomizer but prevent voltage from leaking back the other way. They allow coating material to flow from the grounded pumps or kitchen to charged atomizers, yet block voltage from leaking back from the atomizers to the pumps or kitchen. This means that the hardware in the pump house and distribution system can be virtually the same as for a conventional solvent-based system, or for an indirect charged waterborne system.

Since the primary advantage of voltage block technology is that it limits the amount of hardware at high voltage, it is important to install these devices as close to the atomizer as possible. The connecting hoses between the voltage block and the atomizer are at high voltage, so keeping them short minimizes both the capacitance and the opportunity for accidental grounding. A voltage block for one atomizer is compact, requiring about as much space as a small electrical control box, so it can be mounted inside the spray or ventilation booth close to the atomizer.

The mini-isolated systems created by voltage blocks do not have the problems found in large isolated systems because less hardware is charged with electrical energy. Capacitance is greatly reduced, making the system inherently safer. Safer systems mean easier access to the inside of the spray booths. Often a simple guard rail and warning sign can replace elaborate caging and interlocks. Voltage leakage problems are minimized, since only the atomizer and a short hose are charged, making it easy to keep the TEs up to a high level. By isolating atomizers from each other, mini-isolated systems have some unexpected advantages. First, the NFPA limitation concerning handguns no longer applies. Each handgun is independently isolated from every other handgun so the voltage to idled guns can be turned "off."

In fact, spraying waterbornes with a handgun and voltage block can be easier than spraying the old solvent-based material with the handgun. Solvent-based material is charged at the gun barrel so a high-voltage cable to the gun is required. Since waterborne coating material conducts electricity, however, it can be directly charged at the voltage block and the cable to the gun can be eliminated. With the cable gone, the gun feels lighter and the hose bundle flexes more easily.

Even automatic atomizers, such as rotaries or disks, require less maintenance if the coating material is charged at the voltage block rather than at the atomizer, as it was when spraying solvent-based material. This is because the high-voltage cables last longer when they don't get flexed over and over by the motion of the gun mover or robot.

A second unexpected advantage of making each atomizer into a mini-isolat-

ed system is that every atomizer can operate at a different voltage, or at zero voltage, as desired. For example, in-plant experience might show that the rotary atomizers in a paint line run best at 60,000 V, but the handguns perform better at 45,000 V. With voltage blocks, the handguns and the rotary atomizers can run at different voltages, yet all can be supplied from a common paint distribution system.

Finally, in an application system for waterbornes and using voltage blocks, any atomizer in the system can be shut down and repaired or changed out, even though the other atomizers are operating at high voltage. The ease of access to production application equipment is comparable between a voltage-blocked waterborne system and the solvent-based coating material system it replaces.

CONCLUSION

An often unstated goal when converting a coating application system to waterbornes is to disrupt "the way it's done now" as little as possible, particularly if the existing system has good equipment and is performing well. That goal is not out of reach because the existing process, and much of the existing equipment, can often be used for waterbornes. Usually only the atomizers will need to be modified for waterbornes, or replaced with atomizers specifically designed to handle waterborne materials. The remaining equipment and distribution system can be reused unless made of materials that will corrode in waterbornes or be damaged by exposure to them.

Well-engineered conversions from solvent-based coating materials to waterbornes result in the highest possible operating efficiency at low cost and with maximum operator safety. The operating cost, in terms of TE, should be about the same as that of a good solvent-based paint system. To get high TE, electrostatics must operate at peak efficiency. This means directly charging the material with electrostatic voltage, but limiting the hardware that gets charged.

Voltage-blocking devices confine high electrostatic voltage to only the atomizer and hoses to the atomizer. This means that the rest of the coating material application system can be the same or similar to the system before the conversion is made. The electrostatics will still operate at high efficiency because the coating material can be directly charged so the TE will be comparable before and after conversion. Because system capacitance, or the capacity to store electrical energy, can be controlled to "safe"' levels, safety issues with the converted systems are not prohibitive. In other words, a voltage-blocked waterborne system is as close as possible to the solvent-based material system it replaces with a coating material that conducts electricity.

To summarize, here is how to convert an application system from solvent-based coating materials to waterbornes: (1) Reuse the existing process and hardware if it is up to date and performing well for the existing solvent-based system. Change components where materials are not compatible with waterbornes. (2) Turn each atomizer into a mini-isolated system by installing a voltage block in the coating material hose, as close to the atomizer as possible. Directly charge the material for maximum TE. (3) Lower the voltage to maximize TE, extend equipment life, and reduce shock hazard. (4) Take advantage of the fact that waterbornes conduct electricity. Remove the electrostatic cables from the atomizers and charge at the voltage blocks. Cables will last longer and the guns will move easier.

AUTODEPOSITION OF ORGANIC COATINGS

BY THOMAS C. JONES
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Auto deposition of organic coatings refers to a chemical process for depositing paint coatings onto metal surfaces. This process resembles electrodeposition in that the objects to be coated are submerged in an aqueous bath containing ionized organic materials; however, in autodeposition, the coating is produced by a chemical reaction between the metal surface and the bath constituents as opposed to electrodeposition where the coating is produced by the electrolysis of water due to an imposed electric current. After autodeposition, the wet film is water rinsed and cured by application of heat to produce an inert, corrosion-resistant coating.

COATING MECHANISM

The first step in the coating mechanism for the autodeposition process is the chemical reaction between the metallic surface and the inorganic constituents of the coating bath. The coating deposition step of the autodeposition process involves the controlled destabilization of an aqueous polymer latex dispersion, which is negatively charged, by the positive ions generated at the surface of the metal by the inorganic chemical reaction.

The components of an autodeposition coating bath include a weak acid (hydrofluoric acid, HF) in the range of 0.2% to 0.3% by volume, an anionically stabilized latex and pigment dispersion (latex/pigment), and chelated ferric ion in solution (FeF_3). The total solids content of the bath is less than 10%, and the coating solution has the viscosity of water.

The chemical reactions that result in an auto deposition coating are as follows. For iron dissolution, the major contributor is

$$2\ FeF_3 + Fe \quad 3\ Fe^{+2} + 6\ F^{-1},$$

and a minor contributor is

$$2\ HF + Fe \quad Fe^{+2} + H_2(g) + 2\ F^{-1};$$

deposition occurs when

$$Fe^{+2} + (\text{latex/pigment}) \quad Fe(\text{latex/pigment}).$$

Iron that is not entrapped in the wet film is converted to FeF_4^{-1} by the addition of an oxidizing agent. Since FeF_4^{-1} does not react with the anionically stabilized latex/pigment dispersion, the process is sludge-free.

As the autodeposited film builds, the diffusion of reactants to the surface is slowed, and the rate of film deposition decreases. This self-limiting mechanism results in a final coating that is extremely uniform and conforms to the underlying surface. All areas exposed to the coating bath become coated. This feature

of the autodeposition process is important since even enclosed areas will be protected against corrosion, as long as the solution has wet the surface. Typical coating thicknesses are about 15 to 30 mm (0.6 to 1.2 mils).

FILM PROPERTIES

Analysis of a cured autodeposited film shows the presence of iron throughout the organic layer. It is believed that the positively charged iron reacts with anionic sites (e.g., sulfonate groups and carboxyl groups), formulated into the polymer backbone, to effect the deposition. No additional cross-linking agents are required.

Although many organic emulsion polymers can be autodeposited, there actions are the same; however, the properties of the cured film depend on the chemical nature of the polymer. For example, polyvinylidene chloride (PVDC) latex emulsions are the most widely used at present in the commercial practice of autodeposition. Films deposited show excellent resistance to the penetration of moisture and oxygen to the base metal and, hence, offer superior corrosion resistance, as well as the excellent hardness, formability, and adhesion characteristic of paint films using this type of resin.

Another commercial autodeposition process utilizes acrylic resin polymers to produce films that are resistant to high temperatures (>400°F) in the presence of aggressive fluids (e.g., alkaline polyglycols).

Carbon black pigments, which are effectively encapsulated by the polymers and thus deposit simultaneously with the resin, are highly effective. A nonpigmented version of the polyvinylidene chloride latex is commercially available as a primer for subsequent top coating. While other colored pigments have been successfully evaluated on a laboratory basis, none are at present commercially available.

Zinc and zinc-alloy coated steels can be effectively painted by autodeposition by varying the process chemistry.

PROCESS SEQUENCE

Commercial autodeposition systems employ movement/transfer of the work package from stage to stage by either a continuous conveyor or by an indexing hoist. Conveyorized systems offer the advantage of assured agitation (to bring fresh reactants to the metal surfaces) due to the movement of the work through the coating tank (as well as the cleaning and rinsing tanks). Hoist-operated systems conserve space due to decreased transfer distance.

A typical process sequence is shown below. (Contact times in each stage vary from 30 seconds to 2 minutes, with the exception of the oven where 15 to 30 minutes is common).

Stage 1: Spray alkaline cleaning
Stage 2: Immersion alkaline cleaning
Stage 3: Immersion water rinse (plant water)
Stage 4: Immersion (or spray) deionized water rinse
Stage 5: Autodeposition (immersion)
Stage 6: Immersion water rinse (plant water)
Stage 7: Immersion sealing rinse
Stage 8: Cure

Cleaning

Good cleaning is essential to successful autodeposition. Any residual soils, which

hinder the solubilization of metal ions, can prevent or reduce coating formation. Although most organic soils (e.g., drawing compounds and rust preventive oils) are readily removable by alkaline cleaners, inorganic soils (e.g., weld spatter, scale, and rust) often require cleaning in an acidic material.

Immersion cleaning is usually required to ensure adequate soil removal from recessed areas such as tube interiors and box sections, which are inaccessible by spray. To protect the chemicals in the tank from excessive buildup of soils, a (smaller) spray cleaner stage is used beforehand. A slight overflow of this tank results in decreased cleaner loss.

Rinsing

Plant water rinsing is employed to remove residual cleaner carried through on the workpieces (and racks). This is followed by a rinse with deionized water to remove any hard water salts. The effect of salt buildup over time results in gradually decreasing coating film thickness per unit of immersion time.

Autodeposition

Autodeposition occurs by the reactions given above. The control parameters are paint solids (gravimetric determination), acid level (free fluoride concentration), and oxidation/ reduction potential (in millivolts), which is proportional to the ratio of FeF_3 to Fe^{+2}.

Postcoating Rinsing

A plant water rinse (usually immersion, but low-pressure spray applications have been used) removes traces of unreacted latex. A final sealing rinse contains chemicals that react with any soluble iron in the wet film to eliminate porosity after the film is cured.

Cure

The drying of a polyvinylidene chloride autodeposited coating is simply the removal of water from a coalesced wet film. No solvents are present. Commonly practiced parameters are 15 to 30 minutes at convection oven temperatures of 210 to 230°F. Shorter times (5 to 10 minutes) may be achieved on simple (i.e., line-of-sight to all surfaces) parts by the use of medium-intensity infrared radiation.

Acrylic coatings require a higher temperature (320–350°F) range for complete cross-linking.

FEATURES OF AUTODEPOSITION

A phosphate pretreatment process is not required for autodeposition, minimizing requirements for capital and floor space. Dragout is also minimized because of low paint bath viscosity. There is no coating buildup on hangers because a cured autodeposited film is inert to further reaction. Furthermore, since the coating process relies on chemical reaction, coating of all hidden or recessed areas occurs with even coverage. The coating does not pull away from sharp edges, coats evenly over machined surfaces (e.g., threaded fasteners), and is free from runs, sags, orange peel, and similar defects. This effect is enhanced by the low redispersibility of the wet film, which allows water rinsing to remove excess supernatant prior to oven cure. Very low maintenance is required and energy use is reduced because of the elimination of the phosphate pretreatment process. Finally, autodeposition is environmentally benign with low or no VOC emis-

sion or heavy metal effluent. No fire hazards are present.

Since the autodeposition reaction is diffusion controlled, the supernatant film on freshly coated pieces lifted from the bath continues to deposit paint solids. As a result, there is minimal loss (i.e., transfer efficiency averaging 95%) of solids to the water rinse following the coating bath. This effect is further enhanced by the absence of any external force (e.g., electric current), which would increase the concentration of solids at the immersed surface of the work. Since bath solids are maintained at only 5% to 7% by weight, any dragout effects are minimal.

Autodeposition is a versatile means of coating complex parts and assemblies. For example, in the automotive industry, the following parts are coated by autodeposition: jacks, brake backing plates, fan blower housings, suspension components, headlamp mounting assemblies, intermediate steering shafts, leaf springs (individual and as assemblies), power brake booster housings, seat frames, seat tracks, and miscellaneous brackets, connectors, and fasteners. Some nonautomotive examples include office furniture components (e.g., drawer slides, file frames), appliance accessories, hand tools, exercise equipment, and patio furniture.

EQUIPMENT CONSIDERATIONS

All of the stages for an autodeposition process, with the exception of the coating tank, are identical to those employed in other finishing processes and are not discussed here. For this reason, retrofit of an existing coating system to autodeposition can be relatively simple. The following comments pertain to the coating tank alone:

Materials of Construction: The coating tank is a mild steel tank lined with an acid-resistant material. To avoid damage to the liner by parts or racks falling into the tank, it is advisable to use materials with high impact resistance. Traditionally, three-ply (soft, hard, soft) rubbers have been employed.

Agitation: A gentle agitation of the coating bath is provided by properly spaced mixers with AC variable frequency drive (0.5-hp motors typical). Agitation is required only when workpieces are in the paint tank and may be decreased or stopped during downtime since no paint settling will occur in short periods (e.g., 2–3 weeks).

Cooling Equipment: The temperature of the bath should be controlled in the range of 68 to 72°F. Heating/cooling coils in the bath are required (1) as a safeguard against accidental heat/cold carry-in; or (2) if ambient plant conditions warrant (heating or cooling). Even when a bath is used to process metal at a high rate, there is no measurable temperature increase due to exothermic chemical reactions.

POWDER COATING EQUIPMENT

BY NICHOLAS P. LIBERTO
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There are many ways to apply powder coating materials; however, the material that is to be applied must be of a compatible type. For instance, if the application method is fluidized bed, the powder coating material must be a fluidized bed grade. Conversely, if the method of application is electrostatic spray, the powder material must be an electrostatic spray grade.

Once the material is correctly selected, the application method is chosen by part design and production goals. There are two forms of application methods: fluidized bed application and spray application. These vary as widely as the applications they suit.

FLUIDIZED BED

This application method was the first one used to apply powder coating materials. It is still used on many applications where the cured-film thickness is above 5.0 mils. Typical items are wire products, electrical bus bars, etc.

The fluidized bed application method can be performed in two ways. One way is the nonelectrostatic fluidized bed. This process requires preheating the part so that powder will melt and adhere to it. The hot part is placed into a fluidized bed of powder for coating. The amount of powder that is applied to the part is a function of how hot the part is and how long it is in the bed. It should be obvious that tight film-thickness control is not of primary concern when this method is used, as the total coating thickness often exceeds 10 mils.

To gain more control of film thickness on the part, with a fluidized bed system, the principles of electrostatics are introduced. As shown in Fig. 1, the part

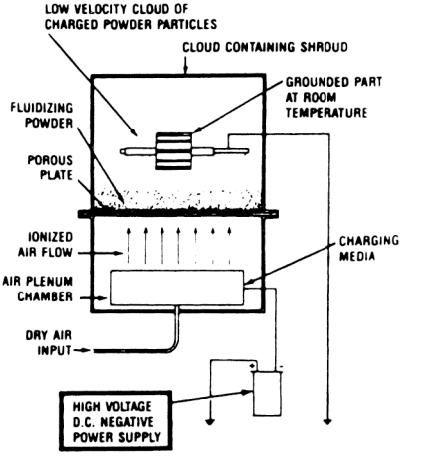


Fig. 1. Electrostatic fluidized bed for powder coating.

is transported above the fluidized bed and the powder is attracted to it. The part requires no preheating prior to being placed above the bed. Powder is attracted to the part by an electrostatic charge on the powder particle. This electrostatic charge is developed in an electrostatic field either above or in the fluidized bed.

Film thickness on the part now is controlled within tighter tolerances not only by the amount of time the part is in the fluidized bed but also according to how much electrostatic charge is on the powder particle. Sometimes, heat still is used in this process to overcome Faraday cage problems caused by part configuration. This process routinely applies powder from 5 to 10 mils thick.

Electrostatic fluid bed application is used for coating electrical motor armatures. These require a high dielectric strength coating with close film-thickness control to allow the wire to be wound properly.

SPRAY APPLICATION

Applying powder coating with electrostatic spray equipment is broken down into two types. In each case electrostatics must be used to attract powder to the part. There is no mechanical attraction or adhesion to hold powder to the part as seen in liquid spray systems. The two types of electrostatic spray equipment are corona-charged spray guns and tribo-charged spray guns.

Corona Guns

This device uses an electrostatic generator to create an electrostatic field between the gun and a grounded part. Powder is sprayed through the field, picks up an electrostatic charge, and is attracted to the part. The amount of charge that is transferred on the surface of the powder is a function of electrostatic field strength and the amount of time the powder particle is in the field. Also of importance is the surface area of the powder particle, as finer powder particles hold less electrostatic charge. The following equations (see Fig. 2) best explain how the powder is charged:

Field Strength: E=V/d
Charge on Particle: Q= 1/2 CEt2

Notice that some factors are more important that others. For instance, electrostatic field strength is directly proportional to applicator electrode voltage. Also, the distance between the part and the applicator (sometimes called the target distance) will directly affect electrostatic field strength.

The charge on the powder particle (which causes the attraction) is most affected by the amount of time the particle is in the field (by its square). The time and field strength will determine how much powder is attracted to the part (i.e., first pass transfer efficiency). The time the powder particle is within the electrostatic field is most easily controlled by adjusting the velocity of the powder pumped through the gun, or applicator, and reducing the speed of the applicator motion. It is a known fact that systems that use reduced powder velocity and slow gun motion will provide the best coating efficiency with the least effort.

The powder coating process is most often used to apply a charged dielectric material (powder coating) and onto a conductive (grounded) part. However, electrostatic powder coating on nonconductive materials (i.e. plastics, rubber, glass, etc.) can be performed using a conductive primer or aiding powder attraction by

heating the surface to be coated. Additionally, electrostatic charging of conductive materials (i.e., blended metallic powders) can be difficult since they can short-circuit the applicator's charging circuit. However, most equipment manufacturers provide electrodes outside the powder path to overcome this problem.

Both positive and negative polarity electrostatic guns are available from most manufacturers to provide efficient charging of widely divergent coating materials. It is worth noting that 98% of all applicators used in powder coating operations are negative polarity devices.

Code requirements insist that certain protection circuits be part of the system. Among these are current limitation to control arcing and grounding of all equipment and products that are coated to dissipate stored charges. System interlocks are required for automatic equipment. Guidelines for this equipment are listed in National Fire Protection Association Code (NFPA) 33.

Tribo Guns

Tribo-charged spray equipment uses the principle of frictional electrostatic charging. This type of charging is best explained by the following analogy: When you shuffle your shoes on a carpet in the winter, you create an electrostatic charge that is stored in your body. This charge is usually dissipated when you come into contact with a ground, such as a light switch. This phenomenon will only occur in a dry (not humid) environment. This is why we are not bothered by static electricity in the humid summertime, but only in the dry air of winter.

Tribo-charge spray equipment will direct the powder stream through a path that it will tumble and rub against a dielectric surface within the applicator, yielding a frictional electrostatic charge on the powder particle. This path is accomplished by lengthening the powder route through the spray equipment in either a straight, radial, or oscillating path. The amount of electrostatic charge that builds up on the surface of the powder particle is a function of several variables, including (1) the amount of time the powder particle is subjected to the frictional charging apparatus; (2) surface area of the powder particle; (3) dryness of air the powder is transported with or comes into contact with; and (4) the type of resin material from which the powder is made.

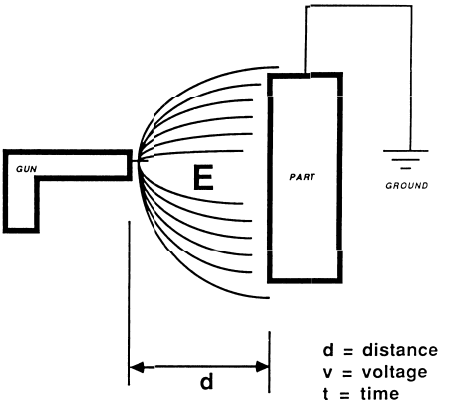


Fig. 2. Principle of corona charging.

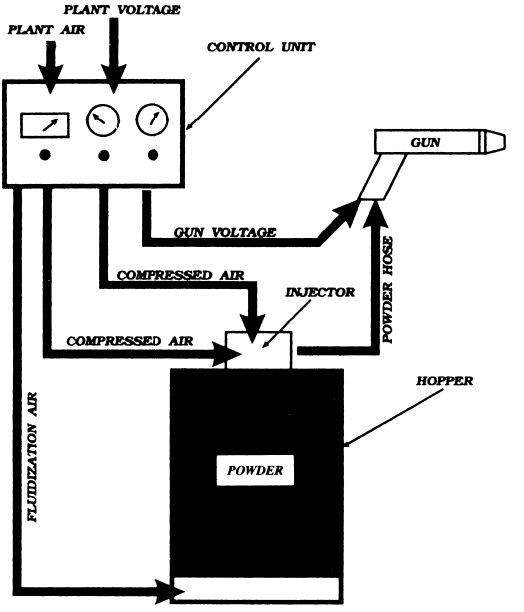


Fig. 3. Powder delivery system.

Controlling these variables is important to assure that the powder particle will be properly charged. Remember: if the powder is not charged, it will not adhere to the part unless the part is hot enough for the powder to stick on contact.

The amount of electrostatic charge that typically is developed by this apparatus is less than that produced by corona equipment. The polarity of the tribo charge is a function of the material being sprayed and the material that it is rubbed against. If the same two materials are used, the polarity will always be the same.

Tribo-charge applicators can often be used to overcome Faraday areas on difficult-to-coat parts, as there is no electrostatic field used to charge the powder. This flexibility, however, is often overshadowed by the additional process and coating materials controls that are required to ensure successful coating.

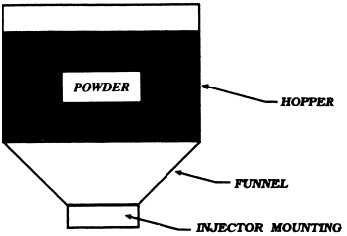
Powder Bells

This device uses an air turbine to rotate a conical cup used to atomize the powder coating. Powder is pumped to the cup where the rotational forces cause complete powder atomization. The feed system used to support this device is similar to that of spray guns. These devices employ the corona charging method, described earlier in this article.

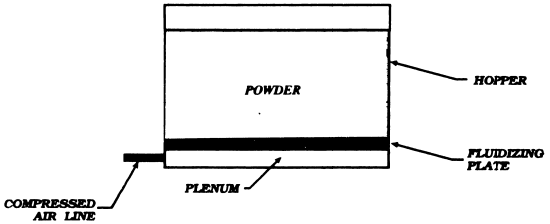
Powder bells are capable of dispersing a large quantity of powder coating over a large area. Therefore, the typical applications for this device are large flat components, such as appliances and automobile bodies.

POWDER DELIVERY

All spray application equipment requires a delivery system (see Fig. 3). This de-



GRAVITY FEED HOPPER



FLUIDIZED HOPPER

Fig. 4. Hopper designs.

livery system consists of a feed hopper, a powder pump, and a powder feed hose.

The feed hopper can be one of two types (see Fig. 4). The first type is called a gravity feed hopper. As the name suggests, this feed hopper uses gravity to move powder to the powder pump located at the bottom. This hopper usually is conical in shape to funnel powder to the pump. Sometimes a mechanical stirrer or vibratory assist is used to maintain an even powder flow. Frequently, without a mechanical assist, powder will bridge across the bottom of the funnel causing uneven feed to the pump. Since there is no air mixed with the powder in the hopper, this device is often employed when spraying blended metallic powders that can be stratified within a fluidized hopper.

The second type of powder feed hopper uses a fluidized bed. It is the same as the fluidized bed system described previously. A compressed-air supply is connected to the plenum chamber below the fluidizing plate. The fluidizing plate causes the air to fluff powder in the hopper to a state resembling water. Now the powder can be drawn out by the powder pump. Since powder is mixed with compressed air from the plenum, the powder within this device is very homogeneous in nature.

Powder pumps are mounted on the hopper and are connected to a pick-up tube to draw powder out of the hopper. These pick-up tubes usually are positioned an appropriate distance into the fluidized bed to assure that the turbulence usually present on the surface of the fluidized plate is not drawn up into the powder pump. This turbulence can cause inconsistent powder feed to the applicators.

Box Feeders

Powder equipment manufacturers also provide methods of pumping powder coatings directly from their shipping containers (box or bag) to the spray gun. This method is called the box feeder and utilizes a tilted vibrating table to support the box of powder. A powder pump connected to a pick-up tube is inserted in the low-

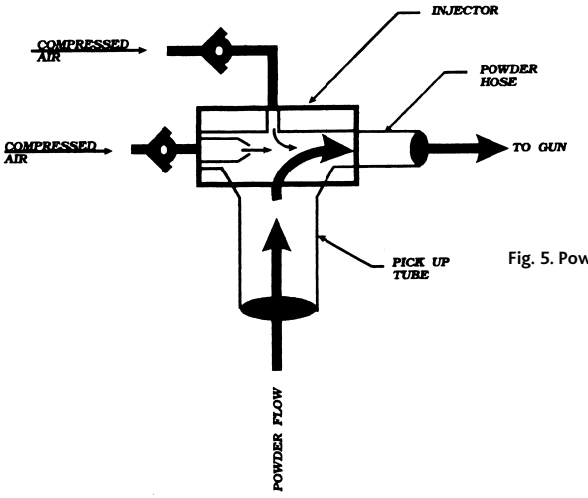


Fig. 5. Powder pump.

est portion of the box. A compressed air jet is employed at the end of this tube to assist powder flow into the tube. Powder is then pumped directly from the box to the spray gun without the need of a feed hopper. This approach makes color change cleanup quick and easy, as only the pick-up tube, pump, and hose need to be cleaned. Changing the powder box completes the color change task.

Pumps

Most powder pumps are designed to work by the venturi principle. Compressed air is directed perpendicular to the venturi pickup, causing a differential in pressure, or vacuum, that siphons powder out of the feed hopper or box feeder. When the powder enters the compressed air stream, it is pushed through the powder hose toward the applicator. An additional compressed air supply is introduced at the point where the powder enters this air stream (see Fig. 5) to dilute the powder and increase its velocity. Increasing powder velocity ensures that the powder stays within the air stream as it proceeds through the hose, reducing surging or pulsing problems. Surging occurs when the powder lays at the bottom of the hose until enough air pressure builds behind it to push it out with a burst. Both air supplies have check valves to force the air to go through the powder hose, allowing independent control of both powder quantity and speed through the feed hose.

Powder hose can be made from several materials, including urethane, vinyl, and certain rubber compounds. Hose diameter and length are critical. Diameter is dictated by the powder pump used; it always should match the manufacturer's recommendation. Length always should be as short as possible to reduce back pressure to the powder pump. This reduces surging of the powder stream to the gun. Avoid bends and kinks in the hose routing.

The more powder you pump using venturi style pumps the faster it travels through the electrostatic field. Consequently, transfer efficiency will be lower at higher feed rates. Applications requiring highly controlled powder flow at a wide range of output rates use high density - low pressure (HDLP) powder pumps. These

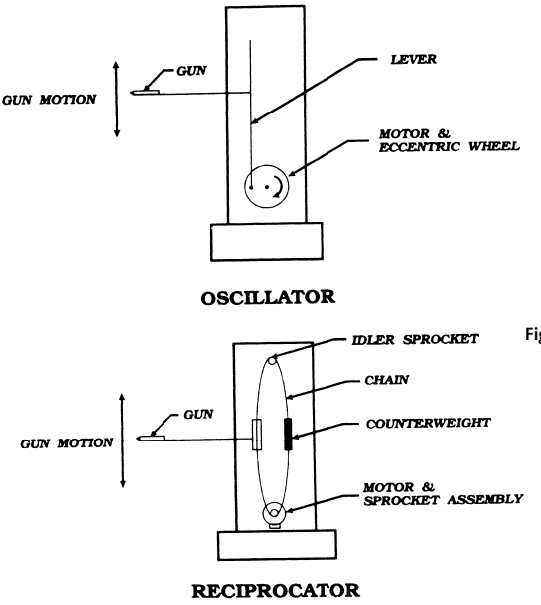


Fig. 6. Gun motion devices.

devices deliver a column of powder to the applicator without having to mix it with compressed air. Reducing the compressed air within the powder stream decreases the velocity of the powder delivered from the applicator, slowing powder speed, increasing powder density, and eliminating aerodynamic issues that may cause coating difficulties on box-shaped parts. Since these pumps employ significantly smaller diameter feed hose, the hose is much easier to clean with compressed air purging, making these pump the preferred choice for "fast color change" systems.

GUN MOTION

Automatic spray devices are often accompanied by some ancillary equipment used to produce spray gun motion. Gun-motion equipment can be broken down into four general categories: oscillators, reciprocators, multi-axis machines and robots.

Each of these gun-motion systems has a different design and is used to fill a specific coating requirement; however, all have one common feature. They are designed to move the spray gun(s) in one or more planes to coat a larger area than a fixed spray gun. Thus, the number of spray guns required to coat a given area can be reduced. This makes for a more efficient and economical system design

Oscillators & Wagglers

One type of gun-motion device is called an oscillator. This design is different from other movers in that it usually has a fixed stroke and speed. Some units have adjustment of these parameters, but they cannot be used while the machine is running. The main component of this type of equipment is an eccentric wheel and lever as shown in Fig. 6. The motor rotates the eccentric wheel. The lever, which is attached to the wheel at some distance from the center, will translate this ro-

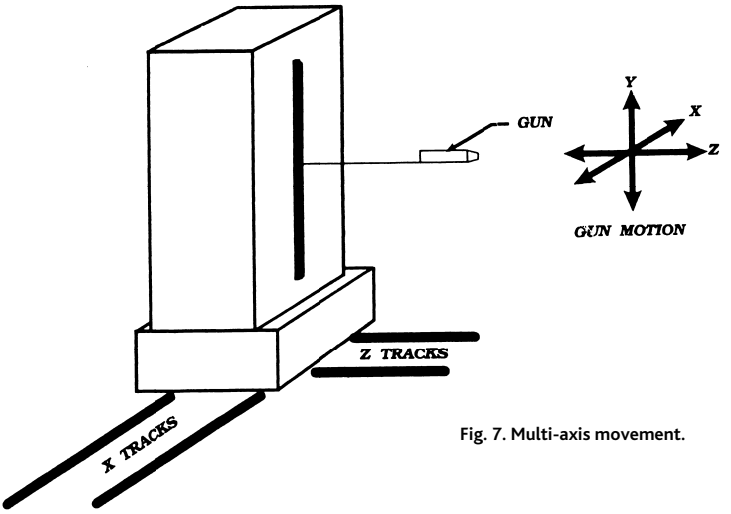


Fig. 7. Multi-axis movement.

tary motion to a vertical motion.

Stroke length is determined by the position at which the lever is attached to the eccentric wheel and by the diameter of the wheel itself. It can be adjusted by locating the lever at different points on the wheel radius. Speed is dictated by the motor and gear reducer used in the design. Sometimes, there are clutches and adjustable belt sheaves that will provide some speed adjustment; however, neither speed nor stroke adjustment can be changed while the unit is running.

Wagglers (radial oscillators) pivot the gun through an arc, where straight oscillators provide vertical gun motion in a straight line. Gun-to-part target distance is affected with radial oscillators, while straight oscillators will not have this problem.

Reciprocators

Reciprocators (see Fig. 6) use a variety of electronics to control both stroke and speed. In these machines, the mechanical linkage between the motor and guns is fixed; therefore, speed and stroke control must be adjusted electrically. These adjustments are sometimes made at the control panel and sometimes at the unit itself. For instance, stroke adjustment can be made by moving electrical limit switches in the unit or by adjusting an electronic feedback loop variable in the control panel.

Speed control is accomplished by a variety of methods depending upon the type of motor used. For instance, those designs that use a DC motor will provide speed control by varying voltage to the motor. Reciprocators that use AC motors have variable speed-control circuits to adjust speed. Both types allow adjustment during operation. This offers some flexibility over the oscillator design when different stroke lengths and speeds are required to coat different parts during the production cycle.

Multi-Axis Machines

Both oscillators and reciprocators provide movement in one plane only. Multi-

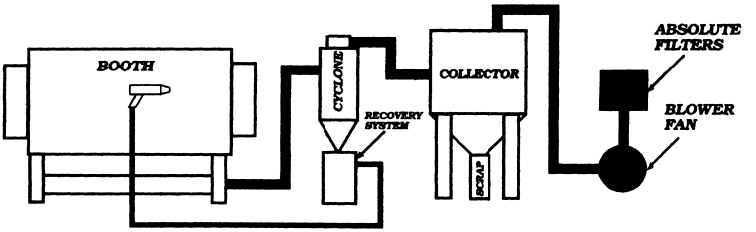


Fig. 8. Conventional powder booth system.

axis machines were developed to provide increased coating flexibility and meet a demand for total automation. Multi-axis machines have been successful in eliminating some or all of the manual touch-up necessary on some products. Though costly, this increased automation often will pay for itself by providing consistent part coating with minimal, if any, touch-up.

The multi-axis machine design is made up of two or three reciprocators that will move the gun(s) in two or three planes. The convention used to label the three axes of motion is as follows (see Fig. 7).

X = parallel to the conveyor travel
Y = up and down
Z = in and out

The design of these units is the same as reciprocators with respect to the control of speed and stroke adjustment; however, because the units must track parts moving along the conveyor, the addition of a programmable logic controller (PLC) is required.

The PLC will accept inputs from encoders (that determine conveyor speed) and photo cells or limit switches (that determine part position). This information is used to determine at what speed the multi-axis machine must run to track the part and when the multi-axis motion program is to be executed. The purpose of this complex tracking and motion system is to provide gun dwell time and powder pattern direction.

Robots

Most robots provide six axes of gun motion by adding wrist movement. Robotic machines can be electrically or hydraulically driven. Because of their cost and complexity, these units are rarely used in powder coating systems. Another detriment to these units is that hydraulic fluid is not something you want to have around powder. Also, powder coating material is very abrasive and can play havoc with hydraulic seals and pistons.

POWDER RECOVERY

A powder booth/recovery system must accomplish two specific goals: contain the powder overspray within the booth and remove the powder from this containment air so that it can be reused or disposed of properly. Powder booths are designed using several filtration techniques to separate the overspray powder from this containment air stream depending upon if the system will reclaim this pow-

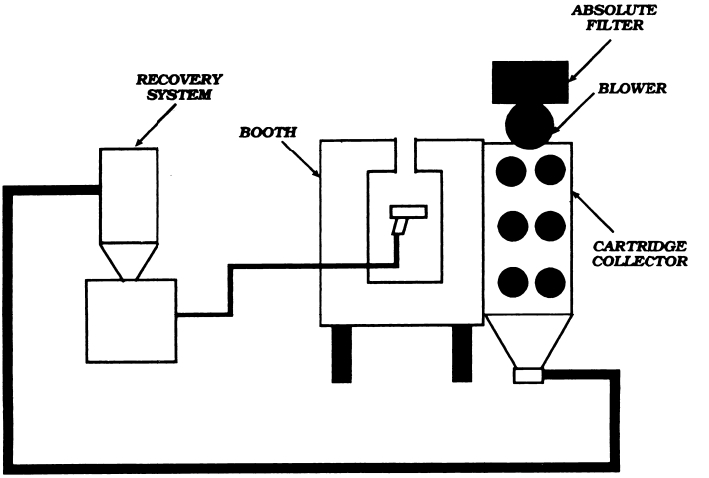


Fig. 9. Cartridge booth system.

der or employ a spray-to-waste strategy, the number of reclaimed powders, and the time available to perform the color change.

Cyclone Booth System

A cyclone powder booth system, as pictured in Fig. 8, is made up of a spray booth, cyclone(s), a cartridge collector, and possibly ductwork.

The spray booth can be made of metal, plastic, or composite sandwich designs. Metal booths provides strength and durability but attract more powder that will prolong color change time. Plastic will allow more light into the booth and will attract less powder, reducing color change time. Composite sandwich designs offer strength and attract the least power, significantly improving color change time. All powder booths should provide a smooth interior to facilitate easy and thorough cleaning.

Ductwork connection(s) can be at one of several locations. The preferred method is to locate the ductwork connection in the base of the booth as this provides a down-draft air flow inside the booth helping to keep it clean.

The booth may have devices, such as baffles, to help control air flow within the booth, touch-up openings to provide access for manual spraying, and gun slots to provide access for automatic equipment.

The cyclone is designed to separate most of the powder from the airflow before entering the filtration section. This has several benefits. First, air entering the filter is "precleaned," which will lower the loading on the filter media. This translates to longer filter life. Second, the powder collected in the cyclone can be easily recycled. Since the cyclone is a cleanable device, color change is attainable without additional equipment. Multiple cyclones are used when air flow is so high that one cyclone isn't practical for a given plant ceiling height. Twin cyclones are used in parallel before the filtration section. Cyclone efficiency can vary by manufacturer and design with some systems delivering in excess of 90% of the powder into the reclaim device.

The filtration section used with a cyclone booth is a cartridge collector, given its name for the cartridges used to separate powder from the air flow. These paper cartridges are cleaned with a "back pulse" of compressed air to shock the powder from the cartridge surface. The cartridges will separate most of the powder out of the air flow from the booth (up to 99% efficiency). These are not cleanable devices for color change. The blower fan that produces the air flow in the booth typically is located on the clean air side of the filtration device. Final filters are used after the fan to remove powder particles, down to 0.3 micron in size, before the air is returned to the work environment.

All of these devices—booth, cyclone, collector, fans, and absolute filters—can be connected by ductwork. The velocity of air within this ductwork usually is above 4,000 fpm and the ductwork is designed to promote laminar flow to assure "self-cleaning" during operation.

Some powder booth manufacturers have taken the approach of reducing the ductwork in this type of booth. This design has numerous smaller cyclones attached directly to the powder booth wall. The booth airflow enters the cyclones directly and without ductwork. These cyclones are much smaller than those used in standard cyclone booths, allowing for simpler cleanup. The blower, filter pack, and final filters are downstream from, and attached to, the cyclones, allowing the air to be returned directly to the plant.

Cartridge Booth System

The cartridge booth system (see Fig. 9) answers the same technical needs that all powder recovery systems must address: safe containment and separation of powder coating overspray. In a cartridge booth system, this is accomplished by filtration of powder from the containment air using a cartridge collector attached to the booth. There are no external filtration devices (or ductwork to connect them) with this system.

The cartridge collector is usually located in the wall of the booth (side draft) or in the base of the booth (down draft). The powder-laden air flow enters the collector. The air passes through the cartridge filter and the powder is deposited on the filter surface. Periodically, cartridges are back-pulsed with compressed air to shock the powder from their surface and deposit it in the collector base. Powder in the base is pumped to a reclaim stand for reuse or to a container for disposal.

The cartridge filter pack can be removed from the blower pack for color change. A separate cartridge pack is required for each recoverable color. Cartridges are made of a paper filter media. The blower pack houses the blower fan and filter assembly. The blower is on the clean-air side of the cartridges. Air from this powder booth system is returned to the plant.

The booth may have touch-up openings and/or gun slots depending upon the application for which it is used. The booth is typically of metal construction, though some manufacturers prefer plastic. This type of powder booth system is known for its compactness. Safety is another important benefit to this design. Since there are no "enclosed" devices the need for explosion venting is eliminated.

POWDER SPRAY GUNS

BY ALAN J. KNOBBE
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Two basic types of electrostatic powder guns are used for the spray application of powder coating materials. They are corona guns and tribo guns, where corona and tribo refer to the predominant process used in the guns for electrostatically charging the powder particles.

CORONA GUNS

Corona charging guns work by bombarding powder particles sprayed from the gun with charged particles called ions. The corona charging process is illustrated in Figure 1.

The corona charging process begins with a potential (or voltage) applied to one or more electrodes at or near the front of the gun. A high-voltage generator is used to produce this voltage of up to 100,000 V. As the voltage on the electrode is increased, an electric field is produced between the gun and the grounded workpiece. When the electric field in the vicinity of the electrode reaches a strength of about 30,000 V/cm, the field is strong enough to break down the air in the vicinity of the electrode. This electrical breakdown of air results in the creation of charged molecules or ions in the form of a continuous discharge known as a corona discharge. Powder particles exiting the gun travel near the electrode where they are bombarded by these ions and accumulate a charge.

Both the charged ions and the charged powder particles are influenced by the electric field between the gun and the workpiece and tend to follow the electric field to the part, as illustrated by lines in Figure 1. Ions that do not become attached to powder particles in flight are known as excess ions or free ions. Typically, only a few percent of the ions generated actually become attached to powder particles in flight. Some powder particles may be shielded from other particles in the charging zone and, therefore, do not accumulate a charge. For these particles, aerodynamic forces resulting from the powder conveying air might propel them toward the workpiece.

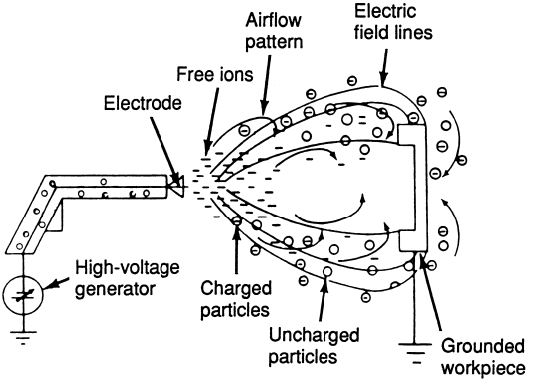


Fig. 1. Corona charging process.

Charged powder particles and excess ions are both deposited on the grounded workpiece. The charged powder particles are held onto the workpiece electrostatically until it is transported into an oven for curing. Heat causes the powder particles to flow together and fuse into a continuous film.

The Pauthenier equation describes the charge, over time, accumulated by a powder particle exposed to a corona discharge:

$$Q(t) = Ar^2Et/(t+\tau)$$

where, A = a constant, which depends on the particle composition, r = particle radius, E = electric field strength = electrode voltage/gun-to-workpiece distance, t = time, and τ = charging time constant.

The charging performance of a corona gun can be affected by the gun-to-workpiece distance. Today, corona guns are available that use specially designed high-voltage generators or gun-control modules to reduce or eliminate this dependency.

The high-voltage generator may be located remotely from the gun in the gun-control module or, alternatively, part of it may be located within the gun body itself. When the high-voltage generator is located in the gun-control module, a high-voltage cable is used to transmit the power to the gun. When a portion of the high-voltage generator is located within the gun body, a low-voltage cable is used.

For spraying most types of finishing powders, a negative-polarity voltage is produced in the high-voltage generator. This results in the powder particles accumulating a negative charge. Positive-polarity generators are also typically available as an option and are used primarily for charging nylon powders.

Two basic types of spray heads are available for shaping the powder particles into a cloud as they exit a corona gun. They are called conical deflectors and flat-spray nozzles. Conical deflectors shape the powder cloud into a circular, hollow, dome-shaped pattern. These spray heads can produce a large, low-velocity spray, 360° SD in circumference. They are best for simple-shaped workpieces and can produce a very high transfer efficiency. Flat-spray nozzles typically have a single slot through which the powder particles exit. The resulting powder cloud is fan-shaped from the side, but has a narrow width. These nozzles may have a higher velocity than a conical spray head and are, therefore, best for spraying parts with deep recesses and corners.

Many equipment manufacturers design their electrostatic corona powder spray guns to comply with the different codes governing the manufacture and use of these products worldwide. Some of the worldwide agencies that test and issue approvals on these spray guns are Factory Mutual (United States), Canadian Standards Association, European Committee for Electrotechnical Standardization (CENELEC), and the Research Institute of Industrial Safety (RIIS, Japan). In the United States, a local fire marshal would typically look for "Approved" equipment or compliance with National Fire Protection Association (N.F.P.A.) Standard 33, Spray Application Using Flammable and Combustible Materials, before permitting an installation to start production.

TRIBO GUNS

Tribo or triboelectric charging guns charge powder particles as a result of the intimate contact and subsequent separation of the powder particles from the gun walls. The word "tribo" comes from the Greek word tribein meaning to rub. The

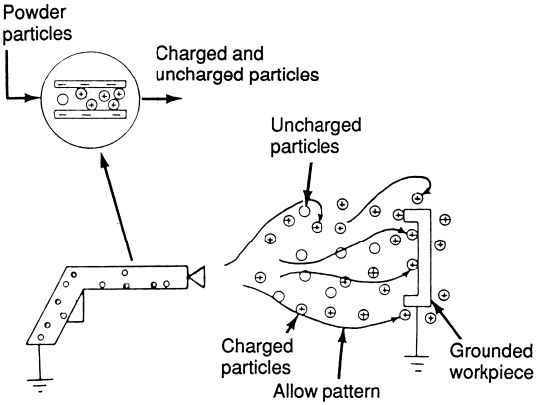


Fig. 2 Tribo charging process.

tribo charging process is illustrated in Figure 2.

When two different materials are brought into contact, there will be a transfer of charge from one material to the other in order to eliminate the imbalance of charge. The magnitude and direction of the charge transfer depends on many factors including the chemical and electronic structure of both materials. Over the years, a lot of testing has been done contacting one material against another and measuring the resulting magnitude and polarity of the charge attained on each of the materials. The results of one such study, presented in the form of a so-called "triboelectric series," are shown in Table I. The farther two materials are away from each other in the series, the greater the triboelectric charge that should be produced when these two materials come in contact. Note that polytetrafluoroethylene (PTFE) is shown at one end of the series as being the strongest electron acceptor and nylon 6/6 is shown at the other end as being the strongest elec-

Electron Donor (+)
Nylon 6/6
Cellulose
Cellulose acetate
Polymethyl methacrylate
Polyacetal
Polyethylene terephthalate
Polyacrylonitrile
Polyvinyl chloride
Polybisphenol carbonate
Polychloroether
Polyvinylidene chloride
Polystyrene
Polyethylene
Polyproplene
Polytetrafluoroethylene
Electron Acceptor (-)

Table I. Triboelectric Series

tron donor. According to this study, all materials that contact PTFE should become positively charged.

PTFE is typically used for the powder contact walls in a tribo gun. Powder particles, of course, are a composition of resin, pigment, fillers, and possibly other additives. Experience agrees well with this series in that most finishing powders become positively charged as a result of their contact with PTFE. Today, most powder manufacturers formulate powders specifically for tribo guns.

Tribo guns charge powder particles as long as the powder particles contact the PTFE gun walls. Compared with corona charging, tribo charging is a highly efficient charging process. The more contacts a powder particle makes with the walls and the harder it hits them, the greater the charge on the particle. Theoretically, the gun walls will be left with a charge equal in magnitude but opposite in polarity to the charge accumulated on the powder particles. This charge on the gun walls must be conducted away or else it will build up inside the gun and the gun will stop charging.

Tribo guns are also available with optional powder-contact parts made out of nylon 6/6. Because of its location in the triboelectric series, nylon parts are ideal for charging PTFE powders. In this case, the PTFE powder particles become negatively charged and the nylon gun walls become positively charged.

Since a tribo gun does not rely on a high-voltage generator or an electrode at high potential, there is only a weak electric field between a tribo gun and the workpiece. The airflow from a tribo gun thus plays a significant role in transporting the powder particles to the workpiece.

The spray head can also play a significant role in the performance of a tribo gun. Since the powder particles are already highly charged by the time they enter the spray head, many spray head designs are possible for optimizing the transport of the particles in just the right quantity, in the right direction, and at the right velocity, onto a workpiece.Tribocharging guns can have a very high transfer efficiency and they can effectively coat the widest variety of workpieces. They are particularly good at coating difficult-to-coat workpieces, which have deep recesses and many Faraday cage areas.

ELECTROCOATING

BY LISA E. MERLO
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Electrocoat (also called E-coat, electrodeposition, or electrophoretic coating) is a widely used coating technology that has provided superior levels of performance on a vast array of industrial metal objects for over 40 years. Electrocoat technology has evolved dramatically since the early 1960s when it was first commercialized as an automobile body primer. Today, over 98% of all car bodies produced globally utilize an electrocoat primer. New end uses for electrocoat continue to be found annually; examples include automotive parts and accessories, appliances, heat exchangers, decorative plated objects,and heat-sensitive components.

Current commercially available electrocoat systems offer superior performance using processes and materials that are both environmentally friendly and economically efficient. Major advantages of the electrocoat process include: total coverage of complex parts with unsurpassed film uniformity; material transfer efficiencies routinely in 95 to 99% range; highly automated, closed-loop systems with excellent productivity and low operating costs; fast line speeds and high part racking densities; very low air and wastewater emissions that foster environmental compliance; and totally enclosed system leading to a cleaner and safer paint application method.

THE ELECTROCOAT PROCESS

There are four major steps in the electrocoat process: cleaning and pretreating, electrocoating, postrinsing, and baking (see Fig. 1)

Cleaning and Pretreating

The cleaning and pretreating of metal prior to the electrocoat bath are critical steps in the process of providing a high-performance paint finish. Alkaline cleaners are employed frequently to remove dirt and oils found on industrial metal parts in manufacturing. Aluminum objects generally receive a conversion coating prior to electrocoat and can be electrocoated simultaneously with ferrous parts.

Phosphate (iron and zinc) pretreatments are used to provide adhesion be-

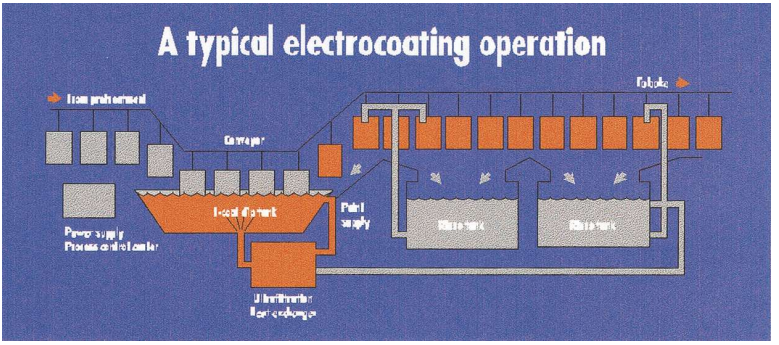


Fig. 1. The electrocoat process has four major steps: pretreat, coat, rinse, and bake.



Fig. 2. Typical electrocoat tank with conveyor.

tween the electrocoat and the substrate and to enhance corrosion protection. A final deionized water rinse is applied to the parts prior to the electrocoat tank. Dry-off ovens are generally not required.

Electrocoating Bath

The electrocoat bath consists of 80 to 90% deionized water and 10 to 20% paint solids. The deionized water acts as the carrier for paint solids, which consists of resins, pigment, and small amounts of solvents. The resin is the backbone of the final paint film and provides properties such as corrosion protection and ultraviolet durability. Pigments provide color, gloss, and corrosion protection as well. Solvents help ensure smooth film appearance and application.

During the electrocoat process (see Fig. 2), paint is applied to a part at a certain film thickness, which is regulated by the amount of voltage applied. The deposition is self-limiting and slows down as the part becomes electrically insulated

by the applied coating. Electrocoat solids deposit initially in the areas closest to the counter electrode and, as these areas become insulated to current, solids are forced into more recessed, bare metal areas to provide complete coverage. This phenomenon is known as throwing power and is a critical aspect of the electrocoat process and materials. Electrocoat bath solids are deposited electrically via a system that includes a number of components: the rectifier, which supplies a DC charge to the bath enabling deposition of ionic species; circulation pumps to maintain proper paint bath uniformity; a heat exchanger and chiller to control the temperature of the bath; filters, which remove dirt particles introduced into the systems; and ultrafilters that produce permeate for rinsing and allow for recovery of excess paint solids.

Postrinsing

As the part exits the bath, excess paint solids not deposited electrically cling to the part and must be rinsed off to maintain process efficiency and optimal aesthetics. Rinse material is supplied from the ultrafilters and is called permeate. The permeate, containing low molecular weight organics and some solvent, is used to rinse the dragout from the parts; the excess solids and permeate are returned to the bath in a counterflow fashion, affording superior levels of transfer efficiency.

Baking

After exiting the postrinses, the coated parts enter the bake oven for curing and cross-linking of the paint film, resulting in a high-quality finish void of runs, drips, and sags (see Fig. 3). Bake temperatures range from 180 to 375°F depending on the type of electrocoat applied.

TYPES OF ELECTROCOAT PRODUCTS

Electrocoat products are referred to as either anodic or cathodic, indicative of where coating deposition takes place (see Fig. 4). The first electrocoats developed in the late 50s and early 60s were anodic systems. Cathodic systems were developed later and were initially commercialized in the appliance industry in the late 60s and early 70s.



Fig. 3. Typical electrocoat finish after baking.

Anodic Electrocoats

Anodic electrocoating involves the use of negatively charged paint particles, which are deposited onto positively charged metal substrates. The polymer species are acid functional and amine solubilized. Anodic electrocoats offer economical finishes with excellent color and gloss control.

The anodic deposition process leads to some dissolution of metal ions from the parts being coated. These ions become trapped in the depo-

sition paint film and, due to their ability to interact with moisture, limit the corrosion performance of these firms. Other undesirable effects can include film staining and discoloration due to the presence of iron in the anodic films.

Cathodic Electrocoats

Cathodic deposition, where positively charged paint particles are attracted to a negatively charged part, involves much less iron incorporation into the deposition film and consequently offers substantially improved corrosion resistance. Additionally, the polymer species are amine functional and acid solubilized, with the alkaline nature of the polymer leading to better inherent corrosion resistance that can be obtained with acid-functional species.

Whenever high coating performance is required, cathodic electrocoat systems are generally specified. Market penetration of these coatings into the appliance and automotive industries over the last 30 years bears evidence to the attractiveness of these coatings.

Typical End Uses

Electrocoats can be segmented into anodic or cathodic, and epoxy or acrylic. Table I illustrates common end uses for the four categories of electrocoats.

CURRENT TECHNOLOGY CAPABILITIES

Electrocoat research and development has fostered many exciting advancements over the past 40 years. Some of the significant advancements enjoyed today by end users include closed-loop systems with close to 100% material efficiency and little wastewater discharge; near-zero VOC electrocoats; HAP-free anodic and cathodic products; lead-free cathodic electrocoat with corrosion protection equal to prior lead-containing products; cathodic acrylic coatings with

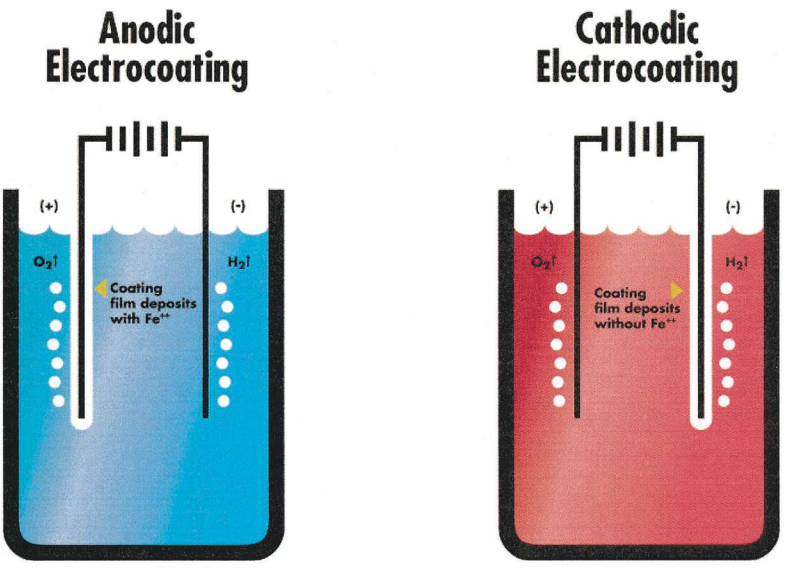


Fig. 4. Principles of anodic and cathodic electrocoat deposition.

Table I. Properties and Applications for Various Electrocoat Systems

	Properties	*End Uses*
Anodic epoxy	Low cure	Agricultural implements
	Corrosion resistance	Automotive parts
	Exterior use	Structural steels
Anodic acrylic	Color control	Metal office furniture
	Gloss control	Air diffusers
	Interior use	Shelving
	Economical	Wire screen and hangers
Cathodic epoxy	Corrosion resistance	Automobiles and parts
	Chemical resistance	Transformers
		Appliances
Cathodic acrylic	UV durability	Lawn and garden
	Corrosion resistance	Agricultural implements
	Color control	Automobile wheels and trim
		Appliance

corrosion and ultraviolet protection as a single-coat finish; anodic electrocoats with cure capabilities below 200°F; two-coat electrocoat systems for ultimate primer plus topcoat performance; exceptional coverage of sharp metal edges; decorative clear electrocoats that can be water-white or tinted to simulate plating; and photoimageable electrocoats.

ELECTROCOAT LIMITATIONS

As with any coating process, electrocoat has inherent limitations and is not suited for all applications. Low production levels of multiple colors favor other coating application methods over electrocoat, which requires a separate tank and postrinse system for each color. High production levels, however, can economically favor the use of multiple electrocoat tanks to handle different colors.

Initial capital outlays for an electrocoat system are often higher than for other types of coating methods such as dip or liquid spray. Justification of the capital to install an electrocoat system has become easier with advances in more efficient equipment design and closed-loop operation.

Because electrocoat is a total coverage process, applications where coating is not desired on all areas of a part can be problematic. Masking of areas to be left uncoated can be costly and time consuming in production.

NEW TECHNOLOGY FOR ELECTROPLATING METAL LAYERS AIMS TO IMPROVE THICKNESS CONTROL

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CMC Laboratories has developed a new technology for electroplating metal layers that results in significant improvements in thickness control.[1] CMC's technology, which is called "Smart Rack," utilizes active control of the plating process to improve thickness versus traditional passive controls such as current thieves. CMC's Smart Rack technology entails a new electroplating circuit as well as a completely different approach to rack design. Though this technology was developed for electronic devices or package applications, it can easily be applied in other areas that utilize precious metal plating.

The focus of this new technology is to narrow the distribution of plated layer thicknesses across a plating rack. Narrowing this distribution can have a significant impact on precious metal plated layers, such as Au, Pt, Pd, Rh, and Ir. When a minimum thickness of these expensive metals is specified, as is typical, a narrower distribution results in less metal used for significant cost savings.

A tighter plating distribution can also be important for other metal plating processes. For example, currently most wafer bump plating is done using low throughput, high tool cost fountain platers. For small wafer size (< 6 inches), it may be possible to use Smart Rack technology to bump multiple wafers at one time in a rack configuration. Since Smart Rack only improves part to part thickness control, not the thickness distribution across a part, the technology would not help for very large wafers.

The ability to plate AuSn at the eutectic composition on die attach pads would also be very important in many high power electronic applications. However, since the composition of AuSn varies with current density, it is very difficult to achieve the 80/20 eutectic across a large plating rack. AuSn compositions that are off eutectic will not melt at the 400°C process temperature.[2]

Traditional electrolytic plating uses a plating rack that is made of a highly conductive metal such as copper or stainless steel. All of the parts being plated are attached to this rack. During the plating process, the rack is attached to a constant current power supply (plating rectifier). Current is pumped through the rack structure, forcing the plating reaction to occur at the interface between the conducting work parts and the plating solution or electrolyte.

The plating rate at each individual part depends on a number of factors:

- **The electrical current density at the individual part**
- **The availability of metal ions in solution at the location of the individual part**
- **The availability of other electrochemical reactants at the plating interface which compete with the plating reaction**

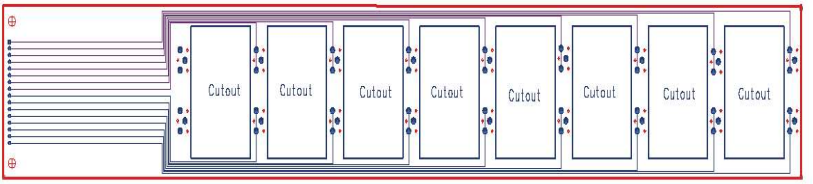


Figure 1a. Electrically isolated rack pieces.

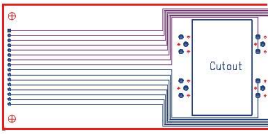


Figure 1b

Macroscopic factors that affect these more microscopic reactions include:

- **Density of plating parts surrounding the individual, part being plated**
- **Resistance drops across the plating rack**
- **Location of the part on the rack**
- **Plating rate**
- **Uniformity of the electrochemical environment including variations in solution chemistry, temperature, agitation**

All of these variations lead to thickness variation in parts from one location of a plating rack to the next. Typically the thickest parts are located along the edge of the rack and the thinnest parts are located near the center. One reason for this trend is that the flow of metal ions to be plated is unimpeded near the edge of the rack, but near the center of the rack, surrounding parts "screen" the metal ion flow from their neighboring parts. This competition for plating ions results in a thinner deposited layer and a lower plating current density.

DESCRIPTION OF SMART RACK CONCEPT

The essential feature of the Smart Rack concept is to individually control the electrical current that flows to each piece during the plating process. This individual current control allows active and direct control of the plating process, which can very significantly narrow the plating thickness distribution. This direct method is much more effective than indirect methods such as current thieves, and the range of adjustment is considerably higher. For example, if desired, the programmed current density of two parts on the same rack could vary by factors of 2 or more. In addition, this method is much easier to implement and control because changes in current densities can be effected by adjusting inputs to the plating program rather than making any physical changes to the plating bath or set up.

To accomplish this requires two significant changes compared to the traditional plating approach. First, the plating rack must be constructed so that individual



Figure 2. Smart Rack for PCBs.

electrical current conductors are connected to each individual piece on the rack, and thus each piece is electrically isolated from all of the other pieces. The rack, rather than being a large conductor, is now an insulator with individual wires or embedded metal traces, to each piece. This is shown in the diagram in Figure 1. In this Figure, you can see the cut out area where 2 parts are located and the traces to each part from the top contact array shows in the detail drawing.

One option for fabricating this type of rack is to utilize standard printed circuit board (PCB) technology which incorporates thick copper traces within a fiber reinforced epoxy insulator. This structure can then be coated to protect it from the aggressive plating chemicals. An example of a PCB technology Smart Rack is shown in Figure 2.

The second significant change is the presence of a new circuit, which can control the current to each individual piece at a preprogrammed value. (There will be a more detailed description of this circuit later in this paper.) This circuit acts like an individual programmable current supply for each piece. However, due to the availability of miniature micro-controllers, the overall size of the control circuit can be made very small, and even mounted on the rack itself.

SMART RACK PLATING RESULTS

Nickel Plating

The first set of results described here are for Ni plating from a traditional nickel sulfamate plating bath. Overall current density was 20 amps/sq. ft. with a bath temperature of 125°C. The pieces plated were copper substrates.

The plating rack held 16 pieces and could be run in two different configurations. If all the plating locations were shorted together, the rack simulated a traditional plating rack. If each conductor was controlled individually, this represented the Smart Rack technology.

Figure 3 shows the width of the plating thickness distribution for two different situations. The first plating configuration has all of the parts shorted together and a constant current run through the entire rack. This configuration is the traditional plating bath set-up. Note that the total distribution width was +/- 20%, which is typical for a Ni bath.

In the second configuration, the individual traces to each part were isolated and a constant and equal current was run through each part. Said differently, the Smart Rack circuit forced the exact same current to flow through each part,

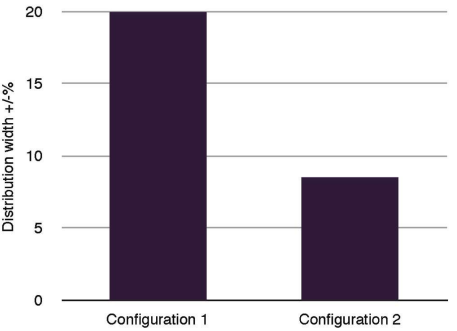


Figure 3. Comparison of plating thickness distribution in two scenarios.

irregardless of location on the plating rack. Note that, in this case, the distribution width dropped to +/- 8.5%, over a factor of 2 improved. This result demonstrates the dramatic reduction in the distribution width that can be accomplished by forcing the same current density through each individual piece during plating.

Because of the significant flexibility inherent in the Smart Rack approach, further improvements can be made by individually adjusting the current density at each point to minimize the distribution width. To do this, small increases in current were programmed into parts with slightly lower than mean thickness, and small decreases in current were programmed into parts with higher than mean thickness. The result, show as configuration 3, had a distribution of +/- 3%. This is shown along with the previous results in Figure 4.

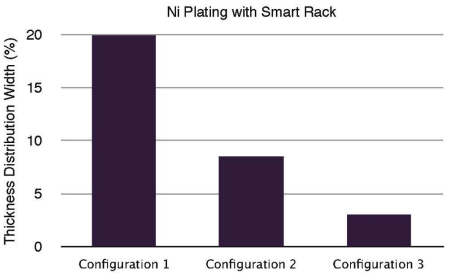


Figure 4.

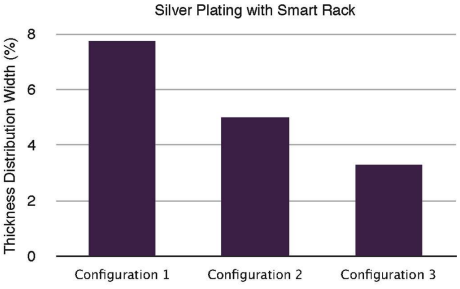


Figure 5.

Silver Plating

Figure 5 right shows the results for Ag plating.

DISCUSSION

The results above illustrate that individual current control can have a dramatic impact in reducing the thickness distribution during electroplating, even for materials like Ni that are typically very difficult to control.

Another interesting aspect of this technology is the comparison between Configuration 2 and Configuration 3. At first pass, it would appear that setting a fixed and equal constant current at each plating site should yield the minimum distribution width.

Since a constant electrical current is flowing through each part, the difference in plated layer thicknesses across the rack in Configuration 2 must be attributable to differences in plating versus non-plating electrochemical reactions at the part surface. By increasing the current density slightly for the lower thickness parts, as is done in Configuration 3, it is clear that the rate of plating reaction can be brought closer to plating rate for the mean thickness parts. Thus, differences in the plating reaction rates from one area on the rack to the next can be minimized by relative adjustments of current density as is shown for Configuration 3. This idea is illustrated schematically in Figure 6.

DESCRIPTION OF THE SMART RACK CIRCUIT

There are three major portions of the control circuitry. A computer (which

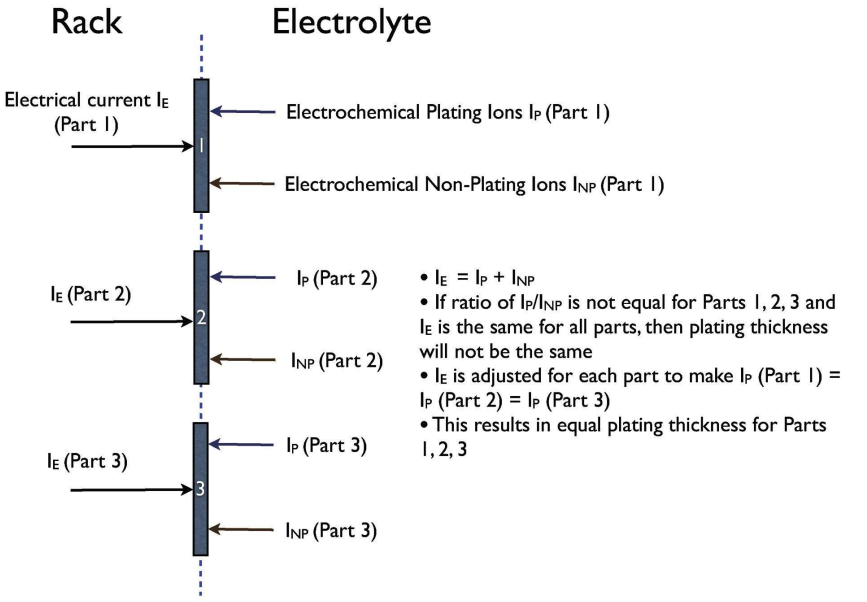


Figure 6. Variation in plating reaction rates from one area of the rack to another.

could also be a micro-controller), a master control circuit and an individual current control circuit for each part. The computer stores all of the programmed information, the Master Control Circuit (MCC) can measure the electrical current flowing in each individual Current Control Circuit (CCC) and send required adjustments to the CCC as needed.

The plating process utilizing the Smart Rack technology has two segments. Programing the control circuit followed by the plating segment.

The key steps in the program segment are:

1. Enter the base current density into the program
2. Enter the plating time
3. Enter the size of the plated surface on each part
4. Input any current density adjustments for each individual part from the base current level, as in Configuration 3 (if no changes are entered, the current density will be the same for all of the parts, as in Configuration 2).
5. Start the program, which initiates plating

Here is what the control circuitry does during the plating cycle:

1. Each individual part is controlled by its own constant current circuit (CCC). During the first phase of plating, the computer sends the desired individual current density value to each individual CCC.

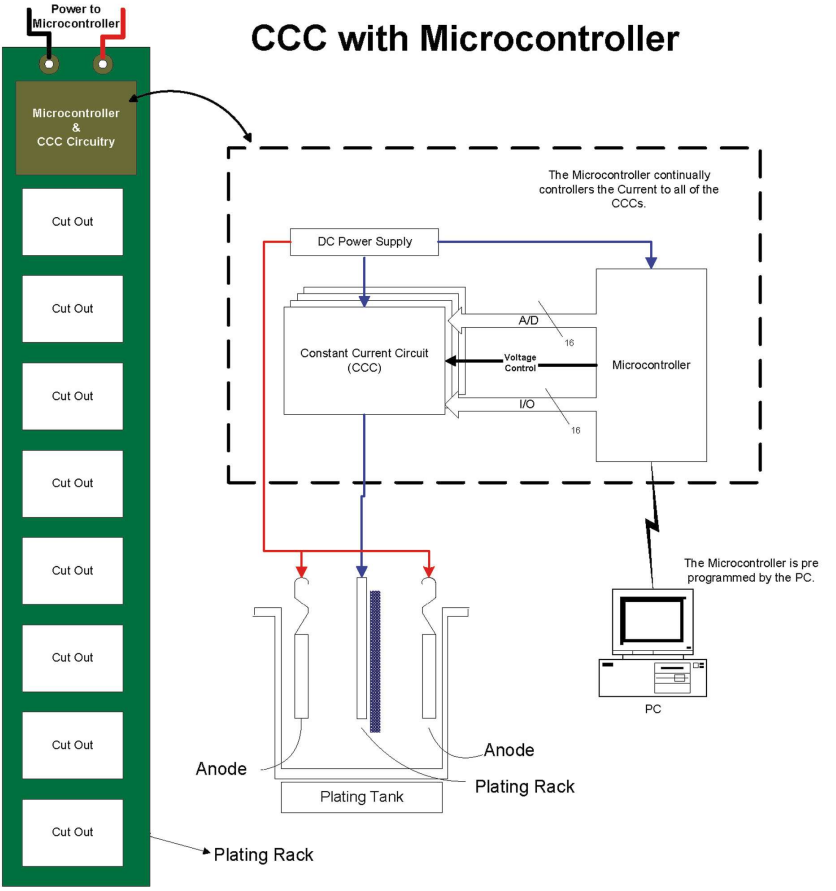


Figure 7. Schematic of the control circuit.

2. Current begins to flow and plating starts
3. A master control circuit (MCC) reads the current value at the first part and compares it to the programmed value. The MCC then sends any required current adjustments to the CCC until the programmed current set point is met.
4. MCC scans to the next part and repeats the same process
5. After the last part is adjusted, the MCC returns to the first part and the cycle repeats.
6. This process continues until the plating cycle is completed.

Thus, the purpose of the CCC is to act as a miniature constant current source

for each individual part. The goal of the MCC is to monitor the CCC output and make any required adjustments to keep the output current at the required value (which is stored on the computer). It is clear that an individual CCC unit for each part is necessary in order to have maximum flexibility in adjusting the electrical current at each part. Furthermore, this flexibility is at the core of the Smart Rack technology's ability to dramatically narrow plating layer thickness distributions.

(A schematic of the control circuit is shown in Figure 7.)

APPLICATIONS FOR SMART RACK TECHNOLOGY

There are a number of applications where Smart Rack technology can have a strong impact in improving performance and manufacturability.

- **Noble metal plating to reduce the amount of material required to meet minimum thickness and, thus, lower cost. Key metals would be Au, Pt, Pd and Rh.**
- **Rack plating AuSn for solder or eutectic die attach. For this application, Au and Sn layers are deposited on plated surfaces and then diffused. The deposited layer thicknesses must be very consistent (+/- 3%) in order to achieve eutectic composition melting.**
- **Uniformity of thick plated layers such as Cu conductors. Because the conductors can be very thick (50–500 µm), large variations in Cu thickness can lead to dimensional tolerance issues for the final plated part.**
- **Bumping wafers that are 6 inches or less on a plating rack rather than using a fountain plater. The advantage is higher throughput and lower tool cost.**

SUMMARY

This paper has described a new electroplating technology that is focussed around individual electrical control at each plating site. This electrical control is achieved by a special control circuit that monitors and adjusts the electrical current during plating at each site to a pre-set value. This approach also requires a plating rack that is made from an electrically insulating material with metal traces to each plating site. This type of rack can be made using PCB fabrication technology to lower cost and weight.

If electrical current is set to the same value at each plating site, a significant improvement in the plating thickness distribution can be achieved. However, if small additional adjustments are made that boost the thickness in areas below the mean value, and reduce the thickness in areas above the mean value, even a narrower distribution can be attained. The basic electrochemistry behind this observed phenomena was discussed.

Data was presented for Ni plating and Ag plating. For Ni, the distribution using a traditional "shorted" rack, where all of the parts are connected to each other and to the cathode, had a distribution of +/- 20%, which is typical for Ni sulfamate. If all parts were run at an individually controlled and equal value, the distribution width dropped to +/- 8.5%. If each plating location current was optimized,

as discussed above, the distribution width dropped to +/- 3%. For silver, the results were similar. The shorted rack had a distribution of +/- 7.8%. The constant current rack dropped the distribution width to =/- 5% and the individually controlled rack had a distribution width of +/- 3.3%.

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ABOUT THE AUTHORS

Thomas Beckett *is a metal finishing specialist and plating consultant for CMC Laboratories, a technology solutions company that provides analytical and labscale plating services, program management, and marketing research for clients focusing on advanced materials and all levels of electronic interconnection.*

Thomas (Tom) Beckett has been working in the metal finishing industry for more than 30 years. Beckett has extensive experience with electrochemical and finishing processes such as cleaning, phosphating, organic finishing, and base metal plating, including nickel-chrome, precious metals, electroless nickels and gold plating. Beckett has expertise in laboratory procedures, wet analysis, and analytical instrumentation. Beckett has also designed and installed plating equipment for PWB's, nickel-gold tab lines and other specialty installations.

Beckett's professional record includes metal finishing engineering at CMC Wireless Components and Nelco, Inc., where he focused on solving existing issues to improve manufacturing processes, productivity and yield. Tom currently provides professional plating engineering assistance through his company, Tom Beckett Electrochemical Consulting.

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DETERMINATION OF PHOSPHORUS IN ELECTROLESS NICKEL DEPOSITS

BY DR. V. PERSITS, ISRAEL AEROSPACE INDUSTRIES LTD, PETAH, TIKVA

The term "electroless process" is used to describe methods of plating by means of chemical reduction. Electroless nickel is produced by reducing nickel ions from solutions which contain phosphite, boron or hydrazine compounds. Electroless nickel deposits are not pure nickel but contain substantial amounts of phosphorus. The phosphorus content can be varied, normally between 2–13%, to control strength, ductility, stress, magnetic properties and structure. The phosphorus content of deposits is strongly affected by the bath pH; phosphorus content increases with decrease in pH. Acid baths in common use produce deposits containing about 7– 13% phosphorus. An increase in hypophosphite concentration increases the phosphorus content of deposits from a bath of given pH. The phosphorus content of deposit is affected by bath temperature. Heat treatment at 400°C results in precipitation of an intermetallic Ni3P phase and grain growth. Deposits containing about 7% (wt) phosphorus consist of 50% (vol) Ni_3P and 50% nickel. Lower phosphorus deposits consist of Ni_3P in nickel matrix and the reverse for higher phosphorus deposits. High phosphorus contents obtained in solutions with a low pH and a high ratio of phosphate to nickel ions favor high strength and low stress. The alloys are supersaturated solid solutions of nickel phosphide in nickel.[1]

With the manufacturing necessity and the inability of the exact determination of phosphorus on the level 7%– 13% in nickel electroless deposits by EDS method (Energy Dispersive Spectrometry) were examined the methods of the determination of phosphorus in nickel electroless deposits, using chemical methods. Phosphorus analyses embody two general procedural steps: conversion of the phosphorus form interest to dissolved orthophosphate and the determination of dissolved orthophosphate, using suitable chemical method. For the determination of phosphorus in electroless nickel deposits were tested gravimetric and photometric methods.

In gravimetric method, the determination of phosphorus- heteropolyphosphormolybdate $(NH_4)_3H_4[P(Mo_2O_7)_6]$ is precipitated washed, dried and weighed.

The gravimetric method for the determination of phosphorus in different samples, for example–steels, cast iron is accurate and often used for the check work, where a substance is determined more than one method [2,3].

SUMMARY OF THE METHOD

The deposit is dissolved in nitric acid and the phosphorus is oxidized by means of potassium permanganate in acidic conditions. Ammonium molybdate is added and reacts with phosphorus (V) to form yellow precipitate of the heteropolyphosphor molybdate $(NH_4)_3H_4[P(Mo_2O_7)_6]$

EXPERIMENTAL

Reagents and apparatus:

All the materials were reagents grade and were used without further purification.

Distilled water was used in the preparation of all solutions. Solutions were stored in glass and polyethylene bottles. Used deionized water (μ – 1-2 microSiemens)

Phosphorus standard solution (1 ml = 1.0 mg P)

Transfer 2.292 g of anhydrous Na_2HP0_4, previously dried to constant weight at 105°C, to a 500-ml volumetric flask. Dissolve in about 100 ml of water, dilute to volume and mix.

Ammonium molybdate solution (acidic):

- **Part A: Add 50 ml NH_4AOH (conc.) to 300 ml water. Add 80g of ammonium molybdate $[(NH_4)_6Mo_7O_{24} \times 4H_2O]$ (M.w. = 1235.9) and heat to dissolve. Cool and mix.**
- **Part B: Add 400 ml HNO_3 conc. (d = 1.41 g/ml) to 300 ml water.**

Finally, add part A dropwise into part B with permanent mixing.

PROCEDURE

Weigh accurately to the nearest 0.001g a sample of a 1.0– 2.0 g of a deposit and transfer the sample to a 250 ml Erlenmeyer flask. Add about 100 ml of 1:1 nitric acid and boil gently to complete dissolution of the sample and to expel brown fumes of nitrogen oxides. Cool, transfer the solution to a 250 ml volumetric flask, fill to the mark and mix. (Solution A)

$$3Ni_3P + 41HNO_3 = 3H_3PO_4 + 9Ni(NO_3)_3 + 14NO + 16H_2O$$

$$Ni_3P + 13HNO_3 = H_3PO_3 + 3Ni(NO_3)3 + 4NO + 5H_2O$$

Transfer 20 ml aliquote sample to a 200-ml beaker, add 100 ml of water and 5 ml of 4% $KMn0_4$. Boil for a few minutes and then destroy the excess of KMn04 and MnO^2 with drop by drop addition of 30% $NaNO_2$. Boil for a few minutes to expel nitrogen oxides.

$$5H_3PO_3 + 2KMnO_4 + 6HNO_3 = 5H_3PO_4 + 2Mn(NO_3)_2 + 2KNO_3 + 3H_2O$$

$$4KMnO_4 + 2H_2O + 4HNO_3 = 4MnO(OH)_2 + 4KNO_3 + 3O_2$$

$$MnO(OH)_2 + KNO_2 + 2HNO_3 = Mn(NO_3)_2 + KNO_3 + 2H_2O$$

Cool and neutralize with 25% NH_40H to pH 7-8 (by pH-meter). Add 1-2 drops of (1:1) $HN0_3$ to dissolve the precipitate. Add 10g of NH_4N0_3. Heat to 45°–50°C (with water bath), add 50 ml of acidic ammonium molybdate solution drop wise and 2 drops of 25% NH_4OH. Mix the solution with precipitate for 1-2 minutes and let it stand for 2-3 hours.

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 = (NH_4)_3H_4[P(Mo_2O_7)_6] + 21NH_4NO_3 + 10H_2O$$

Filter the solution through weighted glass filter ("F" or "4" porosity) with pore size 5 µm maximum. Wash the precipitate 6-8 times with small portions of the solution (2% $HN0_3$ + 5% NH_4N0_3) and cool deionized water (CO_2 free) until the washings are free of acid, as indicated by phenolphtalein test (5 drops of washing water + phenolphtalein + 1 drop of 0.1 N NaOH = pink color). Dry the filter and the precipitate in the oven at 110°C for 1-2 hours. Cool in a dessicator and weigh.

Calculation:

$$P\% = \frac{(A - B) \times 0.0164 \times 100}{C}$$

Where:

A - weight of filter and precipitate $(NH_4)_3P0_4.12Mo0_3$, g.

B - weight of filter, g.

C - weight of sample, taken in aliquote of 20 ml, g.

Photometric method has the advantage of economy in apparatus and is selective. It was found that better precision and greater sensitivity were obtainable by using the determination of phosphorus by the molybdivanadophosphoric acid method [4].

REAGENTS

Phosphorus solution (0.4 mg/ml):

Transfer 40 ml of 1 mg/ml standard solution into a 100- ml volumetric flask. Add 15 ml (1:5) $HN0_3$, dilute to mark and mix.

Ammonium molybdate solution (100 g/l):

Dissolve 100 g of ammonium molybdate $[(NH_4)_6Mo_7O_{24} \times 4H_2O]$ in 600 ml of water at 50°C and dilute to 1 liter. Filter before using.

Ammonium vanadate solution (2.5 g/I):

Dissolve 2.5 g of NH_4V0_3 in 500 ml of hot water. When dissolution is complete, add 20 ml of (1:1) $HN0_3$, cool and filter if necessary and dilute to 1 liter.

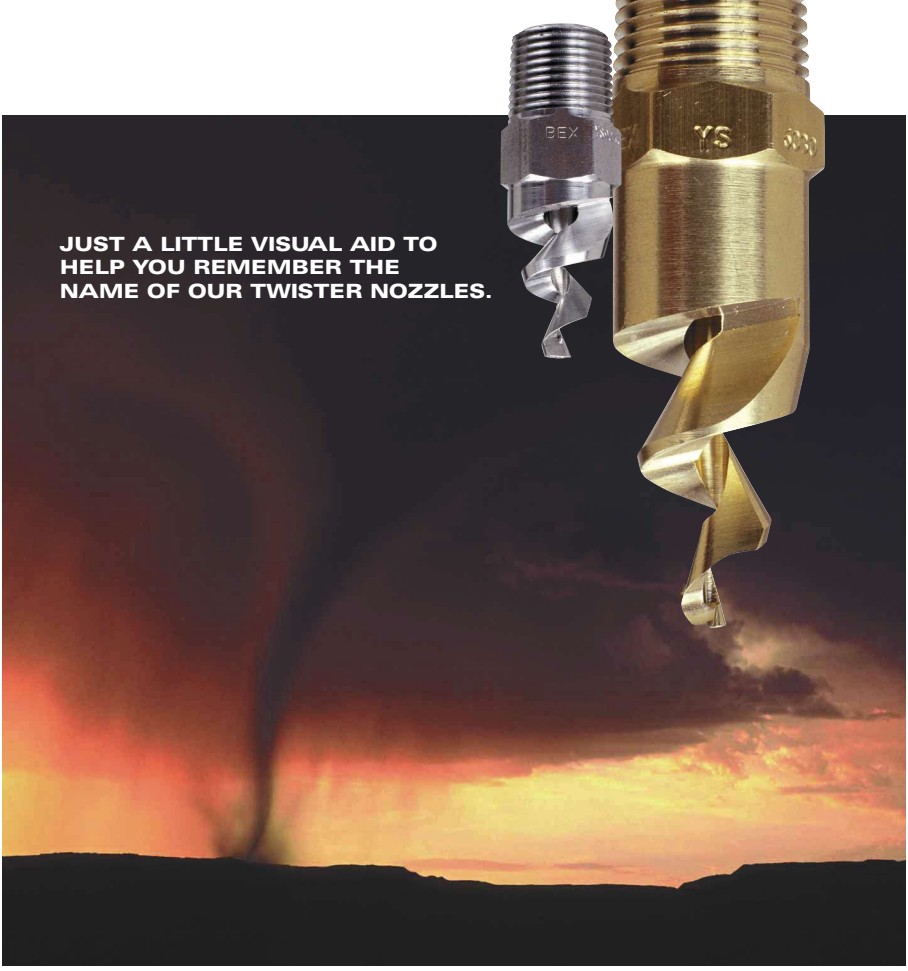
SUMMARY OF PHOTOMETRIC METHOD

Yellow colored complex is formed when an excess of molybdate solution is added to an acidified mixture of vanadate and orthophosphate. Photometric measurement is made at approximately 470 nm.

PROCEDURE

Transfer 1.5 ml aliquote sample (from solution A) to a 150-ml flask and add 20 ml of (1:5) $HN0_3$ and cover. Boil gently for about 1-2 minutes. Add 2 ml of 1% KMn04 solution and heat just to boiling. Add 1ml of 3% H_20_2 solution and swirl the flask until excess of $KMn0_4$ is destroyed and the solution clears. Add 10 ml

plating processes, procedures & solutions



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of a vanadate solution and boil gently until the solution is a clear light bluish-green, which indicates that excess of H_20_2 has been destroyed. Cool to the room temperature. Transfer the solution to a 100-ml volumetric flask and dilute to about 80 ml with water. Add 10 ml of a molybdate solution, dilute to mark and mix. The color of the phosphorus complex develops within 5 minutes and is stable for at least 1 hour.

The recommended concentration range is 0.1–1.2 mg of phosphorus in 100 ml of solution. Measure the absorbance of the sample, reference and calibration solutions at 470 nm. Plot the photometric readings of the calibration solutions against mg of phosphorus per 100 ml of solution. Convert the photometric reading of the test solution to mg of phosphorus by means the calibration curve.

Calculation:

Where:

$$P\% = \frac{(mg\ (P) \times 250 \times 100 \times 1g}{A \times B \times 1000} = \frac{(mg\ (P) \times 25}{A \times B}$$

A- ml of the sample, used for photometry.
B- g of the sample (into 250 ml).

The tables 1, 2 show that the proposed methods can be applied successfully for the simple and precision determination of phosphorus in electroless nickel deposits without a significant systematic error.

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BIO

Dr. Vera Persits was granted her M.Sc. in chemistry from Rostov State University in 1971, earning her Ph.D. in analytical chemistry from Leningrad (currently Saint Petersburg) state university in 1982. The theme of the doctorate was "Investigation of Process of Electro-thermal Atomization and Their Utilization for the Elaboration of Methods for the Determination of Zinc, Cadmium, Lead, Tin, Bismuth and Antimony in Steels and Alloys." Dr. Vera Persits authored and co-authored 20 articles and has two patents in analytical chemistry. Since 1992, Dr. Persits has worked at IAI as a chemistry engineer in the field of plating.

GOLD POST-DIP TO IMPROVE CORROSION-RESISTANCE PROPERTIES

BY OLAF KURTZ, JÜRGEN BARTHELMES, FLORENCE LAGORCE-BROC, TAYBET BILKAY, MICHAEL DANKER, AND ROBERT RÜTHER, ATOTECH DEUTSCHLAND GMBH, BERLIN, GERMANY

Electrolytic or electroless gold depositions are used to provide a conductive and corrosion-resistant final coating for electronic applications. Because copper or copper alloys are the predominant choice for the base material, a nickel or nickel–phosphorus layer is often used as a diffusion barrier.[1,2]

Cost efficiency and reduced precious metal content are the main criteria to satisfy the ever-increasing technical and quality requirements for components used in the electronic, telecommunications and automotive industries. The dramatic increase in the price of gold within the last decade reached its highest position in March 2008, amounting to $1,000 per ounce.[3]

The gold coating thickness must be adequate to ensure pore freedom and provide sufficient corrosion resistance. Each defect or pore formation within the gold or barrier layer can lead to corrosion, resulting in both a reduced contact area and an increase in contact resistance. In general, a pore-free deposit is normally achieved at a deposit thickness of 0.5 to 2 µm,[4,5] depending on the substrate type and pretreatment process used.

For cost efficiency, the combination of palladium–nickel and ultra-thin gold coatings are used as an alternative to conventional gold deposits.1,[6,7]

As an alternative route, special pre-treatment such as electropolishing and the use of "inexpensive" electrolytic nickel–phosphorus barrier layers increase corrosion resistance at the expense of a significant reduction in gold thickness.[8,9]

Post-treatments may also help. However, care must be taken to ensure that they do not impair the essential surface properties (i.e., contact resistance and solder or bonding functions needed for most connector applications). Lubricants are

Process Parameters	*Optimum*	*Process*
pH	5.8	5.7–6.0
Temperature	50°C	20–60°C
Agitation	Required	Required
Immersion time	*Reel to Reel*	*Reel to Reel*
	5 sec	3–10 sec
	Rack and Barrel	*Rack and Barrel*
	2 min	1–3 min

Table 1: Process Parameters for Betatec Gold Post-Dip

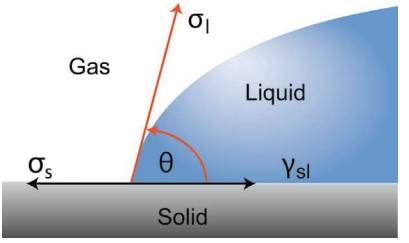


Figure 1: Contact angle determination on a solid surface according to Young.[12]

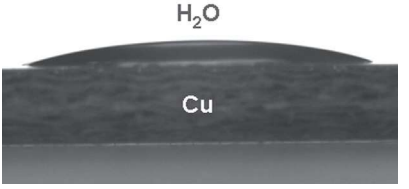


Figure 2: Wetting of an acid-activated copper surface by water measured and recorded with a tensiometer.

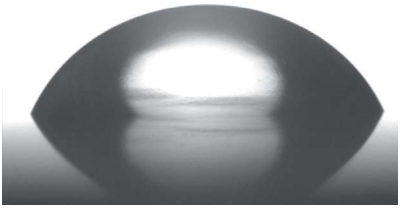


Figure 3: Wetting of an acid-activated copper surface by water after treatment with Betatec gold post-dip, θ = 76°.

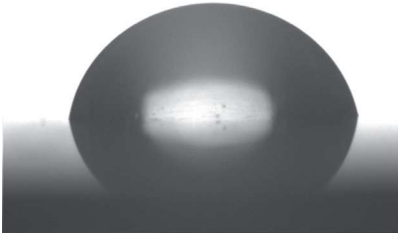


Figure 4: Wetting of an acid-activated nickel surface by water after treatment with Betatec gold post-dip, θ = 92°.

often used as post-dips because they improve lubrication and abrasion properties while simultaneously avoiding fretting corrosion. Nonetheless, because most lubricants, chemically speaking, are insulators a negative influence on the surface contact properties is observed.

This article will describe such an aqueous post-dip treatment, providing corrosion resistance for various types of metal surfaces without impairing the contact resistance and other technical properties, while free from toxic or hazardous substances that may cause harm to the environment and living organisms.

BETATEC*: POST-DIP TO IMPROVE CORROSION RESISTANCE

The innovative Betatec aqueous gold post-dip requires a treatment time of only a few seconds after applying the gold deposit. Table 1 summarizes the process parameters. Properties of the post-dip include:

- **Imparting hydrophobic (water repelling) surface behavior**
- **Repelling the action of corrosive vapor**
- **Improved corrosion resistance.**

CONTACT ANGLE MEASUREMENT

Contact angle measurements were carried out for wetted gold surfaces, before and after treatment, to determine the hydrophobic properties of Betatec post-dip. Measurements were carried out using a contact angle measuring device (tensiometer). A mean of 30 individual measurements was used to minimize errors.

The wetting of a solid surface with a liquid depends on the respective surface

energies. The surface energy consists of the potential energy of the molecules or atoms on a surface (specific surface energy). The energy results from the ratio of work per surface increase ΔW to the surface growth ΔA. For liquids, this surface energy equals the surface tension.[10,11]

$$\sigma = \Delta W/\Delta A \text{ [N/m or J/m}^2\text{]}$$

Thomas Young established the relationship between the free surface energy σ_s of a solid, the interfacial energy γ_{sl} of the solid and the suspended drop, the surface tension sl of the liquid and the contact angle (θ) between the vectors sl and γ_{sl} (see Fig. 1).[12]

Young's formula can be described as follows:

$$\cos\theta = \sigma_s - \gamma_{sl}/\sigma_l$$

(Indices s and l represent "solid" and "liquid," respectively).

The most stable thermodynamic state of a system is that of lowest (free) energy. Therefore, each system strives to avoid surfaces possessing high surface energy or tending to reduce surface contact. It is for this reason that materials are slightly wetted with materials of a low surface energy. The wetting angle can be within the following limits: $0° < \theta < 180°$. A solid can be wetted by a liquid if the contact angle is $\theta < 90°$.

A pure copper surface is nearly completely wetted by water. Figure 3 shows such a wetting with a very small contact angle that lies outside measurement accuracy. In this case, the surface energy of the copper (1.85 J/m^2) is significantly higher than the energy of the water (0.05 J/m^2): $\sigma_l << \sigma_s$.[13]

Surface energy is also influenced by surface preparation. The sample shown in Figure 2 was activated (i.e., all oxides were removed from the surface prior to measurement). For an inactivated copper surface the contact angle increases to approximately 60°. An oxide layer, therefore, leads to a more hydrophobic copper surface.

For meaningful measurements and to remove the aforementioned strong influence, all post-dip treated metal combinations on top of the copper substrate (including copper, nickel, gold, and a combined nickel/gold layer) were activated (removal of the oxide layer) prior to treatment with Betatec.

The copper substrate standard immersed in Betatec post-dip provided an increased contact angle of approximately 76° (see Fig. 3).

Tests were also carried out for a nickel surface (surface energy of nickel is 2.45 J/m2) with a measured contact angle of approximately 92° after treatment with the post-dip.[14] Hence, despite nickel possessing considerably higher surface energy, thereby making it more hydrophilic, Betatec post-dip treatment was very effective at imparting hydrophobic surface properties (see Fig. 4).

Similar testing was undertaken with pure gold surfaces (surface energy of 1.5 J/m2) that were also made water-repellent, achieving a contact angle of 87°.15 In these cases, an almost complete wetting of the gold surface was achieved without the post-dip treatment. For the final contact angle measurements, copper sub-

strate was plated with 1.5 µm nickel (followed by 0.3 µm gold). The non-treated sample showed close to 100% complete wetting effect after activation. These same samples after post-dip treatment provided a contact angle of 76°. The results from all these tests highlight the strong hydrophobic properties of Betatec post-dip for both pure metal surfaces and electrodeposited nickel/gold.

CORROSION RESISTANCE STUDY

Reference standards were used to assist corrosion inspection and sample assessment.[15] Typical laboratory corrosion test conditions utilize an artificial atmosphere provided by a climate chamber. The atmosphere can be carefully controlled with respect to humidity, temperature, and the desired concentration of corrosive gas or gas mixtures (e.g., sulphur dioxide, chlorine, nitric acid, etc.).[16–18]

Salt spray tests are also widely used, particularly the "neutral salt spray test," which simulates the high salt content found in seawater or that used on highways during cold winter periods.[19] In general, the choice of test was dictated by the application and the expected corrosion severity.

	Temp. °C	Components
Step 1	65	Soak Cleaning (Uniclean 260)
Step 2	45	Cath. Cleaning (Uniclean 260)
Step 3	RT	Activation (Uniclean 675)
Step 4	55	Nickel Sulphamate (Nickel Sulphamate HS, 1.5µm)
Step 5	40	Gold-Cobalt (Aurocor HSC)
Step 6	50	Au- Posttreatment (Betatec)

Figure 5: Process sequence for the plating of copper-based samples.

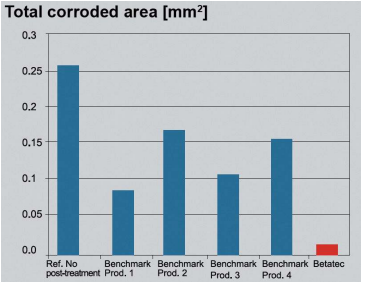


Figure 6: Corrosion inhibitor comparison (as corroded area after NAV testing) for Betatec and conventional products.

NITRIC ACID VAPOR (NAV) TEST

The ASTM B-735 standard uses the "nitric acid vapor test" to evaluate porosity, and the extent of corrosion is microscopically measured by a quantitative pore count per surface area. Test requirements include:

- **Temperature: 20–25°C**
- **Air humidity of approximately 55% (never exceeding 60%)**
- **Acid vapor provided from 70% w/w nitric acid reagent.**

The procedure involves placing nitric acid into a dry chamber or desiccator, followed by a delay period of approximately 30 minutes prior to introduction of the corrosion test samples. The ASTM standard specifies a duration of 60 min for gold thickness to 2 µm.

Required test time as a function of gold deposit thickness20:
60 ± 5 min for Au = 0.6–2.0 µm
75 ± 5 min for Au = 2.0–2.5 µm

The actual duration used for this study was extended to 120 minutes to provide an increased severity of two times the ASTM standard.

The gold thickness used throughout this study was fixed at 0.3 µm (well

Sample	Ni-Sulphamate HS [10 A/dm²]	Aurocor SC [µm]	Post-treatment
0	1.5 µm	0.3	None
1	1.5 µm	0.3	Benchmark 1
2	1.5 µm	0.3	Benchmark 2
3	1.5 µm	0.3	Benchmark 3
4	1.5 µm	0.3	Benchmark 4
5	1.5 µm	0.3	Betatec

Table 2: Part of the Sample Matrix Highlighting the Benchmark Products

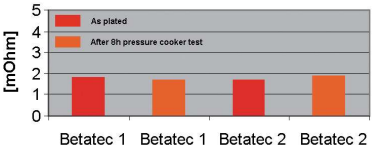


Figure 7: Stable contact resistance values before (red) and after (orange) an 8-hour pressure-cooker test.

below that used in previous studies). Samples removed from the chamber were oven-dried at 80°C prior to pore examination, which was undertaken using a microscope together with Aquinto a4i docu/analysis software. Calculations involved pore count per area and individual pore diameter, providing an overall % corrosion area in accordance with the ASTM specification. Pores were size-categorized as follows:

- **<0.05 mm**
- **0.05–0.12 mm**
- **0.12–0.4 mm**
- **>0.4 mm**

For each test specimen, a target area of 36 mm² was used for each set of measurements. The process sequence used to prepare the samples was as per Figure 5.

A total of 200 samples with a target gold thickness 0.3 µm were prepared and examined alongside samples treated with commercially available corrosion inhibitors (Benchmarks 1–4). Table 2 highlights a small fragment of the experimental matrix used.

After being subjected to 2 hours of NAV testing, all samples were categorized by calculating and evaluating the pore count per corroded surface area. Figure 6 compares the calculated corrosion area of the samples.

CONTACT RESISTANCE MEASUREMENT

Extensive measurements establish that treatment with Betatec post-dip does not cause an increase in contact resistance. The parameters: I = 10 mA, U = 20 mV, F = 5 cN were used to satisfy the EN IEC 512 standard. The mean value of 30 measurements was used for each test sample.

		ZCT	F_{MAX}
Reference	As plated	0.34 sec	1.91 mN
	Pressure cooker 4 h	0.36 sec	1.49 mN
	Pressure cooker 8 h	0.81 sec	0.71 mN
Betatec	As plated	0.33 sec	2.07 mN
	Pressure cooker 4 h	0.35 sec	1.54 mN
	Pressure cooker 8 h	0.80 sec	0.56 mN

Table 3: Results Demonstrating no Loss to Solderability After Post-Dip Treatment

Steam-aging: The "pressure cooker test" is used to promote corrosion, diffusion, and deposit cracking. This test was conducted for a duration of 8 hours, after which contact resistance measurements were carried out. The pressure cooker test parameters included:

- ➢ **high temperature** **105 °C**
- ➢ **high humidity** **100% RH**
- ➢ **high pressure** **1.192 atm**

Results inferred no increase in contact resistance after 8 hours of exposure. Figure 7 depicts little change in contact resistance values for Betatec 1 and 2 test samples, before and after the pressure cooker test, using the very low tracking force of 5cN.

SOLDERABILITY STUDY

This study was carried out to confirm that Betatec post-dip would not effect solderability properties. The gold thickness was reduced to 0.1 µm for these solderability tests.

The lead-free alloy SAC (SnAgCu) was used as solder with the following conditions:

Solder	**SnAgCu**
Temperature	**245°C**
Density	**7.5 mg/mm3**
Immersion time	**10 s**
Sensitivity	**2.5**
Submergence	**3 mm**
Velocity	**21 mm/s**

All tests were conducted in accordance with the IEC-68-2-69 standard using a Litton Kester 950 E3.5 flux. Both zero crossing time (ZCT) and wetting force (Fmax) were used to assess solderability, highlighted in Table 3.

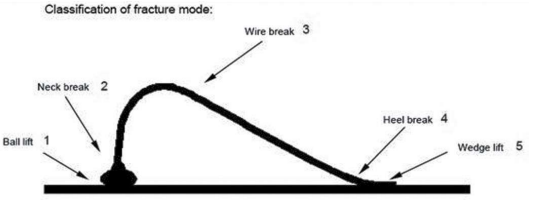


Figure 8: Crack classification rating 1 to 5, with 1 and 5 showing insufficient surface bonding. Ratings 2, 3, and 4 are acceptable.

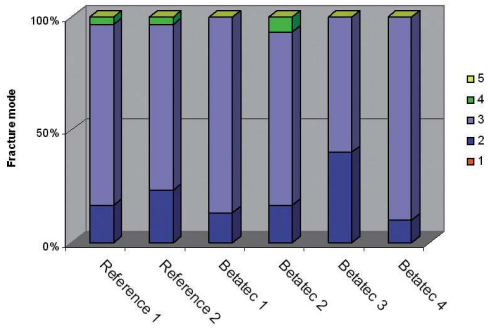


Figure 9: Thin gold wire crack rating distribution (as % of population) for Betatec-treated nickel/gold-plated samples. All samples passed the test.

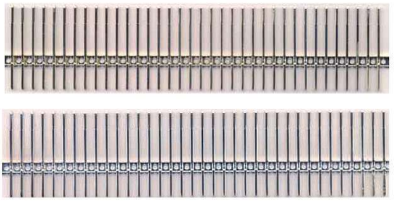


Figure 10: Strong discoloration of untreated samples compared to Betatec treatment (above) showing no discoloration after an 8-hour pressure cooker test.

BONDING PROPERTIES (WIRE PULL TESTING)

Gold-wire loops (25-µm diameter) (Au HD2) were used to determine any loss in bonding properties after Betatec post-dip treatment. A pull tester (DAGE 4000) and TS-bonder (Delvotek 5410) were used for this study.

Wire pull testing determines the quality of the gold wire bond to the surface. It consists of applying a specified upward force under the gold wire attached to the surface. The crack mechanism is studied to evaluate the bond quality.

The crack ratings in Figure 8 highlight the crack at the wire/surface interface. Ratings 1 and 5 indicate an insufficient bond with the surface, whereas ratings 2, 3, and 4 are acceptable.

Sample processing involved nickel sulphamate (Ni-Sulphamate HS) and pure-bond gold (Aurocor K 24 HF) plating, followed by Betatec post-dip treatment. To confirm measurement reproducibility, 4× samples were measured and compared to 2× untreated references. All samples passed the test with no crack ratings of 1 or 5 evident. The majority of samples provided a rating of 3 (central crack), considered the best bonding quality (see Fig. 9).

TIN SURFACE PROTECTION STUDY

To maximize cost-effectiveness (mentioned in the introduction) many connectors are plated with gold only at the functional contact region with the "solder flank" receiving a tin coating. However, the processing sequence does not allow for selective treatment of each region with different post-dips. Hence, the ideal gold post-dip candidate must ensure no detrimental effect on the properties of

		Zero Crossing Time (ZCT)	F_{max}
Reference	As plated	0.35 sec	2.89 mN
	Pressure cooker 8 h	No wetting	–0.55 mN
Betatec	As plated	0.35 sec	2.92 mN
	Pressure cooker 8 h	0.41 sec	1.49 mN

Table 4: Solderability Results for Untreated and Betatec-treated Samples on Tin Deposits

the tin but also provide preferable increased corrosion resistance.

Oxide formation of tin (evident as surface discoloration) greatly impairs solderability properties. Therefore, Betatec-treated samples were subjected to 8-hour pressure cooker tests. The results shown in Figure 10 highlight the beneficial corrosion resistance of the Betatec treatment.

SOLDERABILITY STUDY OF TIN DEPOSITS

The solderability study of tin deposits was undertaken using the same parameters and conditions used for gold. All samples were plated with 1.2 µm nickel and 8 µm tin. It is clearly apparent that without Betatec post-dip treatment, no wetting occurs within the 10-second test period. The solderability results are summarized in Table 4.

CONCLUSIONS

Comprehensive test results have been presented for a new and patented gold post-dip treatment that significantly improves the corrosion resistance of nickel/gold deposits and contributes to the reduction of gold costs. Extended NAV testing (to two times the ASTM B-735 standard) shows a significant increase in corrosion resistance for a 0.3 µm gold thickness.

It has been demonstrated that the Betatec post-dip can impart beneficial hydrophobic properties to the gold surface with subsequent blocking of pores. This hydrophobic and protective mechanism has been evaluated by water contact angle measurements on pure copper, nickel, and gold deposits together with nickel/gold plating on copper (before and after treatment with the gold post-dip).

Results show that this beneficial post-treatment has no adverse effects on electrical, solderability, or bonding properties of the gold electrodeposits. It has also been demonstrated that this treatment can provide a dramatic increase in protection of tin deposits, allowing for easy incorporation into most selective gold plating lines.

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ZINCATE- OR STANNATE-FREE PLATING OF MAGNESIUM, ALUMINUM, AND TITANIUM

BY JOHN W. BIBBER, SANCHEM, INC., CHICAGO, ILL.

For more than 80 years, the plating industry has been dependent on the use of various zincate and/or stannate solutions to assist in the plating of metals such as titanium, aluminum, and magnesium. It is becoming ever more difficult to use these solutions due to restrictive regulations—plus, they are difficult to work with. This article presents an environmentally acceptable and easy-to-work-with alternative process that does not require the metalizing of the metals to be plated or extensive cleaning and deoxidization procedures.

The process presented in this article eliminates the use of "zincates" and/or "stannates" and also negates a large portion of the extensive cleaning and deoxidation that is often required in the plating of these metals. The examples shown in this article involve the use of electroless nickel, as this is one of the more commonly plated materials on these metals and is often used as a base for the plating of other metals.

The lightness, strength, and high melting point of titanium, aluminum and various magnesium alloys make them quite desirable for use in the aerospace industry or many automotive applications. In many instances the metals need to be plated, but transition metals such as copper, chromium, nickel, etc., do not form good bonds with the light, non-transition elements.

For several decades, the plating of these metals has been accomplished by the initial application of a thin film of zinc and/or tin from what are known as zincate or stannate solutions.[1] Simple zincate or stannate solutions are nothing more than solutions of zinc oxide or tin oxide in strong sodium hydroxide or potassium hydroxide, but for best results cyanide is generally added to the solutions.[2] Other variations to the baths include mixing zincate with stannate and changing the pH and/or concentrations of the mixed solutions.[3] In addition, copper is often plated out on these metals in order to smooth out rough areas or to improve the bonding characteristics of the metals being plated out. Due to cost considerations, zincate is by far the most widely used of these solutions.[4]

CLEANING AND DEOXIDATION

With plating, more than just about any other type of metal processing, the most important aspect of the process is proper cleaning and deoxidation of the metal or metal alloy to be plated. Cleaning is the removal of surface oils and/or solid organic material, whereas deoxidation is the removal of unwanted inorganic compounds (oxides and hydroxides) that would interfere with the plating process. The exact cleaner selected will depend on the type of soil being removed and/or the metal or metal alloy being processed.

In general, a strong alkaline cleaner will give the best results on titanium, aluminum, or magnesium and their alloys. This is typically followed by a rinse in high-quality demineralized water—the rinse itself being where the actual clean-



Figure 1: Magnesium alloy "AZ91D" before (top) and after (bottom) plating with electroless nickel.

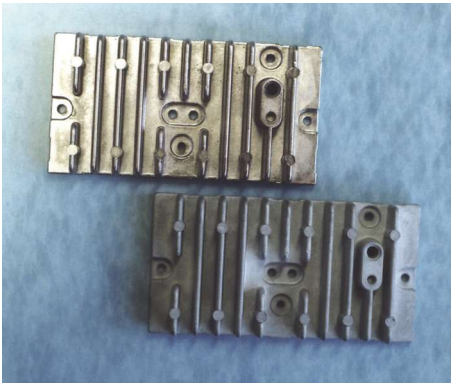


Figure 2: Cast aluminum alloy "383" before (bottom) and after (top) plating with electroless nickel.

ing takes place. The deoxidizer generally used on these metals and their alloys is a mineral acid (nitric, sulfuric, hydrofluoric, and/or hydrochloric) of low or high concentration, depending on the metal or alloy in question, followed once again by a rinse in high-quality demineralized water. In the past, these metals were in many cases deoxidized with chromic acid solutions or given chromate-based conversion coatings as a way of preventing the growth of metal oxides, and, thus, assisting in the application of the zincate and/or stannate solutions. Environmental concerns have now served to stop many of these procedures.

MAGNESIUM

Due to the extreme reactivity of magnesium and its alloys, very little plating of the pure metal or its alloys takes place. Quite often the plating is over a copper strike applied to mitigate any oxidation that may have taken place on the surface of the metal during the cleaning and deoxidation processes or that will take place on the metal after it is plated. In addition, the copper strike acts to smooth over any scratches and/or pits on the surface of the metal.[5] A commonly used procedure for the application of electroless nickel to a magnesium surface would involve the steps listed in Table 1.5 The new process being proposed would involve steps noted in Table 2.

To accomplish the newly proposed process, make the magnesium or magnesium alloy the cathode of an electrolytic cell containing a conductive emulsion of various polyamines and/or polyamides at about 15 amps per square foot for a few seconds, rinse in demineralized water, and go directly into the electroless nickel plating bath to the desired plating thickness (see Fig. 1). Subsequently rinse and then dry. The bonding surface generated by this process is at most about 400-nm thick and is self limiting in that leaving the part in the processing solution for longer periods will not cause any harm. Any excess polymer will simply go back into the processing solution to be used over again or be rinsed off.

Adhesion was excellent (baked at 375°F for one-half hour and quenched in cold water) using this process and subsequent plating of copper on the part was not a problem. In addition, it should be noted that rinsing, drying, and storing the

Step	Temperature	Duration
Alkaline soak cleaner	180–200°F	3–5 minutes
Rinse in demineralized water		
Chromic acid or phosphoric acid pickle	Ambient	30–60 seconds
Rinse in demineralized water		
Phosphoric acid–fluoride etch	Ambient	1–2 minutes
Rinse in demineralized water		
Fluoride-containing "zincate"	155–160°F	3–15 minutes
Rinse in demineralized water		
Copper cyanide strike	130–140°F	6–8 minutes
Rinse in demineralized water		
Electroless nickel plating bath to desired thickness		

Table 1: Common Procedure for Applying EN to a Magnesium Substrate

Step	Temperature	Duration
Alkaline soak cleaner	180–200°F	5–8 minutes
Rinse in demineralized water		
Deoxidize in mild acid solution	Ambient	15–30 seconds
Rinse in demineralized water		

Table 2: Zincate-/stannate-free Pretreatment Process for EN Plating

processed part for several days before going into the electroless nickel bath is possible. One simply needs to soak the part in demineralized water for about half an hour to reactivate the bonding surface before going into the electroless nickel bath. If you only want to paint the part, the surface is excellent for painting.

ALUMINUM

Every aluminum alloy will have certain unique cleaning problems associated with it and, as such, it is not possible to give an all-encompassing cleaning process for all aluminum alloys. It can be stated that plating on aluminum will in almost every instance require a zincate or stannate process after cleaning and deoxidization to maintain a receptive surface.[6]

Step	Temperature	Duration
Degreasing if necessary		
Strong alkaline soak cleaner	180–200°F	5–8 minutes
Rinse in demineralized water		

Table 3: Non-toxic Pretreatment Process for Plating on Titanium



Figure 3: Titanium bolts before (left) and after (right) plating with electroless nickel.

Due to the unusually high silicon content of most aluminum castings, they present a rather difficult surface to properly plate. These castings are generally deoxidized in fluoride-containing concentrated nitric acid solutions because nitric acid will prevent attack on the aluminum and allow the surface silicon to be removed by the fluoride. In the newly proposed process, a cleaned and deoxidized "383" cast alloy was cleaned and deoxidized, rinsed in demineralized water, and then made the anode in the polyamide and/or polyamine emulsion at 15 amps per square foot for a few seconds to generate the plating surface (in the case of aluminum it is sometimes more desirable to generate the plating surface by making the metal the anode). The casting was then rinsed and placed in the electroless nickel bath to the desired plating thickness, removed, rinsed, and then dried.

The casting showed no signs of adhesion failure when heated to 375°F for half an hour and then quenched in cold water. A freshly formed electroless nickel–plated surface could easily be plated with any one of a number of different metals. As in the case of magnesium, the parts may—if so desired—be rinsed, dried, and stored to be plated or painted at a later time. However, it is generally recommended that the parts be plated shortly after forming the bonding surface (see Fig. 2).

TITANIUM

Titanium is a rather noble metal that quickly forms a thin film of titanium dioxide when exposed to oxidizing conditions, making it very difficult to plate or paint. Quite a number of patents have been issued on the plating of titanium, most of which require extremely toxic and/or corrosive cleaning conditions,[7] and in some cases a zincate solution will be used. The new process uses the non-toxic and relatively simple process noted in Table 3.

To accomplish this process, make the titanium the cathode in a electrolytic cell containing a conductive emulsion of various polyamines and/or polyamides at about 15 amps per square foot for a few seconds, rinse, and then go into your electroless nickel bath to the desired plating thickness (see Fig. 3). Once again, the

process is self limiting in that leaving the part in the emulsion for a longer period of time will have no adverse effect, and the excess polymer will simply go back into the emulsion or be rinsed off.

This process exhibits excellent adhesion (baked at 375°F for one-half hour and quenched in cold water and/or bending 180° to check for loss of adhesion), and other metals could easily be plated on a freshly formed electroless nickel–plated surface. As with the other metals, the parts can be rinsed, dried, and stored for several days and then be reactivated for plating by soaking in demineralized water for half an hour if so desired. In addition, the surface can be coated due to excellent paint adhesion characteristics.

CONCLUSIONS

The electrolytic deposition of a thin film of various polyamides and/or polyamines on the surface of a magnesium, aluminum, or titanium surface and their alloys will allow the metals to be easily and quickly plated with other metals. This can be accomplished with far less difficulty than via the application of a thin film of zinc or tin by the use of a zincate or a stannate.

NOTES

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AESF, an officer of ASTM and a member of ACS.

HIGH-TEMPERATURE ACID COPPER PROCESS FOR PLATING THROUGH-HOLES

BY MARIA NIKOLOVA, JIM WATKOWSKI, DON DESALVO, AND RON BLAKE, MACDERMID, INC., ELECTRONICS SOLUTIONS, WATERBURY, CONN.

Electrolytic copper plating solutions are employed for many industrial applications. They are used in the automotive industry to deposit base layers for subsequently applied decorative and corrosion protection coatings. They are also used in the electronics industry, especially during fabrication of printed circuit boards (PWB).

During circuit fabrication, copper is electroplated over selected portions of the surface of the printed circuit board and onto the walls of through-holes passing between the surfaces of the circuit board base material. The walls of the through-holes are metallized to provide conductivity between the circuit layers of the printed circuit board. Thus, in many printed circuit board and semiconductor fabrication processes, electroplating has been adopted by industry as the primary deposition means for copper metallization.[1-3]

The most widely used copper plating electrolyte is based on an aqueous solution of copper sulfate, an acid electrolyte such as sulfuric acid, and various plating additives. Commonly used additives for copper metallization include inhibitors/suppressors, brighteners/accelerators, and/or levelers. The brighteners/accelerators change the nucleation process, enhancing the formation of new deposit nuclei as opposed to the growth of existing nuclei. The suppressors/inhibitors adsorb at the cathode surface uniformly, increasing the deposition over-potential. The levelers are selectively adsorbed on the protruding features or at the flat surface, and the leveling effect is a result of the diffusion control of the leveling species. The adsorption and inhibition may be further

Component	*Target*	*Range*
$CuSO_4 \times H_2O$	75 g/l	65–85 g/l
Sulfuric acid	200 g/l	190–220 g/l
Chloride	75 ppm	60–90 ppm
HT 100 Make-up	8 ml/l	6–10 ml/l
HT 100 Wetter	Dosing during the plating	
HT 100 Brightener	0.8 ml/l	0.6–1 ml/l
Temperature		22–40°C
Current density	2.0–2.5 ASD	1.0–4.0 ASD

Table 1: Process Parameters

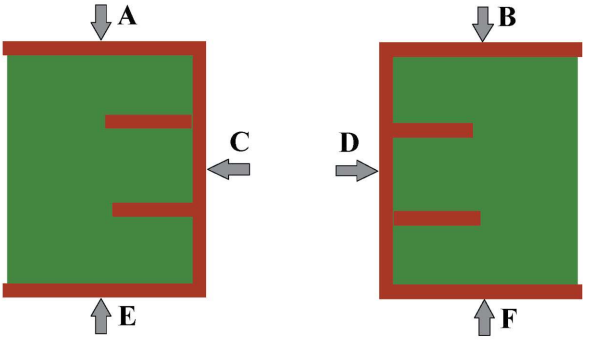


Figure 1: Thickness of copper plated on the surface and in the through-hole.

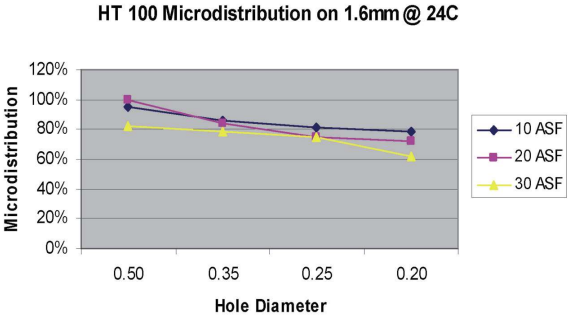


Figure 2: HT 100 microdistribution on 1.6 mm measured at 24°C..

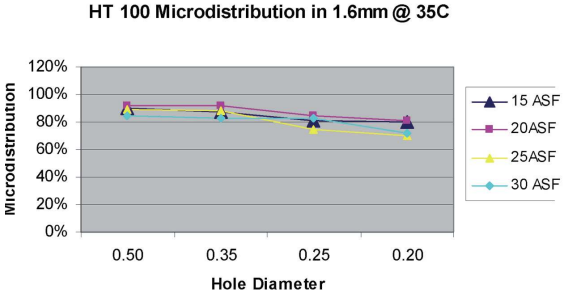


Figure 3: HT 100 microdistribution on 1.6 mm measured at 35°C.

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The thermal charac-
ratures are adversely
affected and reliabili-
ty performance
decreases. Failure
occurs during the sol-
dering operation that
follows plating.Over
the past few years,
printed circuit board
fabrication has dra-
matically increased in
geographic areas with
hot climates. In order
to maintain the
desired temperature
in these areas, chillers
or other cooling
methods are general-
ly needed. Thus, it is
desirable to simplify
the process in these
warmer areas to elim-
inate the need for
chillers or other cool-
ing methods while
still obtaining a
desired plating
deposit.

A new direct-current process for plating smooth, bright, and planar copper layers at temperatures up to 40°C (104°F) is described in this article. The method outlined herein yields excellent microdistribution. The organic brightener used assists in reducing the surface-to-hole thickness ratio, as well as improving the ductility and tensile strength of the copper deposit. Furthermore, the thermal characteristics of the deposited copper are excellent.

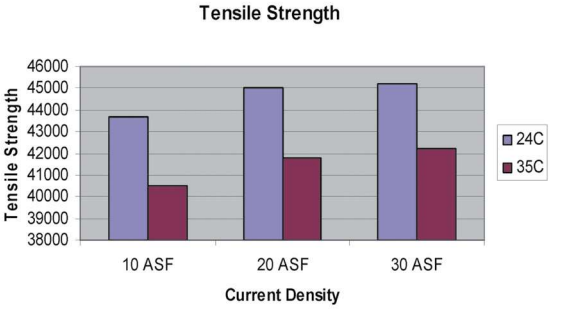


Figure 4: Tensile strength measured at 24°C and 35°C..

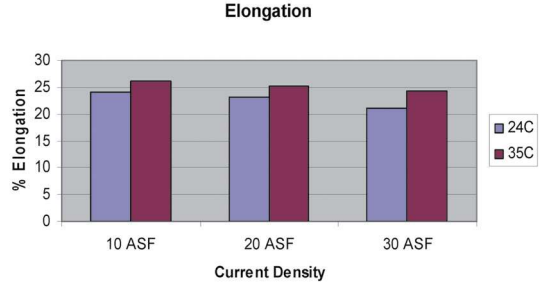


Figure 5: Elongation measured at 24°C and 35°C.

ACID COPPER BATH CONSTITUENTS

The developed process was formulated for high-volume rigid PWB production. A sulfate-based copper plating system that is well established for PWB fabrication was utilized. The method presents low operational costs and is easy to control. The development work goal was to achieve a process that is temperature tolerant up to 40°C (104°F). The bath composition, as well as the plating parameters, are given in Table 1.

HT 100 Make-up is a mixture of wetter/suppressor that aims to improve start-up and decrease dummy plating time for new baths. It is used only for new make-ups and after carbon treatments. HT 100 Brightener is responsible for copper grain refinement and internal stress reduction. It also has a leveling effect to smooth rough holes. HT 100 Wetter is a combination of organic additives that is used for replenishment during the plating process.

TEST VEHICLES

The test vehicle used in the process evaluation was 1.6-mm thick boards with various-sized through-holes. The through-hole diameters were 0.2, 0.25, 0.35, and 0.5 mm. The process flow included the following operations:

Acid cleaner: Wets the hole and removes light soils.

Rinse Micro-etch: Etch undercuts and remaining debris to ensure excellent copper-to-copper adhesion.

Rinse Acid dip: Acidifies copper surface prior to plating.

The plating was performed at current densities of 1.0, 1.5, 2.0, 2.5, and 3.0 ASD. The solution temperature was in the range of 22–40°F.

PROCESS FEATURES

Surface Appearance. Fine-grained deposits were obtained from this electrolyte. Plated copper was smooth and leveled inside the hole. No thin copper at the knee of the holes was observed. In addition, no plating folds or thin areas inside the through-hole were measured. Plating thickness was consistent throughout the

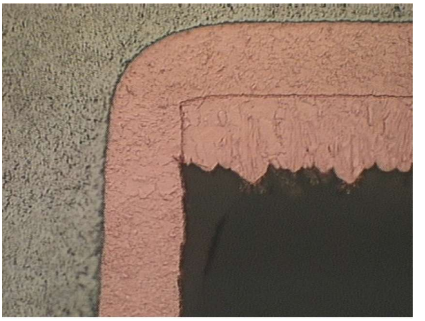


Figure 6: Cross section of 0.5-mm through-hole after 6× solder shock test.

barrel of the hole.

Microdistribution: Through-Holes. The throwing power of the plating electrolyte is very important for plating through-holes. Poor throwing power can result in non-uniform copper thickness in the hole, which will result in poor component contact.

The microdistribution was the measurements of the amount of copper plated in the center of the hole as a percentage of the copper thickness on the board surface, as shown in Figure 1. The microdistribution values were calculated using the following equation:

$$\text{Microdistribution} = [(C + D)/2 \cdot 100]/[(A + B + E + F)/4]$$

Figures 2 and 3 show the data for microdistribution obtained at various current densities and temperatures. Good distribution values were measured across a wide current density range. Bath performance was consistent across temperatures ranging 24–35°C.

Tensile Strength and Elongation. Tensile strength and elongation of plated copper were measured in accordance with IPC TM-650 Test Methods Manual, 2.4.18.1. The results from the measurements are demonstrated in Figures 4 and 5. Plating at all conditions meet IPC specifications. According to the results, increasing current density increases tensile strength, whereas increasing current density lowers elongation.

Through-Hole Reliability: Thermal Characteristics. Solder shock resistance testing per IPC TM-650 2.6.8 was used to study the thermal characteristics of plated boards. Solder shock conditions were 10-second float at 288°C for six times. The thermal integrity was excellent for all of the tested through-hole sizes. Neither corner cracks nor barrel cracks were observed, as shown in Figure 6, across the temperature range studied.

Process Control. The additives are easily controlled using conventional CVS analysis, but Hull cell tests can also be used to control bath performance. The additive consumption changes insignificantly with the temperature increase, and the organic additive can be mixed together for auto-dosing during plating.

Equipment. Air/no air solution agitation were studied, and eductor nozzles were used. There was no difference in the appearance properties of the plated copper with respect to air agitation or the eductor nozzles.

CONCLUSIONS

A new process has formulated for high-volume rigid PWB production, one that

is tolerant of temperatures up to 40°C. Excellent results were achieved at high temperatures, but this new process also runs very well at lower temperatures. Furthermore, the process can be used with either air or eductor nozzles, and the electrolyte is CVS analyzable or Hull cell controllable. Copper deposited using this system is bright, leveled, with enhanced microdistribution, and has excellent mechanical and physical properties that meet the IPC standards.

NOTES

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DECORATIVE CHROMIUM PLATING

BY DONALD L. SNYDER
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Electrodeposition of decorative chromium is the principal means of imparting the physical and chemical properties of chromium to the surface of less expensive and easier-to-form materials such as steel and plastics. The most desirable properties of chromium as a metal coating are its inherent protective and decorative characteristics. The deposit's high reflectivity is retained in service because of chromium's excellent lubricity and resistance to tarnish, corrosion, wear and scratches.

Decorative chromium is almost exclusively plated over a nickel electrodeposit, which can be plated over substrates such as plastics, steel, aluminum, copper alloys, and zinc die castings. Nickel is preferred because it protects the substrate from corrosion, helps to give chromium a pleasing bluish-white decorative appearance, and is protected from surface oxidation by the chromium. Stainless steel is the only substrate that is frequently plated directly with chromium, but a nickel preplate before chromium is also used. Multiple or single layers of nickel and copper can precede the chromium deposit depending upon the intended use of the part. The appearance of the chromium deposit can be significantly altered by using bright, dull, satin or mechanically modified nickel deposits preceding the chromium deposit. Decorative chromium deposits typically are plated in the 2-20-millionths-of-an-inch range. Thicker deposits are usually referred to as functional chrome and tend to be duller and contain visible cracks.

The traditional chromium deposit is produced from an electroplating electrolyte containing hexavalent chromium ions. About 1975, a chromium electrolyte containing the less toxic and less hazardous trivalent chromium ion was introduced to replace decorative hexavalent chromium electroplating. Depending upon the process, trivalent chromium electrolytes can either produce a metallic white deposit almost identical in appearance to the bluish white hexavalent chromium deposits, a deep-looking pewter or stainless steel appearing deposit or almost black decorative deposits. In almost all chromium plating applications, both hexavalent and trivalent chromium deposits are interchangeable with each other; however, one or the other process might offer unique advantages. For example, the cost for hexavalent chromium solutions is typically lower than that for trivalent. However, the fluoride used in many hexavalent chromium processes will etch substrates, such as copper and steel, resulting in metallic contamination of the plating bath which could increase operating problems and rejects. Trivalent chromium processes typically do not contain fluoride but will dissolve copper and iron. However, metallic contamination is easier to remove from a trivalent chromium electrolyte. This makes it possible to produce nickel, free nickel/chrome looking decorative parts by plating trivalent chromium directly over white copper alloys. Doing this with hexavalent chromium solutions would be problematic.

HEXAVALENT CHROMIUM PROCESSES

Hexavalent chromium electrolytes require a source of chromium and one or more

catalysts in order to plate. The formulation of the traditional process (called the conventional, Sargeant or single catalyst process) contains hexavalent chromium and sulfate as the only catalyst. When fluoride is added as an additional catalyst to the conventional hexavalent chromium plating bath formulation to enhance particular plating operations or the deposit's properties it is typically called a mixed-catalyst or dual catalyst bath. Proprietary organic additives can also be used to produce dual or triple catalyst baths to further enhance the plating operation and deposits.

Mixed-catalyst baths are used when their special properties are required, but they are more expensive and slightly more difficult to operate than conventional processes. They typically plate at faster speeds, have better coverage, have wider bright ranges, and are more tolerant to impurities. They are also less sensitive to current interruptions and can be plated over more passive surfaces.

The basic formulations of hexavalent chromium processes are very similar. They consist of chromic trioxide (CrO_3), which when combined with water forms chromic acid (H_2CrO_4), and the sulfate ion (SO_4^{+2}) which is added in the form of sulfuric acid or a sulfate salt. Even though chemically incorrect, solid chromic oxide is commonly referred to as chromic acid, its hydrated form.

A number of sometimes conflicting theories have been proposed to explain the very complex mechanism of hexavalent chromium electroplating. In a simplified form, they all contain the following multiple reactions.

$$CrO_3 + H_2O \rightarrow H_2CrO_4 \quad CrO_4 \rightarrow^{-2} +2H^+ \qquad (1)$$

$$2H_2CrO_4 \rightarrow H_2Cr_2O_7 + H_2O \rightarrow Cr_2O_7 \rightarrow^{-2} +2H_+ + H_2O \qquad (2)$$

Deposition reaction:

$$Cr_2O_7^{-2} + 14H^+ + 12(e) + CAT \quad 2Cr0 + 7H_2O \qquad (3)$$

CAT is the required catalyst, e.g., sulfate in addition to fluoride and/or an organic catalyst, while (e) refers to an electron. The plating efficiency of reaction (3) is approximately 20% or less depending upon the catalyst, bath chemistry and the current density.

Side reactions:

$$2H^+ + 2(e) \rightarrow H_2(gas) + a\ mist(H_2SO_4 + Cr^{+6} + H_2O) \qquad (4)$$

This side reaction consumes most of the available power not used by reaction (3). The mist, a major HSE concern, can be trapped within the plating tank by the use of mist control agents or surface tension reducers.

Trivalent chromium ions are created and oxidized by:

$$Cr_2O_7^{-2} + 14H^+ + 6(e) \quad 2Cr^{+3} + 7H_2O \qquad (5)$$

$$2Cr^{+3} + 3O_2 - 6(e) \quad 2CrO_3 \qquad (6)$$

Reaction (6) is catalyzed by a PbO_2 film that naturally forms on the lead anode.

Dilute conventional formulations consist of approximately 250 g/L (33 oz/gal) chromic trioxide ("chromic acid"), and 2.5 g/L (0.33 oz/gal) sulfate. Concentrated conventional baths contain approximately 400 g/L (53 oz/gal) chromic trioxide and 4.0 g/L (0.53 oz/gal) sulfate. In practice, however, concentrations in between these are widely used.

The dilute formulation offers good coverage, moderate nickel substrate activation, and consistent current efficiency. It also has a lower solution cost, plates faster, and produces less waste to treat. The concentrated formulation gives better coverage and greater resistance to impurities and requires lower operating voltages; however, it is more expensive to make up because of its higher chromium concentration and more chromium is dragged out resulting in higher waste treatment coat.

A critical point in all bath formulations is the requirement for close control of the CrO_3/SO_4 weight ratio needed to produce consistent plating results. Ratios of between 80:1 and 130:1 are typical, with a ratio of around 100:1 being common for conventional processes. A low ratio results in relatively poor throwing and covering power and an increased limiting current density. Higher ratios result in slower deposition rates, duller deposits, increased covering power, and decreased limiting current density.

The addition of a fluoride catalyst necessitates an adjustment in the CrO_3/SO_4 weight ratio. Ratios of 170:1 to 210:1 are required, with 190:1 being most typical. The chromium concentrations for both the dilute and concentrated mixed-catalyst formulations are the same as for conventional baths; however, the sulfate concentration is lowered due to the use of the secondary catalyst.

Unlike most plating baths in which the metal, M, is present in solution as a cation, M^+, chromium is present as an anion complex, $Cr_2O_7^{-2}$, which very likely undergoes further complexing with ions such as the sulfate catalyst to permit chromium deposition. Fluoride or silicofluoride ions are extensively used today in mixed-catalyst formulations, especially in self-regulating baths. Self-regulating formulations are obtained by using sparingly soluble salts of the fluoride catalysts. This controls the catalysts' concentration because only the required amount of catalyst will dissolve. For this reason, less frequent catalyst analysis is required. Much more routine analyses and chemical control of the catalysts are needed in non-self-regulated formulations since the catalyst must be added to the bath as they are depleted. However, this offers a much wider range of operating conditions.

Chromic acid concentrations may be maintained by making frequent specific gravity determinations of the operating solution using a hydrometer. Occasionally, more accurate chromium analyses should be conducted by an analytical method specific for chromium. Chromium is consumed and dragged out of the bath. Since lead anodes are used, the chromium must be replenished by additions of chromic acid (chromic trioxide).

Sulfate concentrations should be determined frequently by using a centrifuge to measure the volume of the sulfate precipitated by the addition of barium. Occasionally, gravimetric analyses should be conducted to confirm this quick, less accurate method. Sulfate concentrations may be raised by adding sulfuric acid. To add 0.05 g/L sulfate (SO_4), add 0.0295 ml/L concentrated (66° Bè) H_2SO_4. Sulfate can be dragged into as well as dragged out of the tank. To lower the concentration of sulfate by 0.05 g/L of H_2SO_4, add 0.01 g/L barium carbonate to pre-

cipitate the sulfate. Sulfate is an impurity in other chemicals such as chromic acid. For this reason, sulfate should be controlled carefully and any sulfate present as impurities should be accounted for.

Plating tanks are typically lined with polyvinyl chloride, (PVC, Koroseal). The historical use of lead lined tanks is no longer recommended. Auxiliary equipment should be constructed of PTFE (fluorocarbon resin) or tantalum. Titanium can be used except when a fluoride catalyzed chromium process is used. A ripple filter on the rectifier is used to reduce plating current problems. A non-PFOS surfactant must be used in regions that it is restricted by regulations. Table II contains additional information.

TRIVALENT CHROMIUM PROCESSES

Decorative trivalent chromium, a safer and more efficient system, was commercialized in the mid 1970s as an alternative to hexavalent chromium processes with its many HES issues. In addition, trivalent chromium eliminated most of the operational problems associated with hexavalent chromium chemistry: high toxicity, low current efficiency, poor metal distribution, lack of coverage around holes, burns in high-current-density areas, and "white-wash." Depending on the design of the part being plated, productivity might be improved because these advantages might permit a higher rack density and lower reject rate compared to hexavalent chromium processes.

The literature contains far less information on the chemistry of trivalent chromium processes than for hexavalent. This is the result of the relative newness of the commercially successful processes, the proprietorships of the processes, and the wider differences in the chemistries used. Basically, the significant reactions in all the trivalent chromium processes are very simple.

Deposition reaction:

$$Cr^{+3} + 3(e) \rightarrow Cr^{0}\text{(metallic chromium)} \qquad (7)$$

Side reaction:

$$Cr_{+3} \rightarrow Cr^{+6} + 3(e) \qquad (8)$$

Reaction (7) requires only 3 electrons compared to the six required by hexavalent chromium processes thus doubling the electron efficiency of the process. The unwanted reaction (8) can take place at the anode under some conditions.

The electrolytes for the different trivalent chromium plating processes differ in chemistry, but they all contain a source of trivalent chromium, that is typically added as a sulfate and/or chloride salt. They also contain a stabilizing material (called a catalyst in hexchrome processes) that combines with the chromium to permit it to plate in the desired form. Salts are also added to increase conductivity in the solution. Wetting agents are used to help in the deposition reaction and to reduce the surface tension of the solution. This essentially eliminates the formation of a mist at the anode and cathode. It also helps lower the solution viscosity resulting in more solution draining from the part when compared to hexavalent chromium processes.

Historically, the two general formulations of trivalent chromium processes obtain their generic names by the method they used to eliminate the side reac-

tion (8) – single and double cell processes. The original single-cell process uses graphite anodes immersed directly into the plating solution. An interaction between the anodes and the chemistry of the process eliminated the formation of hexavalent chromium. A secondary chemical mechanism converts hexavalent to trivalent if any does appear in the solution. The anodes, which are destroyed only by mechanical means, are placed below solution level to eliminate misting. Since this process utilizes both sulfate and chloride (and boric acid), as in nickel baths, it is now commonly referred to as a mixed salt trivalent process. Just as with nickel electrolytes, the mixed chloride-sulfate formulation enhances the operation of the process. This is most noticeable in plating rate and deposit thickness (Table I). The chloride helps to make it easier for the mixed process to meet the automotive company's specification for 0.25 to 0.5 microns of chromium. Other factors are listed in Table II.

The double-cell process originally reduced the side reaction (8) by isolating the chromium containing solution from the anode through a membrane box. Because of maintenance problems and the amount of space that the anode boxes took from the plating area inside the tank, they have been almost completely replaced by insoluble metallic catalytic composite anodes with a projected life of 3 to 5 years. With the elimination of the need for an isolated anode, today this process is commonly referred to as a sulfate process. The electrolyte contains no chloride ions.

Once through the learning curve, control of trivalent chromium plating processes is typically easier than for hexavalent chromium processes. The literature says that an operator should "think nickel plating not chromium plating" when controlling a trivalent chromium process. The troubleshooting guides for trivalent chromium processes are a few lines long as compared to several pages for hexavalent chromium.

The additives are added based upon amp-hours, specific gravity, and pH. In addition, chemical analysis on a monthly basis appears to be sufficient for control. All trivalent chromium processes are far more sensitive to metallic contamination than hexavalent processes. Metallic impurities darken the deposit and alter the throwing and covering powers. However, most trivalent processes utilize a regenerateable resin to remove all common metallic contaminates directly from the working solution. Less desirable, but a quick chemical purification method or a slow dummying method can also be utilized. These methods eliminate the problems attributed to metallic contamination.

Today, most industries using decorative chromium deposits, such as the automotive/truck industry, approve the use of trivalent chromium for both interior and exterior parts. The almost complete elimination of the color difference between hexavalent and trivalent chromium deposits and the demonstrated corrosion resistance is greatly responsible for this wide acceptance. Some trivalent chromium deposits have also been found to be much more resistant to calcium chloride corrosion (Russian Mud) than hexavalent chromium deposits.

OPERATIONS

The typical operating conditions for trivalent compared to hexavalent chromium electroplating processes are shown in Table I.

EQUIPMENT

Trivalent chromium tanks and equipment are very similar to the design of nick-

	Trivalent Chromium		Hexavalent Chromium
	Mixed	Sulfate	
Chromium, g/L	15 - 25	10 - 20	100 - 200
pH	2 – 3	3.2 – 3.8	<1
Temperature, °F	70 – 120	120 - 140	90 - 120
Cathode Current Density, A/ft^2	70 - 150	70 - 150	175 - 300
Anode-Cathode Ratio	2:1	2:1	1:1 – 3:1
Anode material	Carbon	Precious metal coated titanium	Lead-Tin (7%)
Rectifier voltage	Up to 12	Up to 12	4 - 12
Agitation	Mild air	Mild air	Optional
Maximum deposit thickness, µm	> 1	≈ 0.3	> 5
Deposition rate, µm/min	0.15 – 0.25	0.02 – 0.03	0.1 – 0.18

Table I. Chromium Plating - Typical Operating Conditions

el tanks. Tank linings must be made from suitable synthetic material such as PVC, plastisol or polypropylene. Air agitation design can be identical. The sulfate/chloride mixed trivalent process uses graphite insoluble anodes that only need to be replaced when mechanically damaged. The sulfate process uses insoluble anodes with a recoatable catalytic coating. Titanium or Teflon spaghetti coils are used for heating and cooling in both trivalent processes. When converting from a hexavalent to a trivalent chromium process it is almost always better to reline or replace the tank and remove the old ventilation equipment. Even a small amount of residual lead can cause plating problems. An operational hexavalent chromium rectifier usually can be used.

The current carrying capacity of the plating racks must be designed for the amperage they will carry. They should also be designed so that the parts on the racks will utilize the bath's plating benefits and minimize the bath's negative plating characteristics. The plating amps for trivalent chromium processes are at least one half those used for hexavalent processes so the racks can be designed for the lower current. In general, racks designed for hexavalent chromium processes can be used in trivalent processes, but the reverse is not true.

Since trivalent chromium processes will not "burn" and they have greater covering and throwing powers than hexavalent processes (see Table II), parts many times can be placed closer together on the racks and high current density areas can face the anodes. The racks can be designed for optimum nickel plating. Racks used with hexavalent chromium are designed to accommodate the deficiencies of the chromium process. This increases productivity and makes shielding and robbing of the part's high current density areas, as is required for hexavalent chromium processes, unnecessary. Auxiliary anodes are sometimes necessary with hexavalent processes to obtain coverage in the recesses but might

	Trivalent Chromium		Hexavalent Chromium
	Mixed	Sulfate	
Throwing power	Good	Good	Poor
Covering power	Good	Good	Poor
Current interruptions	Completely tolerant	Completely tolerant	Intolerant
Rectifier ripple	Completely tolerant	Completely tolerant	Intolerant
Deposit structure	Amorphous	Amorphous	Crystalline
Micro-discontinuous	Yes as plated	Some	Need particle nickel
High current density	No burning	Some misplate	Burning
Ease or rinsing	Easy	Easy	Moderate (viscous)
Filtering	Occasional	Daily with carbon	Never
Conditioning/ dummying	Very seldom	Routinely on start up	Routinely on start up
Passivity of unplated surfaces	Needs post-treatment	Needs post-treatment	Natural "chromating" gives mild protection
Waste treatment	Easy ≈ 1/10 the sludge, no PFOS	Easy ≈ 1/10 the sludge, no PFOS	Moderate
Relative safety	Similar to nickel	Similar to nickel	Similar to cyanide
Misting	Almost eliminated	Almost eliminated	Heavy, need to be controlled
Odor	Almost eliminated	Almost eliminated	Strong and dangerous
Removal of impurities	Easy	Easy	Hard
Chromium contamination	Hexavalent chromium destroyed	Occasional treatment for hexavalent chromium	Treatment for trivalent chromium

Table II. Trivalent and Hexavalent Chromium Comparison

not be used with trivalent processes.

Trivalent chromium processes do not require scrubbers and, if the room is adequately ventilated, tank ventilation might not be required. In many regions, the same practices used for nickel baths apply to trivalent chromium. This is due to the almost complete elimination of misting and odor. Trivalent chromium processes have a non-PFOS mist suppressor, a low chromium concentration, and a greatly reduced toxicity and oxidizing properties as compared to hexavalent chromium. Trivalent chromium solution drains and rinses easily, thus greatly reducing the amount of chromium drag-out. If any solution does dry on the part, it is less hazardous since the chromium is in the trivalent state. It also does not stain the part.

	Bath A	Bath B	Bath C
Chromic acid, g/L	250	340	250
Fluosilicic acid, g/L	-	0.34	0.25
Acetic acid, g/L	216	-	-
Barium acetate, g/L	7.6	11	-
Temperature, °F	100	70	90
Current density, A/ft^2	40 – 90	200	150 - 450

Table III. Decorative Black Chromium Formulations

	Bath A	Bath B
Chromic acid, g/L	525	340
Sulfate, g/L	1	0.98
Fluorsilicate, g/L	7	6
Temperature, °F	90 – 105	Room - 95
Voltage	6 – 18	6 - 18
Time of plating (minutes to produce 10 millionths)	8	10

Table IV. Hexavalent Chromium Barrel Formulations

SOLUTION MAINTENANCE

The best waste treatment method is to minimize the amount of solution dragged out of the plating tank. Secondly, return as much dragged-out material as possible back to the tank. Any plating solution that cannot be recovered must be waste treated. Even though this reduces plating solution waste, reduced drag-out keeps contaminants in the plating solution, thus complicating the requirement to maintain a pure enough plating solution to obtain the required deposit properties.

Due to hexavalent chromium's poor draining characteristics and its misting, a large amount of solution is unavoidably removed from a decorative chromium plating tank. Vacuum evaporators and ion exchange are examples of methods used to return dragged-out hexavalent chromium back to the plating tank in order to save chemical and waste treatment expenses; however, due to the difficulty of removing metallic impurities from hexavalent chromium plating solutions, it is common to send a solution containing an excess of metallic impurities out for recovery.

Trivalent chromium is much more sensitive to metallic impurities than hexavalent chromium; however, the chemistry of most trivalent chromium processes makes it easy to remove metallic impurities. This eliminates the need to ever discard the solution due to normal metallic contamination. Atmospheric evaporators can be used to reduce solution volume so all the trivalent chromium that can be captured is returned to its plating tank. In most trivalent chromium processes, metallic impurities can be removed quickly by chemical precipitation or slowly by dummying. The most effective way is to use a resin treatment

directly on the plating solution to remove all common metallic impurities. This eliminates the build up of metallic impurities and excludes any change in deposit color or properties associated with metallic impurities. If a trivalent chromium plating solution has to be waste treated its cost is approximately one-tenth that of treating an equal volume hexavalent chromium.

Hexavalent chromium processes are essentially insensitive to organic contamination since the hexavalent chromium ion destroys most organics, resulting in the formation of trivalent chromium ions. Being a contaminant, an excess of trivalent chromium must be reconverted back to hexavalent chromium. The common way is to dummy at a high cathode current density (e.g., anode current density of 12 A/ft^2, cathode current density of 600 A/ft^2). Trivalent chromium processes are also relatively insensitive to organic impurities but sometimes organics must be removed. Occasional carbon filtering is sufficient for some processes while routine carbon/peroxide treatments are needed for others.

CORROSION PROTECTION

Decorative chromium deposits play an important role in the base metal protection provided by nickel/chromium systems. They offer hardness, appealing color, tarnish resistance, wear resistance, and corrosion resistance. Even though decorative trivalent and hexavalent chromium deposits are used interchangeably, there are some important differences. For example, hexavalent chromium ions impart short-term corrosion protection on non-chromium plated surfaces by "chromating" the part. Trivalent ions do not and so post-plating treatments are necessary to obtain the equivalent protection

When corrosion resistance is important, most specifications encourage or require micro-discontinuous chromium deposits. With a controlled pattern of microscopic pores or cracks, the corrosion potential between the chromium and underlying nickel deposits is spread out over thousands of corrosion sites. This reduces the anodic current on the nickel at any one site thus greatly reducing the individual corrosion rate. This results in a fine pattern of corrosion sites (Active Sites) uniformly spaced over the surface. A typical standard will specify a minimum of 10,000 micropores per square centimetre or over 30 microcracks per millimetre. Without micro-discontinuity all the corrosion potential is concentrated in a few sites resulting in unsightly, irregularly spaced, large corrosion sites.

Hexavalent chromium deposits must undergo special treatments to produce micro-discontinuity. Plating chromium over very fine inert particles that are codeposited in a nickel strike (particle nickel) over the bright nickel deposit is the typical way of producing microporous chromium. Lightly spraying the hard, brittle chromium deposit with hard 60 to 80 mesh particles produces microporous chromium at the contact points. Some trivalent chromium deposits are microdiscontinuous as plated. Deposits under about 20 millionths are microporous. Deposits over about 25 millionths are microcracked. Under some conditions these trivalent chromium deposits might not need particle nickel to obtain the desired number of Active Sites.

If micro-discontinuity is not induced, hexavalent chromium will typically macrocrack (visible to unaided eye) in service if plated over 20 millionth in thickness. Most chromium specifications requiring corrosion protection specify between 0.25 to 0.5 microns of chromium (10 to 20 millionths). Hexavalent chromium processes labelled as "Crack-free" deposits will typically macrocrack

in service since, like all chromium deposits, they are hard and brittle. Because the appearance of the part after corrosion is very important, in North America most specifications have eliminated microcracked deposits from use because they tend to lose their reflective appearance much faster than microporous deposits.

DECORATIVE BLACK CHROMIUM

Thin black chromium deposits are used for functional and decorative applications. Important functional applications include solar energy collectors for heat production and anti-glare surfaces. Decorative functions include furniture, plumbing fixtures, optical equipment, boat equipment, and automotive and builders' hardware. The decorative jet black finish enhances users' appeal for the product and so its popularity depends upon the customers' changing desire for black finishes.

As plated, black hexavalent chromium deposits have a decrease in wear and corrosion resistance. However, black chromium deposits have a greater degree of microporosity, which helps absorb oil, waxes, and paint. Along with other post-treatments, this property might be used to improve its corrosion resistance, wearability, and appearance. Dark trivalent chromium deposits have properties similar to standard chromium deposits. If extended corrosion protection is required, some post-treatments might be required. These deposits have become very desirable to designers for interior and exterior automotive parts.

Most black chromium processes are proprietary because of the difficulty of obtaining consistent plating characteristics and deposit properties. In many applications, plating black hexavalent chromium over regular chromium is recommended. For all decorative and most functional black chromium deposits, the typical thickness is [approximate] 0.25 microns. Three general formulations for black hexavalent chromium processes are given in Table III. Low carbon steel anodes can be used with plating times of up to 10 min. Most formulations will only produce a maximum deposit thickness and then stop plating due to the nonconductive nature of the deposit. To produce black deposits, barium salts are typically added to remove any traces of sulfate. Dark trivalent chromium process are all proprietary due to their complex chemistry.

BULK CHROMIUM PLATING

Plating racks are typically used to hold parts, transfer parts to and from the plating solution, and to carry the direct current to the part. Very small parts such as eyelets, screws, nuts, and bolts have high labor costs when placed individually on racks so they are sometimes bulk plated in barrels or trays; however, even under the best of plating conditions, the chromium reject rate can be very high. This is due to incomplete coverage and black/gray deposits mostly resulting from poor cathode contact and current interruption.

Under special conditions, both hexavalent and trivalent chromium processes have been used for bulk plating of parts. Table IV contains simple barrel hexavalent chromium formulations. Hexavalent chromium has been used primarily and special proprietary formulations have been developed that can produce near 100% coverage if precise control is used. Since current interruptions are not avoidable in barrels and trays, highly complexed-fluoride-containing solutions are normally used. It is extremely important that the bright nickel used prior to chromium not be passive. This is typically accomplished by plating a minimum of 0.1 mil of nickel in a barrel and, with a few rinses in between, transferring the

parts directly into the chromium tank. Since the parts are not held by a rack, poor or no contact with cathode leads is common. Contact must depend upon gravity, while being dampened by the solution, to hold the part against the cathode contact points.

To increase the likelihood of good contact and satisfactory plating, platers use low current density, low temperatures, and specially designed barrels and trays. Cathode contact points in barrels are constructed from wire mesh, solid steel liners, button contact points less than an inch apart, or steel bars that tumble the parts as they move. Large barrels with small loads also help to increase the frequency of contact and reduce temperature build up inside the confined space of the barrel. In general, the highest practical current density possible, without burning, should be used.

Screw and spiral design plating equipment are also used. The parts are put into the barrel at one end and transferred through the barrel for plating inside the threads of the screw. This permits a continuous flow of plated parts. Vibratory agitation and centrifugal force barrels are also available. In all cases, the barrels must be constructed so that the hydrogen gas generated during plating can escape from the barrel rather than being trapped and possibly exploding. Tray plating requires that parts be layered onto a metallic screen and vibrated or tumbled during plating.

Trivalent chromium solutions have recently been tried for barrel and tray plating of chromium. Since current interruptions do not hurt the deposit in trivalent chromium processes, and burning is not a problem, this technology will probably become more popular in the future.

FUNCTIONAL CHROMIUM PLATING

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INTRODUCTION

Hard chrome plating, also known as functional chrome or engineering chrome is different than decorative chrome. Decorative chrome is used as a top coat typically over a nickel or copper-nickel layer and is used to lower corrosion, give tarnish protection and improve abrasion resistance of surfaces of parts such as automotive trim, faucets and appliances. With functional chrome the essential difference is that the focus is on the properties of the deposit as they relate to wear resistance, low coefficient of friction and its resistance to corrosion. In these applications, the deposit is typically applied in thicknesses greater than 2.5 microns (0.0001"). As a functional coating it is used in a variety of industries such as hydraulic devices; automotive shocks, and valves; steel and textile industries for rolls; mold dies for plastic and steel; medical instruments; aerospace application as well as a host of other industries that enable parts to mitigate billions of dollars of loss due to wear and corrosion. Functional chrome plating has been part of our industrial life for over 85 years and while under a great deal of pressure to find alternatives it remains an essential process for industry around the world.

Over the past several years the process has come under critical review due to the toxic nature of the hexavalent electrolyte as well as some misunderstanding of some regulations. The European directives such as ELV for automobiles and RoHS, list "hexavalent" chrome as a hazardous substance. This reference is to hexavalent chromium ions within a coating: chromate on zinc or aluminum, for example, and not as it's used to produce chrome deposits. This leaves the main issue with hex chrome with the hexavalent chrome chemistry used to plate it. Both the Clean Air Act and the Clean Water Act limit the amount of chromium ions that can be discharged into the environment either through discharge of water or fumes discharged into the outside air. The Occupational Health and Safety Act (OHSA) also have restrictions on chrome to prevent the hazardous products from affecting workers that work in such environments. OSHA has done studies to determine the toxic levels and has set a Permissible Exposure Limit or PEL to ensure worker safety. The industry as a whole has embraced the regulations and as a group met their obligations. Through the efforts of the industry and its willingness to work together, the reported discharge of hex chromium ions to the water and to the atmosphere has been dramatically reduced.

CHEMISTRY

Hexavalent chromium or hex chrome is used as the electrolyte to plate functional chrome deposits. The typical bath runs between 150 to 450 g/l of chromic acid and uses one or more catalyst to create the reaction that deposits chrome. Three types of chemistries are commercially available: an ordinary chrome bath which contains chromic acid with a sulfate as a catalyst; a mixed catalyst bath which uses sulfate as well but also incorporates a fluoride compound as a secondary catalyst;

a third bath is a mixed catalyst bath that also uses sulfate but the secondary catalyst is a highly stable organic compound based on sulfur chemistry. Fluoride is typically not used in this type of bath except in special circumstances. The primary catalyst for all types of baths remains to be sulfate. Without sulfate no chrome will deposit.

The ordinary or basic formulation is still used in many applications. It is cheap and easy to maintain but does not give the enhanced physical characteristics that the mixed formulations give. In the ordinary bath the efficiency is between 7 to 15%. This means that from 93% to 85% of the electrical energy is going to generate hydrogen and oxygen as gases as shown in the basic reaction section and only 7 to 15% is going to deposit chrome.

Another type of chemistry is the mixed catalyst baths that contain a secondary catalyst system. The first of these baths was introduced in the 1950's. These baths use a fluoride type catalyst in addition to the sulfate to give faster deposit rates due to its higher efficiency. The fluoride or mixed catalyst baths were first introduced as Self Regulating High Efficiency (SRHS). They were able to control sulfate catalyst and the fluoride catalyst based on temperature adjustments. In the early days of its development these baths could operate as a decorative bath by day and a hard chrome bath by night to plate thicker deposits. The major drawback to these and all fluoride baths is that they are more aggressive and etch, or attack, unprotected parts of the work. To use these types of baths, extensive masking was required so unprotected work would not be etched or destroyed. While the fluoride chemistry was used in decorative applications as well, the short duration of plating did not give as bad an effect as the longer plating time used in functional chrome. This was a major drawback when the ID of work was not protected or masking required a lot of labor. The attack of steel or copper substrate from the fluoride etching also contributed significantly to impurities in the bath and made bath control difficult.

It was not until the late 1980's that a new type of catalyst was introduced that did not cause etching. The new chemistry used chromic acid and sulfate but now used a highly stable sulfur-based catalyst. The new bath was no more aggressive than an ordinary sulfate solution. This made the control of the bath significantly easier; reduced deterioration of fixtures, tank linings and allowed for less expensive equipment for heating and cooling. It also gave a superior deposit in terms of physical qualities. The deposit was harder and showed improved corrosion resistance.

CATHODIC REACTIONS

The deposition of chrome metal from the hexavalent state is a complex reaction but for a practical working knowledge there are three basic reactions at the cathode that allow the deposit of chrome metal to take place. First, however, we need to clarify that powered "chromic acid" is really chromium trioxide (CrO_3) and does not become chromic acid ($H2CrO_4$) until dissolved in water.

$2CrO_3 + 2H_2O \rightarrow 2H_2CrO_4 \rightarrow H2Cr_2O_7 + H_2O$ (Chromium Trioxide to Chromic acid)

$(Cr_2O_7)^{-2} + 12\ e^- + 14H^+ \rightarrow 2Cr^0 + 7H_2O$ (metal is formed)

$2H^+ + 2e^- \rightarrow H2$ (Generation of hydrogen gas)

$(Cr_2O_7)^{-2} + 6\ e^- + 14H^+ \rightarrow 2Cr_{+3} + 7H_2O$ (Formation of Cr (III)[1])

ANODE REACTIONS

It is estimated that between 5 to 10% of the reaction goes to generating trivalent chrome. How much trivalent chrome is formed depends on several factors. Introduction of impurities into the bath also causes Cr(3) to form. The formation of trivalent occurs within the reaction of plating and it is also reduced in the operation at the anode in the following reaction:

$2PbO + O_2 \rightarrow 2PbO_2$ (lead peroxide)

$2H_2O \rightarrow O_2 + 4H^+$ (oxygen evolves)

$Cr^{+3} - 3e^- \rightarrow Cr^{+6}$ (trivalent chrome oxidized at the anode back to hexavalent state)

While this anodic reaction seems at first very simple, the oxidation only takes place while current is applied. The lead (typically an alloy of Pb/Sn/Sb) is being oxidized and forming an oxide that is distinguished as a dark brown coating. When the anodes are inactive they form a yellow film of lead chromate ($PbCrO_4$). This lead chromate film can grow until it develops a scale that blocks the flow of current. It is typical for plating operations, both functional and decorative, to activate the anodes by "dummying." This allows the current to blow off the chromate film and reform the peroxide film. When the film gets too heavy, anodes should be cleaned. Caution: *Remember that lead is highly toxic and all necessary protection should be worn to avoid contact or breathing the dust. The best practice is to soak the scaled anodes in a proprietary anode cleaner design for this purpose.*

The current applied to the anode is very important to generating and maintaining this dark brown film. Too low an anode current density will not cause the peroxide to form and trivalent will continue to build. The anode current density should be between 5 to 8 ASD or 0.35 to 0.5 asi. If the anode hook is hot then as a general rule the anode area is too small and more anodes or larger diameter anodes should be used.

Pure lead anodes will quickly dissolve. They need to be alloyed to inhibit corrosion and also to add stiffness to the soft metal; 7% tin has been used successfully for this purpose. Antimony is also added in a smaller quantity and adds rigidity to the anode; 2-3% antimony is generally sufficient to keep the anodes stiff and straight. Long anodes will generally have a core to aid in getting current evenly distributed to the anode and to provide more rigidity. If good distribution is needed, i.e, for I.D. of gun barrels or oil field pipe, the anodes will generally have a copper core. When using copper the manufacturer should silver the copper. This prevents the copper from being attacked by the chrome solution should a hole develop in the lead. Sometimes a steel core is used but if used it should be tinned and/or silver plated to prevent attack. This is particularly important when using the mixed fluoride chemistry.

Proper sizing of the anode relative to the work area is very important. Anodes sized too small will warp. This can also occur with high or low current. For example, burning the hook into the anode gives the best connection. These are areas that should be advised by the manufacturers of anode materials. To effectively convert trivalent chrome back to hex, the anode area should be sized to be twice the area of the work size. Any signs of build up in Cr (III) the anodes should be checked for scale and size. Since lead anodes are consumed they will become smaller over time and the effective area will be reduced, limiting their abil-

ity to oxidize Cr (III) to Cr (VI).

Proper filming of the anodes is very important. New anodes should be dummied at plating current for several hours to develop the proper lead peroxide film. If the bath sits idle for several days it should be dummied again for 2–3 hours to reactivate the anodes. If the bath is to be idle for long periods of time it would be best to remove the anodes altogether.

Some chrome platers will use rippled anodes, believing that such will give more surface area. As the anode works, however, the anode forms lead chromate in the groves of the ripple and the effective anode area is reduced. A smooth round anode is preferred to flat or rippled anodes.

In addition to lead or lead alloy anodes there are specialized anodes that utilize platinized titanium as anodes. These are relatively expensive but allow for very precise chrome deposits. There are applications where the work is centered into a circular platinized titanium anode array and parts are plated to very close tolerances. In this case the cost is greatly justified as it eliminates post grinding operation and the need for excess chrome for grind stock. In the printing industry, for example, many companies utilize platinized titanium as gravure rolls are plated with chrome. Some very precise plating is done with platinized-titanium for I.D. plating of small ports on engines or other types of aircraft components. Some specialized equipment use platinized titanium for plating shock absorber rods.

While it is not generally recommended, shops have successfully used steel wire to plate into I.D. ports or small diameter holes. These, however, eventually lead to rapid bath contamination.

OPERATING CONDITIONS

Typical operating conditions for functional or hard chrome are given in the following Table 1.

	Ordinary chemistry	Mixed fluoride chemistry	Mixed non-fluoride chemistry
Temperature °F/°C	120°F to 140°F 49°C to 60°C	130°F to140°F 54°C to 60°C	130°F to 150°F 54°C to 66°C
Cathode Current Density	0.25 asi to 2.5 asi 4 asd to 38 asd	1asi to 4asi 15 asd to 62 asd	1asi to 6 asi 15 asd to 95 asd
Solution Agitation	Mild Air (blower) or mixer	Mild Air (blower) or mixer	Mild Air (blower) or mixer
Anode-to-Cathode Area	1:1 to 3:1	1:1 to 3:1	1:1 to 3:1
Anode Material	Lead-7%Tin or Lead 6% Antimony	Lead-7%Tin	Lead-7%Tin or Lead 6% Antimony

Table 1, Operating Conditions

As operating temperatures rise, the efficiency of the bath decreases. However, this can be offset by the ability to plate at higher current densities to further gain a faster plating rate. Table 2 shows the efficiency differences between two temperature variables and the resulting efficiency. This effect is even greater with the mixed catalyst chemistries. A benefit of operating at a higher temperature is this

Current Density, Asi (ASD)	Ordinary Bath 130°F 54°C	140°F 60°C	Mixed Fluoride Bath 130°F 54°C	140°F 60°C	Mixed Non-Fluoride 130°F 54°C	150°F 66°C
1.0 (15.50)	10.9	10.8	15.0	14.2	15.0	14.2
1.5 (23.25)	12.4	12.0	18.5	17.9	18.5	17.9
2.0 (31.00)	14.0	13.6	21.4	20.6	21.4	20.6
3.0 (46.66)	16.3	14.9	24.0	23.4	24.0	23.4
4.0 (62.21)	18.1	17.0	26.0	25.3	26.0	25.3
5.0 (77.76)	19.4	18.2	26.8	26.2	26.8	26.2
6.0 (93.31)	20.7	19.3	27.5	27.0	27.5	27.0

Table 2, Temperature versus Cathode Efficiency

allows smoother deposits with less burning or nodulation. As we view the temperature current relationship, it can be seen that efficiency does increase as current density increases. The bath formulations also play a role in this as well. In the ordinary baths we would seldom see the high current density without special conditions. Mechanical conditions, (tank material, fixtures), will prevent obtaining these higher temperatures. The mixed catalysts baths using fluoride will typically make control of the fluoride catalyst very difficult to control. The non-fluoride mixed catalyst, however, will allow operating at much higher temperatures and thus higher current densities. To take advantage of this, special materials of construction would be required that would resist attack of hot chromic acid solutions.

As temperature rises the physical characteristic of the deposit decreases. Hardness of the deposit is affected and the appearance of the deposit becomes frosty or dull. The microcrack density is also reduced at the high temperature. These effects can be overcome in most cases with higher current densities.

Chromic acid concentration obviously is important since in plating chrome the chrome metal comes from the reduction of soluble chromic acid to the metal state. The chromic acid also is the conductive media that allows current to flow between the anode and cathode. The chromic acid bath is different in this respect to other plating chemistry whereby the metal reduced from solution is replaced by metal being dissolved at the anode. As the source of chrome metal and the conducting media, the concentration of chromic acid is important. Higher chromic acid concentrations result in better conductivity of the bath. Most of the chemistries in commercial operation start off running at 250 g/l. The higher concentration of chromic acid also reduces the energy requirements.

Chromic acid baths also differ from other types of plating baths in the effect that impurities have on the bath. Trivalent chrome is formed during the normal deposition process and is in effect a "self-contaminating" reaction. The formation of trivalent is, to a degree, mitigated by the anode reaction that oxidizes it back to the hexavalent state. The effect of trivalent chrome as well as other metallic impurities is that they lower the conductivity of the bath, requiring more energy to be consumed. Chart 1 shows the almost linear decrease in ohms as the impurities increase.

To a limited extent lowered conductivity by impurities can be overcome with an increase in chromic acid. As a rule of thumb, 7.5 g/l of impurities will be overcome by 60 g/l of chromic acid. So we have now increased the chromic acid from

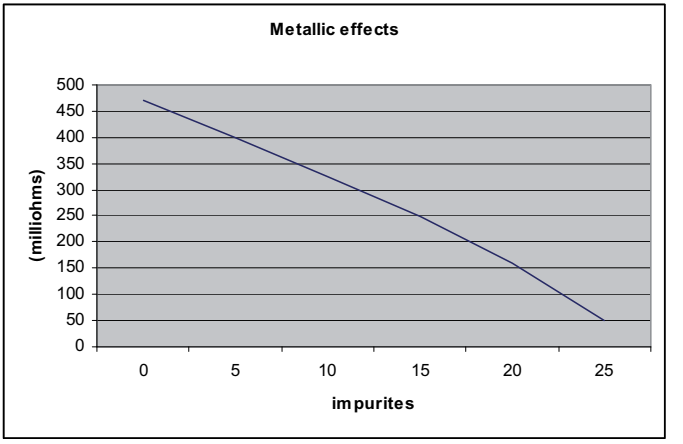


Chart 1, Impurities (g/L) versus Milliohms

250 g/l to >300 g/l. Further increase in chromic acid does not seem to give additional benefits.

Other impurities, such as chlorides, phosphates, nitrates and organics, will not only have an impact on the solution but will also affect the deposit characteristic. The goal should be to maintain a bath free of such impurities.

FIXTURES FOR FUNCTIONAL CHROME PLATING

A fixture is essentially a rack and is used to hold the work and to transfer current to the work or workload. This area is probably an art for functional chrome plating and is the heart of getting the deposit to the areas needed. The work of fixturing is beyond the scope of this article but an excellent book, *Hard Chrome Plating* by Robert Guffie, provides a great deal of information on this subject.

The requirement for many chrome plating jobs is to deposit chrome onto a specific area. This requires masking areas of the work piece(s) so that plating does not occur on unwanted areas. To accomplish this, a wide range of products from waxes to paints and lacquers are used. Care should be given in selecting the materials used for masking, as the wrong material can contaminate the chemistry. Shields and thieves are also employed to prevent deposits on certain areas or minimize the deposit and improve distribution of the deposit into other areas. Again, this is a highly specialized area of plating and is beyond the scope of this article.

POWER SUPPLY

As with other plating operations, a source of power delivering a direct current (DC) is required. With hard chrome or any hexavalent process, this source of DC power must be relatively pure with respect to ripple or AC component of DC. Most modern-day DC power sources for plating are provided by converting AC to DC by a rectifier. The rectifier suppliers all have special means to filter this AC component that will deliver a direct current with no more than 5% ripple.

Problems from high ripple can range from poor adhesion and cohesion to

roughness, poor covering or throwing power, and will show dull deposits with slow plating speeds. If ripple current is suspected it is easiest to have a qualified electrician check the AC line balance of the incoming AC power source. They should also check to assure diodes are functioning. Today's rectifiers are controlled by electronic signals generated by a thyrister firing circuit. If these devices are defective they also can be a source of problems. (See the chapter on DC Power Supplies for more information.)

SPECIAL CHROMIUM CHEMISTRIES

Some applications for chromium require special or unique adjustments to the basic chemistry to give the quality needed for that application. Cast iron, for instance, has been a particular difficult substrate to plate. Alteration of the chrome bath chemistry along with preplate conditioning will allow for a satisfactory deposit with good adhesion.

Some applications benefit from thin hard chrome deposits (also know as thin dense chrome) that can be used for bearing surfaces. These applications take advantage of the high lubricity of the chrome layer but with thin deposits that will not crack under the pressure of such applications. These thin layers of chrome also give some corrosion protection in lubricated conditions.

Porous chromium had a wide use during WW II through its ability to develop channels for oil flow. This was excellent for propeller-driven aircraft. This is still used in some industries today, although the channels are created post plating.

Crack-free chromium was used for many applications. The crack-free deposit is created by high temperature operation, with specific catalyst concentrations. The drive behind this is to develop a layer of chrome that will not have the network of cracks (micro or macro) typical of most hex chrome deposits. Based on the hardness of even the thinnest layer, cracking will occur. The application today is left only to very highly specialized applications.

Black chrome is a deposit that had applications for solar panels due to its absorbance and low emissivity of light. Today it is used more as a decorative process.

More and more applications are being used where inert anodes such as platinized-titanium is utilized. There are tremendous benefits from such use of these anodes but the under laying problem is the creation of trivalent chromium. However, unlike processes that use lead anodes, the trivalent is not easily converted back to hexavalent. Some have tried to resolve this by adding chemical lead into the bath to form thin lead peroxide or the use of lead anode in conjunction with the inert anodes to help develop the lead film. These types of applications have problems as they try to maintain bath purity and deposit quality. Some chemistries are available that can help resolve this issue.

IMPURITY REMOVAL

Perhaps the major complication to chrome plating that makes a simple chemistry into a difficult control problem is the introduction of impurities. As stated before, even the chrome plating chemistry creates its own impurity: trivalent chrome. Under normal conditions this will be converted back to hexavalent chrome at the anode. The formation of trivalent is further complicated by poor anode (Pb alloy) maintenance. Typical lead anodes will be consumed and the dimensions change, thus limiting their effectiveness in oxidizing Cr (III) to Cr (VI).

In addition to the natural formation of Cr (III), any organic materials will be rapidly attacked by the chrome bath reacting to form Cr (III). The source can come from oils, grease or other dirt from parts, especially the unclean ID of tubular work, or the use of compressed air that forces oils into the bath, or normal shop dirt that is drawn into the system from the pull of the ventilation system. Trivalent is fortunately one contaminant that can be reduced by taking the advantage of the reaction at the anodes in a process called dummying. A larger anode-to-cathode area between10-to-30:1 will reduce Cr (III) back to Cr (VI) state. Your chromium supplier, especially those that supply proprietary types, will be able to help.

Other metals can also accumulate in the bath. If reverse etching is done in the same plating bath, significant concentrations of iron (Fe) can build. If copper (Cu) is exposed, it, too, can build in the bath. Nickel (Ni), while more of a contaminant for the decorative process, it can also develop in functional chrome bath if stainless steel is used in various areas of construction. All of these metals, when combined, will lower the conductivity of the solution (see chart 1), resulting in poor quality deposits and higher energy cost. If allowed to increase, the eventual result is the need to replace the bath with new chemistry and waste disposal of the old solution.

Several systems are available for impurity removal and all have had some degree of success. Perhaps the least expensive is the porous pot system. This system utilizes a cathode inside a ceramic pot. The system may use its own anodes or use tank anodes already in the tank. As the cathode compartment is electrolyzed, it releases hydrogen gases that raise the pH of the solution in the pot until impurities precipitate. The solution inside the pot must be pumped out typically daily or per shift and replaced with solution from the tank. The one contamination that does reduce is Cr (III) since the anode area is typically larger than the cathode in the pot. There has been mixed results as to the effectiveness with other impurities and also the cost of operating since energy from a rectifier has to be used.

Electro-dialysis has been of interest for many years. It consists of using a resin membrane that will allow only positive ions to flow through. Similar to the porous pot, a cathode is used in a compartment and the metallic cations are deposited onto the cathode. As the cathode builds with impurities resistance builds and the effectiveness is reduced. The cathodes must then be removed and scraped clean in a typical operation. There have been many attempts to design a system based on this basic principle and such systems are available commercially. There are, however, mixed reactions as to the effectiveness of the devices.

Ion exchange (IX) units have found success in many applications. In this type of system, a portion of the bath is diluted and cooled. It is then directed into the IX unit which is filled with a cationic resin bed. Metallic (cationic) impurities are exchanged on the bed for hydrogen ions. The bed is then purged of the residual chrome solution and rinsed. The bed is reactivated by pumping an acid which displaces the metal ion with hydrogen ions from the acid. It is rinsed and the process is restarted on the chrome bath. The major limitations are: 1) a full concentrated bath cannot be sent through the bed—it must be diluted first. 2) The volume of wastewater generated is typically high. The system can, however, be combined with evaporation devices, and waste and chrome can be recovered.

ENVIRONEMNETAL ISSUES

Hexavalent chrome is a highly hazardous substance and proper knowledge of its nature is essential to maintain a safe workplace. The Occupational Health and Safety Act (see OSHA Hazard Communication Standard (29 CFR 1910.1200)) sets the limit of exposure as the Permissible Exposure Limit (PEL). It is the responsibility of each operation to assure that workers are not exposed beyond these limits. There is an action level at which point a plan must be developed to decrease exposure. More information is available on requirements through your supplier's material safety data sheet (MSDS) which should be kept on file and available to all personnel.

Other regulations also give requirements for the use of hexavalent chrome for plating applications. These include the Clean Air Act and the Clean Water Act, which sets limits as to how much hexavalent chrome is allowed to be discharged to the outside by exhaust or by wastewater. These laws are enforced by the United States Environmental Protection Agency (EPA) who set the standards. A full discussion of the laws and their requirements is beyond the scope of this article, but a review of the section on Industrial Ventilation and Pollution Control would be beneficial. The section on Waste Water Treatment is also beneficial to understanding the requirements for plating in general.

The use of stable surfactants as fume and mist control has been an acceptable means of controlling the mist generated during hexavalent chrome plating. The gases generated by the electrolysis from both the cathode and the anode reactions are high and carry droplets of the hexavalent chrome into the ambient air. These hazardous fumes and mist can be minimized to a significant degree by reduction in the surface tension through the use of these surfactants and in some applications may meet the requirements of OSHA and the USEPA. In addition to use of suppressants as a means of minimizing fumes and mist, it is also found to be beneficial in keeping air ventilation and scrubber systems low in contaminants and reduces down time, wear and maintenance.

When using mist suppressants as a means of controlling copious amounts of foam formed by the generation of hydrogen and oxygen, gases can generate an explosive condition if a spark ignites the gases in the foam. This can lead to the foam containing the hazardous hex chrome to leave the confinement of the tank, possibly causing a danger to workers. Low foaming mist and fume suppressants are available and would be preferable to the foaming type that intentionally build the foam blanket to suppress the misting. There recently have been several articles covering the use of these type of mist and fume suppressants. One of these issue is the persistent, bioaccumulative and toxic (PBT) of some of the chemistries and in particular PFOS-based products used as mist/fume suppressants. It is anticipated that chemicals that are non-PFOS containing with lower PBT will become available. It is anticipated that the PFOS types will be banned. On a global level, many countries have already eliminated the use of PFOS based products in all industries.

[1]Cr (III) is not the same as chromium trioxide

COPPER PLATING

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COPPER CYANIDE BATHS

Copper cyanide plating, with its accompanying health hazard and waste disposal problems (also shared with other cyanide plating baths), is still essential in many plating operations as a strike and, to a decreasing extent, for thick deposits. In dealing with the chemistry of the copper cyanide bath, a distinction must be made between total cyanide and free cyanide. Cuprous cyanide must be complexed with either potassium or sodium cyanide to form soluble copper compounds in aqueous solutions. The major complexed form is considered to be either potassium copper cyanide, $K_2Cu(CN)_3$, or sodium copper cyanide, $Na_2Cu(Cn)_3$. The sum of that required for the complexation of copper cyanide plus the amount of cyanide required for the proper functioning of the bath (free cyanide) is the total cyanide. The total cyanide required by weight is given in the following equation:

Total potassium cyanide = (Copper cyanide required × 1.45) + free potassium cyanide required

Total sodium cyanide = (Copper cyanide required × 1.1) + free sodium cyanide required

As an example:

A plating bath needs 2.0 g/L of copper cyanide and 0.5 g/L of free potassium cyanide. How much potassium cyanide is required for the bath?

Total potassium cyanide = (2.0 × 1.45) + 0.5 = 3.4 g/L

The plating bath formulations provided here are suitable for the majority of uses in cyanide copper plating and are easy to control. These formulations can be modified by the plater after reading the operating parameters and notes on maintenance and control. It is recommended, whenever possible, that the potassium formulations be used for extended plating range and a greater tolerance to deviation from recommended operating parameters.

Anodes for all baths should be high purity copper that is oxide free. They can be bagged copper slabs or bagged steel baskets containing copper nuggets. Plain steel anodes may be mixed with the copper to control copper cyanide content if copper content in the plating bath tends to increase with use. Anode/cathode ratio should be 1:1 to 2:1.

General Purpose Strike

The general purpose strike (see Table I) is used for improved adhesion, activation of passive substrates, or as an insurance step in the cleaning cycle. When used for zinc die castings, the hydroxide concentration should be kept at a maximum of 3.75 g/L (0.5 oz/gal). Deposits are usually in the range of 0.5-2.0 µm (0.02-0.08 mil) in thickness.

Table I. General Purpose Copper Cyanide Strike

	Potassium	*Sodium*
Copper cyanide	30.0 g/L (4.0 oz/gal)	30.0 g/L (4.0 oz/gal)
Total potassium cyanide	58.5 g/L (7.8 oz/gal)	—
Total sodium cyanide	—	48.0 g/L (6.4 oz/gal)
Potassium hydroxide	3.75-7.5 g/L (0.5-1.0 oz/gal)	—
Sodium hydroxide	—	3.75-7.5 g/L (0.5-1.0 oz/gal)
Potassium carbonate	15.0 g/L (2.0 oz/gal)	—
Sodium carbonate	—	15.0 g/L (2.0 oz/gal)
Rochelle salt	30.0 g/L (4.0 oz/gal)	30.0 g/L (4.0 oz/gal)
Free potassium cyanide by analysis	11.25-15.0 g/L (1.5-2.0 oz/gal)	—
Free sodium cyanide by analysis	—	11.25-15.0 g/L (1.5-2.0 oz/gal)
Temperature	24-66°C (75-140°F)	
Current density	0.5-4 A/dm^2 (5-40A/ft^2)	
Time	30 sec to 2 min or until fully covered	
Cathode efficiency	30-60%	
Recommended agitation	None or mechanical	

Strike-Plate Bath

The strike-plate bath (see Table II) is the one most used for the plating of zincated aluminum. It is also used for zinc die castings and other metals that are subject to attack by subsequent plating baths or finishing operations that require more than a strike deposit for protection. This formulation eliminates the need for two baths—a strike followed by a plate in a high efficiency bath. Deposits range from 3.0 to 5.0 µm (0.12-0.20 mil) in thickness for the parameters given in the formulation.

High-Efficiency Bath

The high-efficiency bath (see Table III) is used when a rapid buildup of a sig-

Table II. Copper Cyanide Strike-Plate Bath

	Potassium	*Sodium*
Copper cyanide	42.0 g/L (5.6 oz/gal)	42.0 g/L (5.6 oz/gal)
Total potassium cyanide	66.6 g/L (8.9 oz/gal)	—
Total sodium cyanide	—	51.9 g/L (6.9 oz/gal)
Potassium carbonate	30.0 g/L (4.0 oz/gal)	—
Sodium carbonate	—	30.0 g/L (4.0 oz/gal)
Rochelle salt	60.0 g/L (8.0 oz/gal)	60.0 g/L (8.0 oz/gal)
Free potassium cyanide by analysis	5.7 g/L (0.8 oz/gal)	—
Free sodium cyanide by analysis	—	5.7 g/L (0.8 oz/gal)
pH	10.2-10.5	
Temperature	40-55°C (100-130°F)	
Current density and time	Initial (strike) 2.5-3.0 A/dm^2(25.0-30.0 A/ft^2) for 2 min. Final (plate)1.0-1.5 A/dm^2 (10.0-15.0A/ft^2) for 3-5 minutes.	
Cathode efficiency	30-50%	
Recommended agitation	None or mechanical	

Use diluted tartaric acid or acetic acid to lower the pH; hydroxide to raise it.

Table III. High-Efficiency Copper Cyanide Bath

	Potassium	*Sodium*
Copper cyanide	60.0 g/L (8.0 oz/gal)	75.0 g/L (10.0 oz/gal)
Total potassium cyanide	102.0 g/L (13.6 oz/gal)	—
Total sodium cyanide	—	97.5 g/L (13.0 oz/gal)
Potassium carbonate	15.0 g/L (2.0 oz/gal)	—
Sodium carbonate	—	15.0 (2.0 oz/gal)
Potassium hydroxide	15.0 g/L (2.0 oz/gal)	—
Sodium hydroxide	—	15.0 g/L (2.0 oz/gal)
Rochelle salt	45.0 g/L (6.0 oz/gal)	45.0 g/L (6.0 oz/gal)
Free potassium cyanide by analysis	15.0 g/L (2.0 oz/gal)	—
Free sodium cyanide by analysis	—	15.0 g/L (2.0 oz/gal)
Temperature	60-71°C (140-160°F)	
Current density	up to 80 A/ft²	
Cathode efficiency	90-99%	
Recommended agitation	Mechanical, solution or air	

nificant copper thickness is required. The copper cyanide can be as high as 120.0 g/L (16.0 oz/gal) for applications such as wire plating. Although the brightness and grain refinement of the deposit can be improved by the use of periodic reverse current or current interruption, the best results are obtained by using suitable additives.

Barrel Plating

The strike bath, high-efficiency bath, or both in combination, can be used for barrel plating. Typical compositions for barrel plating are shown in Table IV.

Bath Preparation

Dissolve potassium or sodium cyanide in cold water. In a separate container, mix copper cyanide with water to form a thin slurry and slowly add to the potassium or sodium cyanide solution while mixing. The dissolving reaction is exothermic and the solution should not be allowed to overheat, as this may decompose some of the free cyanide. Add the rest of the required materials after dissolving the copper cyanide. Carbon treatment of the bath before use is recommended. All salts should

Table IV. Copper Cyanide Baths for Barrel Plating

	Potassium	*Sodium*
Copper cyanide	45.0-60.0 g/L (6.0-8.0 oz/gal)	45.0-60.0 g/L (6.0-8.0 oz/gal)
Total potassium cyanide	80.3-109.5 g/L (10.7-14.0 oz/gal)	—
Total sodium cyanide	—	64.5-88.5 g/L (8.6-11.8 oz/gal)
Potassium carbonate	15.0 g/L (2.0 oz/gal)	—
Sodium carbonate	—	15.0 g/L (2.0 oz/gal)
Potassium hydroxide	7.5-22.5 g/L (1.0-3.0 oz/gal)	—
Sodium hydroxide	—	7.5-22.5 g/L (1.0-3.0 oz/gal)
Rochelle salt	45.0 g/L (6.0 oz/gal)	45.0 g/L (6.0 oz/gal)
Free potassium cyanide by analysis	15.0-22.5 g/L (2.0-3.0 oz/gal)	—
Free sodium cyanide by analysis	—	15.0-22.5 g/L (2.0-3.0 oz/gal)
Temperature	60-71°C (140-160°F)	

be sulfur free to prevent dull, red deposits in low current density plating areas.

Maintenance and Control

Constituents

It is recommended that all constituents in the formulation be controlled to within 10% of their nominal values, especially the free cyanide. The copper cyanide concentration controls the allowable plating current density in combination with agitation. The free cyanide concentration controls efficiency, plating range, throwing power, and anode polarization. The hydroxide concentration controls conductivity and throwing power. Carbonates buffer the solution and reduce anode polarization. Although high carbonate concentration of 90.0 to 120.0 g/L (12.0-16.0 oz/gal) decreases the plating range, it is added to new baths to stabilize their initial operation. Rochelle salt enhances anode corrosion and provides some grain refinement. Potassium formulations have a broader plating range than sodium formulations.

Temperature

Temperature above 71°C (160°F) in the high-efficiency and barrel formulations promotes the breakdown of cyanide and the rapid buildup of carbonates.

Agitation

Mechanical and/or solution agitation is recommended. Use air agitation only when required, as air agitation promotes carbonate buildup.

Contamination

Organic contamination causes nonuniform, dull, rough, or pitted deposits. In severe cases of organic contamination, the anodes may polarize. Carbon treatment will remove organic contamination. A copper strike should not be considered to be a cleaner and should be carbon treated periodically to prevent organic contamination from spreading to other plating baths. Hexavalent chromium contamination causes skip plate in the low current density plating area, blisters, and nonuniform deposits.

The best method for eliminating the problem of chromium contamination is to eliminate the source. Hexavalent chromium in the bath can be reduced to trivalent by using proprietary reducing agents. Zinc contamination causes nonuniform or brass-colored deposits and can be removed by dummying the bath at 0.2-0.4 A/dm^2 (2-4 A/ft^2). Sulfur and its compounds cause dull, red deposits in the low current density plating areas and usually appear in new baths because of impure cyanides or leaching from tank linings. Small amounts of a zinc salt, such as zinc cyanide, will eliminate sulfur red from the deposits. Most other common types of metallic contamination cause deposit roughness and can usually be removed by dummying and filtration.

Carbonate

Excessive sodium carbonate can be removed by freezing out at a low temperature because of its limited solubility below -3°C (26°F). Both potassium and sodium carbonate can be removed by precipitation with calcium oxide, calcium hydroxide, or calcium sulfate.

COPPER PYROPHOSPHATE PLATING BATHS

Copper pyrophosphate plating baths require more control and maintenance than

Table V. Pyrophosphate Copper Strike

Copper pyrophosphate ($Cu_2P_2O_7 \cdot 3H_2O$)	25.0-30.0 g/L (3.3-4.0 oz/gal)
Potassium pyrophosphate ($K_4P_2O_7$)	95.7-176.0 g/L (12.8-23.4 oz/gal)
Potassium nitrate	1.5-3.0 g/L (0.2-0.4 oz/gal)
Concentrated ammonium hydroxide	0.5-1 ml/L
pH	8.0-8.5
Temperature	22-30°C (72-86°F)
Current density	0.6-1.5 A/dm² (6.0-15.0 A/ft²)
Agitation	Mechanical and air
Filtration	Continuous
Operating parameters by analysis are:	
Copper metal	9.0-10.7 g/L (1.2-1.4 oz/gal)
Pyrophosphate	63.0-107.0 g/L (8.4-14.2 oz/gal)
P_2O_7/Cu ratio	7:1 to 10:1

cyanide baths; however, the solutions are relatively nontoxic. The main uses of copper pyrophosphate baths have been for electroforming, plating on plastics, and printed circuits.

The chemistry involved in copper pyrophosphate plating is the formation of potassium copper pyrophosphate complex [$K_6Cu(P_2O_7)_2 \cdot 6H_2O$] from copper pyrophosphate ($Cu_2P_2O_7 \cdot 3H_2O$) and potassium pyrophosphate ($K_4P_2O_7$). The ratio of pyrophosphate ($P_2O_7^{4-}$) to copper (Cu^{2+}) in the compound is 5.48 to 1. Any pyrophosphate in excess of this ratio is called "free" or "excess" pyrophosphate. Free or excess pyrophosphate is essential for the operation of the bath in providing conductivity and anode corrosion. This is done by running a pyrophosphate to copper (P_2O_7/Cu) ratio of 7:1 to 8:1 in the plating bath. A strike bath may have a higher ratio. Potassium pyrophosphate baths are recommended over sodium formulations for better conductivity and higher solubility of the potassium copper complex.

Anodes for all baths should be high purity copper that is oxide free. Anodes can be copper slabs or copper nuggets in titanium baskets. Anode bags are not recommended. Anode to cathode ratio should be 2:1. Copper pyrophosphate baths tend to build orthophosphate (HPO_4^{2-}) concentration by the hydrolysis of pyrophosphate. Small amounts of orthophosphate are not harmful; however, higher concentrations in excess of 100.0 g/L (13.3 oz/gal) may cause banded deposits with decreased plating range and conductivity in the standard plating baths.

In the printed circuit bath, the orthophosphate concentration should not be allowed to exceed 40.0-60.0 g/L (5.5-8.0 oz/gal) because, beyond this point, there is a decrease in both the throwing power of the solution and ductility of the deposit. Orthophosphate concentration is lowered by dilution or replacement of the bath. The anode and cathode efficiencies of copper pyrophosphate baths are essentially 100%. Maximum agitation is required for the best results. When using air agitation, the volume of air required should be 1 to 1.5 times the surface area to be plated. Ultrasonic agitation may also be used.

Strike

Copper pyrophosphate plating baths can form immersion coatings, similar to acid

Table VI. Copper Pyrophosphate Bath for General Use

Copper pyrophosphate ($Cu_2P_2O_7 \cdot 3H_2O$)	52.5-84.0 g/L (7.0-11.2 oz/gal)
Potassium pyrophosphate ($K_4P_2O_7$)	201.1-349.1 g/L (26.8-46.5 oz/gal)
Potassium nitrate	3.0-6.0 g/L
Concentrated ammonium hydroxide	3.75-11.0 ml/L
pH	8.0-8.7
Temperature	43-60°C (110-140°F)
Current density	1.0-8.0 A/dm² (10.0-80.0 A/ft²)
Agitation	Mechanical and air
Filtration	Continuous
Operating parameters by analysis are:	
Copper metal	18.8-30.0 g/L (2.5-4.0 oz/gal)
Pyrophosphate	131.6-225.0 g/L (17.5-30.0 oz/gal)
P_2O_7/Cu ratio	7.0:1-7.5:1

copper, on steel and zinc die castings, and cause poor adhesion. A cyanide- or pyrophosphate-copper strike is used for steel, and a cyanide strike for zinc is recommended. The pyrophosphate-copper strike is a diluted version of the plating bath, which can have a P_2O_7/Cu ratio of 10:1 or higher. A typical formulation would be as shown in Table V.

Typical Pyrophosphate Bath

The copper pyrophosphate bath formulation in Table VI can be used for all plating applications except printed circuits. Current interruption or periodic reverse current can further refine the grain structure.

Printed Circuit Bath

The use of nonproprietary or proprietary additives that improve the throwing power and ductility of deposit is recommended for printed circuit application. A typical formulation is shown in Table VII.

Copper pyrophosphate baths are sensitive to contamination, especially organic con-

Table VII. Copper Pyrophosphate for Printed Circuits

Copper pyrophosphate ($Cu_2P_2O_7 \cdot 3H_2O$)	57.8-73.3 g/L (7.7-9.8 oz/gal)
Potassium pyrophosphate ($K_4P_2O_7$)	231.0-316.5 g/L (30.8-42.2 oz/gal)
Potassium nitrate	8.2-15.8 g/L (1.1-2.1 oz/gal)
Concentrated ammonium hydroxide	2.7-7.5 ml/L (0.3-0.75% by volume)
Addition agent	As required
pH	8.0-8.4
Temperature	49-54°C (120-130°F)
Current density	2.5-6.0 A/dm² (25.0-60.0A/ft²)
Agitation	Mechanical and air
Operating parameters by analysis are:	
Copper metal	20.7-26.2 g/L (2.75-3.5 oz/gal)
Pyrophosphate	150.0-204.4 g/L (20.0-27.2 oz/gal)
P_2O_7/Cu ratio	7.2:1-7.8:1

tamination, and are made from purified liquid concentrates.

Maintenance and Control

Constituents
Ammonia aids in anode corrosion and acts as a grain refiner. Ammonia is replenished daily because of evaporation loss. Nitrate increases the high current density plating range and is a cathode depolarizer. The pH is controlled by using pyrophosphoric acid or potassium hydroxide as required.

Temperature
Operating the baths above 60˚C (140˚F) causes the rapid hydrolysis of pyrophosphate to orthophosphate.

Agitation
Copper pyrophosphate baths need vigorous agitation for a normal operating current density plating range. The most common form used is air agitation, by itself or in combination with mechanical agitation. Ultrasonic and solution jet agitation can also be used.

Contaminants
Copper pyrophosphate baths are sensitive to organic contamination such as oil, breakdown products, or organic addition agents. Organic, cyanide, and lead contamination can cause dull, nonuniform deposits with a narrow plating range. Carbon treatment will remove organic contamination and treating with hydrogen peroxide or potassium permanganate before carbon treatment will remove cyanide and severe organic contamination. Lead can be removed by dummying.

Orthophosphate
In addition to high temperature, localized overheating or too low a pH can cause the rapid buildup of orthophosphate.

OTHER ALKALINE BATHS

There has been work on the development of other types of alkaline, noncyanide copper plating baths; but their use in industry has been too specialized or limited to discuss at this time.

COPPER SULFATE BATHS

Copper sulfate baths are economical to prepare, operate, and waste treat. They are used in printed circuits, electronics, semiconductor, rotogravure, electroforming, decorative, and plating-on-plastics applications.

The chemistry of the solution is simple, with copper sulfate and sulfuric acid forming the ionized species in solution. The baths are highly conductive. Previous problems with throwing power have been overcome with the advent of the modern high throw formulations and additives. Steel parts must be cyanide copper- or nickel-plated in strike formulations to prevent immersion coatings and poor adhesion. Zinc die castings and other acid sensitive metals must have sufficient deposit to prevent attack by the sulfuric acid. The baths are operated at room temperature for most applications. Anodes should be phosphorized (0.02-0.08% by weight phosphorus), oxide-free, high-purity, rolled copper. Copper anode nuggets in titanium baskets can be used. Anodes should be bagged. The anode current density should range from 15 to 30 A/ft^2. Excessively high current densities can cause

Table VIII. Standard Acid Copper Baths

General formulation:	
Copper sulfate	26-33 oz/gal (195-248 g/L)
Sulfuric acid	4-10 oz/gal (30-75 g/L)
Chloride	50-120 ppm[a]
Current density	20-100 A/ft^2
Semibright plating (Clifton-Phillips):	
Copper sulfate	33 oz/gal (248 g/L)
Sulfuric acid	1.5 oz/gal (11 g/L)
Chloride	50-120 ppm[a]
Thiourea	0.0001 oz/gal (0.00075 g/L)
Wetting agent	0.027 oz/gal (0.2 g/L)
Bright plating (Beaver):	
Copper sulfate	28 oz/gal (210 g/L)
Sulfuric acid	8 oz/gal (60 g/L)
Chloride	50-120 ppm[a]
Thiourea	0.0013 oz/gal (0.01 g/L)
Dextrin	0.0013 oz/gal (0.01 g/L)
Bright plating (Clifton-Phillips):	
Copper sulfate	26.5 oz/gal (199 g/L)
Sulfuric acid	4 oz/gal (30 g/L)
Chloride	50-120 ppm[a]
Thiourea	0.005 oz/gal (0.0375 g/L)
Molasses	0.1 oz/gal (0.75 g/L)

[a]10 ml of reagent grade concentrated hydrochloric acid per 100 gallons is equivalent to 12 ppm.

the anode to lose its black, protective film and cause rough deposits; excessively low current densities can cause copper sulfate buildup, which can cause a reduction in throwing power, and a thick anode film, which can reduce the anode's conductivity. Anode and cathode efficiencies are essentially 100%. Since copper sulfate plating has become of major importance to the industry, a troubleshooting guide is given in this section (see Table X).

Standard Acid Copper Plating

Table VIII lists the standard formulations for copper sulfate baths. Air agitation or solution sparging with or without mechanical agitation, is recommended.

High-Throw Bath

The formulation shown in Table IX is used in printed circuit, barrel plating, and other applications where high throwing power is required.

Table IX. High-Throw Acid Copper Bath

Copper sulfate	8.0-10.0 oz/gal (60.0-75.0 g/L)
Sulfuric acid	25.0-30.0 oz/gal (187-225 g/L)
Chloride	50-100 ppm[a]
Proprietary additive(s)	Per vendor recommendations

[a]10 ml of reagent grade concentrated hydrochloric acid per 100 gallons is equivalent to 12 ppm.

For circuit board plating, copper is most commonly plated following an electroless copper metallization of the through holes. Recently, a number of technologies have been developed that replace the electroless copper with other means of imparting conductivity to the through holes. They fall into two general categories: carbon-based and palladium-based systems. They use conventional acid copper sulfate electrolytes to plate up through the holes.

Pulse and periodic reverse plating are being used to improve throwing power, deposit characteristics, and productivity with the development of specialized additives. New additives have been developed with DC current to maintain throwing power at higher cathode current densities, improving productivity.

Bath Preparation

Baths can be made by dissolving copper sulfate in water and then adding sulfuric acid. Carbon treatment is recommended. Cooling to room temperature is recommended prior to adding proprietary additives. Baths can also be made using either purified liquid copper sulfate (generally around 36 oz/gal as copper sulfate pentahydrate) or commercial premade solutions without the organic additives. Carbon polishing is recommended prior to adding proprietary additives.

Maintenance and Control

Constituents

Copper sulfate is the source of copper ions in solution. Because the anode and cathode efficiencies normally are close to 100%, the anodes replenish the copper ions so that the copper concentration remains fairly stable in solution. The sulfuric acid increases the conductivity of the solution and reduces the anode and cathode polarization. It prevents precipitation of basic salts and improves throwing power. In high throw formulations, the weight ratio of copper metal to sulfuric acid should be maintained at less than 1:10. To further enhance the throwing power, the copper sulfate may be reduced to 6.0-8.0 oz/gal (45.0-60.0 g/L) to give metal-to-acid ratios as high as 1:30. This may be useful in plating high aspect ratio printed circuit boards; however, the lower copper content decreases the allowable plating current densities and increases the plating times. Copper sulfate is reduced in concentration in high throw formulations to prevent common ion precipitation effects as the sulfuric acid is increased. Sulfuric acid concentrations above 11% by volume begin to reduce cathode efficiency. Chloride ion, in bright and high throw baths, reduces anode polarization and eliminates striated deposits in the high current density areas.

Temperature

These baths are operated at room temperature for the majority of applications. If the temperature is too low, cathode efficiency and plating range will be reduced. Baths used where bright deposits in the low current density are not required may be operated at temperatures as high as 50°C (120°F) to increase the plating range in electroforming, printed circuit, or rotogravure applications.

Agitation

Air, mechanical, solution jet, or rotating work agitation can be used. The more vigorous the agitation, the broader the allowable plating current density.

Contaminants

Organic contaminants are the ones most commonly dealt with in acid copper plat-

Table X. Troubleshooting Guide for Acid Copper Sulfate Plating

Problem	*Cause*	*Corrective Action*
High current density burning	Low copper, high acid	Analyze and adjust
	Low temperature	Heat bath
	Insufficient agitation	Lower current, unless agitation can be improved
	Organic contamination	Carbon treat
	Low chloride (bright baths)	Analyze and adjust
Loss of brightness (in bright formulations)	Low additive	Determine addition by Hull cell
	Organic contamination	Carbon treat
	Low chloride	Analyze and adjust
	High temperature	Cool the bath
	Low copper	Analyze and adjust
Rough deposit	Particles in solution	Filter bath
	Torn anode bags	Replace torn bag
	Improper anodes	Use phosphorized copper anodes
	Low chloride	Analyze and adjust
Pitting	Organic contamination	Carbon treat
	Anode slough	Bag anodes
	Low chloride	Analyze and adjust
Poor distribution	Low or nonuniform agitation	Improve and adjust
	Excessive anode area	Adjust
	Improper anode film	Dummy
	Current supply AC ripple	Adjust to below 10%
	Organic contamination	Carbon treat
Low current	Organic contamination	Carbon treat
	Low sulfuric acid	Analyze and adjust
	Low additive	Determine addition by Hull cell
	High chloride	1. Wash off anode film and dummy to reform film 2. Precipitate with silver sulfate or nitrate and carbon filter 3. Dilute
	Current density too low	Increase current
	High temperature	Cool bath
Anode polarization	Tin, gold contamination	Dummy with a copper foil (no current)
	Low temperature	Heat bath
	Improper anodes	Bright baths require phosphorized anodes
	High chloride	1. Wash off anode film and dummy to reform film 2. Precipitate with silver sulfate or nitrate and carbon filter 3. Dilute
	High sulfuric acid	Analyze and dilute bath
	Low copper sulfate	Analyze and adjust
	Organic contamination	Carbon treat

Table XI. Copper Fluoborate Baths

	High Concentration	*Low Concentration*
Copper fluoborate	60 oz/gal (459 g/L)	30 oz/gal (225 g/L)
Fluoboric acid	5.4 oz/gal (40.5 g/L)	2 oz/gal (15 gal/L)
pH (colorimetric)	0.2-0.6	1.0-1.7
Temperature	65-150° F	65-150°F
Baum|fe	37.5-39.5°	21-22°
Current density	125-350 A/ft²	75-125 A/ft²

ing. Major sources are decomposition products of brighteners, drag-in of previous process chemistries, tank liners, unleached anode bags, stop-offs, resists, and impure salts or acid. Contaminants will adversely affect the appearance and the physical properties of the deposit.

A green coloration of the bath indicates significant organic contamination. Organic impurities are removed by treatment with activated carbon. In cases of severe contamination, potassium permanganate, hydrogen peroxide, or even bleach, if the chloride ion is monitored, may be necessary to break down the organics so that the activated carbon can effectively remove them. Carbon itself may contaminate or have no effect if the activated carbon was not designed for use in high acid baths. Cellulose filter aids should not be used.

Some common metallic contaminants and their effects are as follows:

Antimony (10-80 ppm): rough, brittle deposits. Gelatin or tannin added to the bath will inhibit its codeposition.
Arsenic (20-100 ppm): same as antimony.
Bismuth: same as antimony.
Cadmium (>500 ppm): can cause an immersion deposit and polarization of the anode during idle time. Can tie up chloride ions.
Iron (>1,000 ppm): reduces bath conductivity and throwing power.
Nickel (>1,000 ppm): same as iron.
Selenium (>10 ppm): anode polarization, roughness.
Tellurium (>10 ppm): same as selenium.
Tin (500-1,500 ppm): immersion deposits and polarization of anodes during idle time.
Zinc (>500 ppm): same as cadmium.

A guide for troubleshooting acid copper baths is given in Table X.

COPPER FLUOBORATE BATH

This bath allows the use of high current densities and increased plating speed, as copper fluoborate is extremely soluble and large amounts can be dissolved in water. The main drawback is its corrosivity, consequently, construction materials are normally limited to hard rubber, polypropylene, polyvinyl chloride (PVC), and carbon/Karbate. In all other aspects, the copper fluoborate bath is similar to copper sulfate plating.

The anodes should be high-purity copper that is oxide free. Anode bags should be made of Dynel or polypropylene. Normally, the bath is made up with copper fluoborate concentrate (1.54 g/ml or 50.84°B|fe), which contains 92.0 oz/gal cupric fluoborate (26.9% by weight copper metal), 1.4 oz/gal fluoboric acid, and 2 oz/gal boric acid (to prevent the formation of free fluoride due to fluoborate hydrolysis). The fluoboric acid (1.37 g/ml or 39.16°Bé typically contains 90 oz/gal of fluoboric acid and 0.9

oz/gal of boric acid.

Typical formulations for copper fluoborate baths are given in Table XI.

Maintenance and Control

Contaminants

Organic contaminants can affect the deposit appearance/uniformity and mechanical properties, especially ductility. These can be removed by carbon treatment. Cellulose filter aids, free of silica, can be used. These baths are often carbon filtered continuously. Lead is the only common metallic contaminant that causes problems, and it can be precipitated with sulfuric acid.

Additives

Normally, no organic additives are used. Molasses can harden deposits and minimize edge effects. Some of the same additives (e.g., acetyl cyanamide) used for copper sulfate baths can also be used with the fluoborate formulations.

GOLD PLATING

BY ALFRED M. WEISBERG
TECHNIC INC., PROVIDENCE, R.I.; www.technic.com

All types of gold and gold alloy electroplates are used for many different applications by many different industries; however, there are eight general classes that may be listed that include much of present-day gold plating:

Class A—Decorative 24K gold flash (2-4 millionths of an in.), rack and barrel.
Class B—Decorative gold alloy (2-4 millionths of an in.), rack and barrel.
Class C—Decorative gold alloy, heavy (20-over 400 millionths of an in.), rack. These deposits may be either C-1 karat color or C-2 karat assay.
Class D—Industrial/electronic high-purity soft gold (20-200 millionths of an in.), rack, barrel, and selective.
Class E—Industrial/electronic hard, bright, heavy 99.5% gold (20-200 millionths of an in.), rack, barrel, and selective.
Class F—Industrial/electronic gold alloy, heavy (20-over 400 millionths of an in.), rack and selective.
Class G—Refinishing, repair and general, pure, and bright alloy (5-40 millionths of an in.), rack and selective brush.
Class H—Miscellaneous, including electroforming of gold and gold alloys, statuary and architectural, etc.

To further simplify an enormous and diverse subject, gold and gold alloy plating solutions may be considered to belong to five general groups:

Group 1—Alkaline gold cyanide for gold and gold alloy plating; Classes A-D and occasionally F-H.
Group 2—Neutral gold cyanide for high-purity gold plating; Classes D and G.
Group 3—Acid gold cyanide for bright, hard gold and gold alloy plating; occasionally Classes B, C, E-G.
Group 4—Noncyanide, generally sulfite, for gold and gold alloy plating; occasionally Classes A-D and F-H.
Group 5—Miscellaneous.

There are literally hundreds of formulations within these five classes of gold plating solutions.

Physical, engineering, or aesthetic considerations will determine which of these groups should be considered for a particular job, but economics will usually be the determining factor in selecting a specific formulation and plating method. The price of gold per troy ounce is only one aspect of the economics that must be considered in deciding among rack, barrel, brush, continuous, or selective plating. For any individual applications it is necessary to balance and optimize the following variables:

1. *Cost of the bath.* This includes the volume necessary for a particular method and the gold concentration.
2. *Speed of plating.*(This determines the size of the equipment) and the bath and the cost for a given desired production.
3. *Cost of drag-out loss.* This will depend on the gold concentration used; the shape of the part; whether it is rack, barrel, continuously, or selectively plated; and must include the probable recovery of dragged-out gold by electrolytic or ion-exchange recovery.

Table I. Gold and Gold Alloy Flash Baths (Classes A and B)

	24K or English	*Low Cyanide English*	*Hamilton Colors*			*White No. 1*	*White No. 2*	*Green*	*Pink*	*Rose*
			Yellow	*Pink*	*Green*					
Gold as potassium gold cyanide (g/L)	1.25-2	1.25-2	1.25-2	1.25-2	1.25-2	0.4	0.325	2	0.82	6
Free potassium cyanide (g/L)	7.5	7.5	7.5	2.0	2.0	15	15	7.5	4	4
Dipotassium phosphate										
oz/gal	2	2	2	2	2	2	2	2	2	—
g/L	15	15	15	15	15	15	15	15	15	—
Sodium hydroxide (g/L)	—	—	—	—	—	—	—	—	—	15
Sodium carbonate (g/L)	—	—	—	—	—	—	—	—	—	30
Nickel as potassium nickel cyanide (g/L)	—	0.025-1.4	0.025	0.025	0.025	1.1	—	—	0.2	—
Copper as potassium copper cyanide (g/L)	—	—	0.13	1.1	—	—	—	—	2.7	—
Silver as potassium silver cyanide (g/L)	—	—	—	—	0.05	—	—	0.25	—	—
Tin (g/L)	—	—	—	—	—	—	2.1	—	—	—
Temperature (°F)	140-160	140-160	150-160	140-160	140-160	150-160	150-160	130-160	150-160	150-180
Current density (A/ft2)	10-40	10-40	10-35	20-50	10-40	30-60	30-50	10-30	30-40	20-50

4. *Cost of control and maintenance.* Some high-speed and high-efficiency baths require almost constant attendance and analysis.
5. *Cost of longevity of the bath.* High-speed and especially high-purity baths with good drag-out recovery must be changed periodically to maintain purity. This results in a certain loss on changeover.
6. *Cost of money* (interest) to keep the bath.
7. *Initial cost of the equipment.*
8. *Overhead cost of the equipment* (whether it is operating or not operating), that is, the interest cost per hour or per day.

Sometimes, a simple manual rack or barrel method will be cost-effective; at other times, a high-speed fully automated plant is justified.

Gold today is a freely traded commodity with a different price every day. To plate successfully it is necessary to watch and control costs.

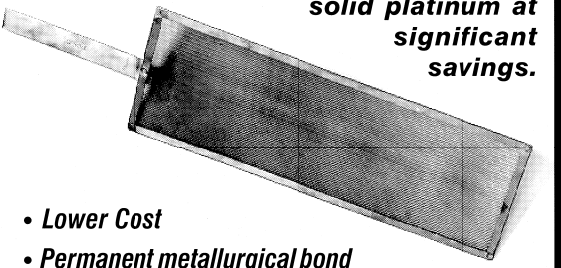
DECORATIVE GOLD PLATING (CLASSES A-C AND, SOMETIMES, G)

Much, but not all, decorative plating is applied to jewelry, watch attachments, and other items of personal use and adornment. The thicknesses of gold or gold alloy are usually 0.000002 to 0.000005 in. and the time of plating is 5 to 30 sec. The recommended trade practice rules for the jewelry industry require that this deposit be called gold flash or gold wash. (To be called gold electroplate it is necessary to have a minimum of 0.000007 in.) These deposits are usually applied over a bright nickel underplate and are bright as plated. They do not require any brightening or grain-refining agents. There are hundreds of different colors and hues, but the Class A and B baths, shown in Table I, will give a representative sample of colors.

All of the "coloring" baths in Table I

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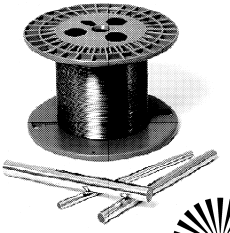


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Rhodium
Sidearm Hoists
Silver
Silver Anodes
Silver Reclaim
Tab Platers
Tank Liners
Timers
Tank Saddles
Tin
Tin/Lead
Tri-Axis Hoists
Tumbleplater
Ultrasonic Systems
Vibarrel

Table II. Antique Baths

	Bright Yellow Highlights, Orange-Brown Smut	*Green Highlights, Green-Black Smut*
Gold as $KAu(CN)_2$ (g/L)	6	2
Silver as potassium silver cyanide (g/L)	—	0.3
Sodium hydroxide (g/L)	15	—
Sodium carbonate (g/L)	30	—
Ammonium carbonate (g/L)	—	38
Sodium cyanide (g/L)	4	15
Temperature (^{O}F)	160-180	70-90
Agitation	None	None
Current density (A/ft^2)	30-40	10

should use 316 stainless steel anodes. The ratio of anode to cathode area is best at 1:1 or 3:1. Very high ratios, when the tank is used as an anode, tend to give an uneven color and thickness of deposit, and the end pieces will frequently burn. No agitation should be used to ensure a uniform color. Sliding or tapping on the cathode bar will increase the deposition of gold and make each color richer but will quickly deplete gold and unbalance the bath. Gold and alloying metals should be added periodically, based on ampere-hour (A-hr) meter readings. The baths, with the exception of the white, green, and rose solutions, should operate at approximately 6% cathode current efficiency. Every 11 A-hr of operation 5 g of gold should be added, together with the proper amount of alloy.

All operating conditions should be controlled as closely as possible. Any variation of the conditions will affect the cathode current efficiency of the gold or the alloy, or both. Changes in the amount of the metals deposited will change the color of the deposit. Other factors that will alter the color of the deposit are the following:

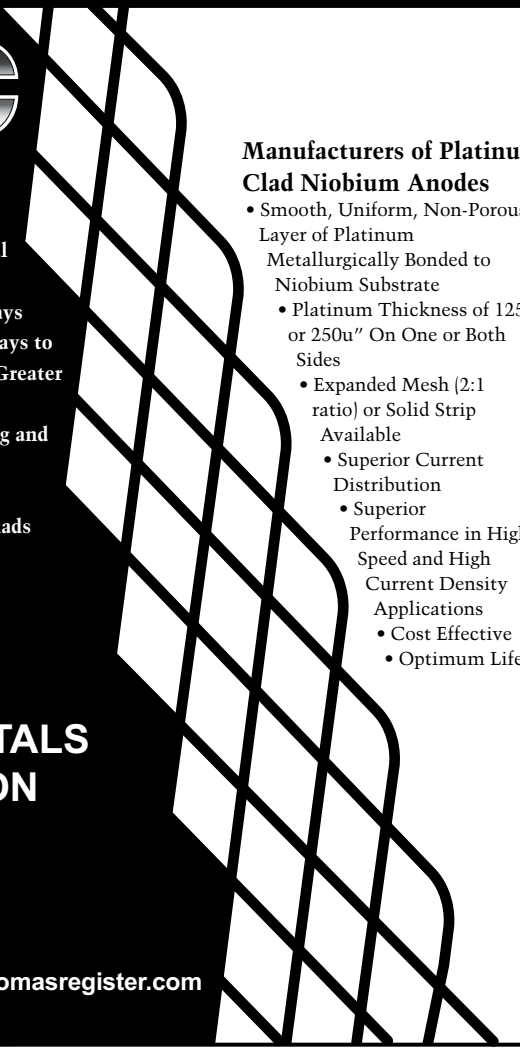
1. *Surface finish.* The surface finish of the basis metal will change the apparent color of the deposit. This is particularly noticeable when a single item has both bright and textured areas. Plated in the same bath, they will appear to be two different colors.
2. *Color of basis metal.* The color of the basis metal alters the color of the gold deposit by adding its color to the gold until the deposit is sufficiently thick to obscure the base. Most gold alloy deposits, if properly applied, will obscure the base after 2 millionths of an in. have been applied. Proprietary additives will allow the gold to obscure the base with as little as 1 ½ millionth of an in. to allow richer colors with the use of less gold.
3. *Current density*. Too low a current density tends to favor the deposition of gold and causes the alloy to become richer. Too high a current density at first favors the alloy and pales out the color. Raising the current density further causes the development of pink, orange, or red tones.
4. *Free cyanide.* Solutions containing copper are very sensitive to changes in the free cyanide content. Low cyanide causes an increase in the pink and red shades, and high cyanide significantly increases the yellow by holding back the copper.

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Table III. A Selection of Typical Acid Gold Color Baths for Thick Deposits

	22k Yellow	*24k Yellow*	*Hamilton*		
			1N	*2N*	*3N*
Gold (g/L)	4-8	4-8	4-8	4-8	4-8
Conducting salts (g/L)	120	120	120	120	120
Nickel as nickel metal (g/L)	0.2	—	7-10	4-6	1-3
Cobalt as cobalt metal (g/L)	1	0.5	—	—	—
pH	4.0-4.5	4.4-4.8	4.0-4.2	4.0-4.2	4.0-4.2
Temperature (°F)	90-100	80-90	120-140	100-120	90-100
Current density (A/ft²)	10-20	10-20	10-20	10-20	10-20
Agitation	Required	Required	Required	Required	Required

5. *Temperature.* The effect is similar to current density. Low temperatures favor the gold yellows, and higher temperatures favor the alloy colors. Temperatures over 160°F should be avoided, except in the case of rose golds, because of the rapid breakdown of cyanide and the darkening of the color.
6. *pH.* It is rarely necessary to adjust the pH of a gold or gold alloy bath. They are usually buffered between pH 10 and 11. Only pink, rose, or red golds are favored by higher readings.

BARREL PLATING (CLASSES A AND B)

Gold as $KAu(CN_2)$, 0.4 g/L
Free cyanide as NaCN, 30 g/L
Disodium phosphate, 23 g/L
Temperature, 100-120°F
Anodes, stainless steel (1:1 or better)

In typical jewelry barrel plating about 6 V is necessary. A decorative finish of 0.000002 in. is deposited in 3 to 4 min. If the parts are small and densely packed in the barrel it may be necessary to plate up to 8 min to get even coverage.

The above formulation may be altered to achieve various colors. Champagne or light Hamilton colors may be achieved by adding 1.5 to 3 g/L of nickel. Lowering the temperature will also produce a lighter and more uniform color.

ANTIQUE GOLDS (CLASSES A AND B)

The art of the 19th-century platers was to produce a finish that looked as if it had been mercury gilt over silver or copper (vermeil) and buried or weathered by the elements for a century or so. Each master plater developed an antique finish that was his trademark. The basic modern method to achieve this effect is as follows:

Table IV. Industrial/Electronic Gold Plating

	Purity	*Knoop Hardness No.*	*Surface*	*Plating Method*		
				Rack	*Barrel*	*Continuous*
Semiconductors	99.95%	60-80	Matte	Yes	Yes	Yes
Printed/etched circuits	99.5-99.7%	120-180	Bright	Yes	No	Yes
Contacts/connectors	99.5-99.7%	120-180	Bright	Yes	Yes	Yes

Table V. Electronic Gold Plating Solutions

	Alkaline Cyanide	*Neutral Cyanide*	*Acid Cyanide*	*Noncyanide*
Semiconductors	Class D	Class D	—	—
Printed circuits	—	—	Class E	—
Connectors	Class E	—	Class E	—

Table VI. Alkaline Cyanide Baths

	Matte	*Bright*
Gold as potassium gold cyanide (g/L)	8-20	8-20
Silver as potassium silver cyanide (g/L)	—	0.3-0.6
Dipotassium phosphate (g/L)	22-45	—
Potassium cyanide (g/L)	15-30	60-100
pH	12	12
Temperature (°F)	120-160	60-80
Anodes	Stainless steel	Stainless steel
Anode/cathode ratio	1:1	1:1-5:1
Agitation	Moderate to vigorous	None to moderate
Current density (A/ft^2)		
Rack	3-5	3-8
Barrel	1-2	1-2
Current efficiency (%)	90-95	90-100
Time to plate 0.0001 in.	8 min at 5 A/ft^2	7 min at 6 A/ft^2
Replenishment	1 oz gold/4 A-hr	1 oz gold/4 A-hr

1. "Burn on" a dark smutty finish.
2. Relieve the highlights on a deeply recessed piece or the flat surface on a filigreed piece by either hand rubbing with pumice and sodium bicarbonate or wheel relieving with a cotton buff, tampico brush, or a brass or nickel-silver wheel. Other methods are possible.
3. Flash gold or a gold alloy deposit on the imperfectly cleaned highlights.

Typical formulations for antique gold baths are provided in Table II. The more the solutions in Table II are abused and the more the operator violates good plating practice and good cleanliness the better and more distinctive the finish will be.

An expensive finish requiring double-racking, but a beautiful finish, is Russian antique. This may be produced by relieving the green-gold antique in Table II and then flashing over with the 24K or English gold.

The old antique baths of the 1940s and 1950s that did not require double-racking or stringing are no longer practical because of the high price of gold.

HEAVY DECORATIVE GOLD (CLASSES C-1 AND C-2)

It is necessary to distinguish between the actual karat assay of a gold alloy electroplate and the apparent karat color of the plate. In general a decorative karat deposit will appear to be a much lower karat than it actually will assay. A 14K color deposit may actually assay 20 to 21K. The formulas in Table III will deposit karat colors but will actually assay a higher karat. (In computing costs it is best to assume that the deposit is pure gold.)

INDUSTRIAL/ELECTRONIC GOLD PLATING

Gold is electroplated for many different electrical and electronic purposes; however, today the majority of gold plating is applied to three specific classes of components: semiconductors, printed/etched circuits, and contacts/connectors.

Table VII. Neutral Cyanide Solutions

	Rack or Barrel Plating	*High-Speed Continuous Plating*
Gold as potassium gold cyanide (g/L)	8-20	15-30
Monopotassium phosphate (g/L)	80	—
or		
Potassium citrate (g/L)	70	90
pH	6.0-8.0	4.5-5.5
Temperature (°F)	160	120-160
Agitation	Desired	Violent
Anodes	Platinum-clad columbium	Platinum-clad columbium
Current density (A/ft²)	1-3	100-400
Current efficiency (%)	90	95-98
Time to plate 0.0001 in.	12 min	10-20 sec
Replenishment	1 oz gold/4 A-hr	1 oz gold/4 A-hr

Table VIII. Acid Cyanide Plating Solutions

	Barrel Plating, Matte Bath 1	*Rack or Barrel Plating, Matte Bath 2*	*High-Speed Continuous Plating, Bright Bath 2*
Gold as potassium gold cyanide (g/L)	8	8	8-16
Citric acid (g/L)	60	60	90
Cobalt as cobalt metal (g/L)	—	0.2-0.5	0.7
or			
Nickel as nickel metal (g/L)			
pH	3.8-5.0	3.8-4.5	3.8-4.3
Temperature (°F)	120-140	70-90	70-120
Anodes	Platinum clad	Platinum clad or stainless steel	Platinum clad
Agitation	Desirable	Desirable	Violent
Current density (A/ft2)	1-5	5-20	100-400
Current efficiency (%)		30-40	30-40
Time to plate 0.0001 in.		10 min at 10 A/ft²	15 sec at 400 A/ft²
Replenishment		1 oz gold/12 A-hr	1 oz gold/12 A-hr

The requirements for the deposit of each of these components and the methods of plating that are used are listed in Table IV.

The gold plating solutions that are actually used by the electronic plater may be conveniently classified by pH range: alkaline cyanide, pH >10; neutral cyanide, pH 6 to 9; acid cyanide, pH 3.5 to 5 (below pH 3.5 the gold cyanide is generally unstable and precipitates); noncyanide (usually sulfite), pH 9 to 10. Table V lists the baths that are primarily used by the industry.

Low-karat gold alloys [Group 2 or 3 (Class F)] have not found much application in the United States. The alloying metal generally affects the electrical properties of the gold

adversely. As little as 1% of iron will increase the electrical resistance of gold over 1,000%, and similar amounts of other metals have less, but still unacceptable, effects on the conductivity of the gold deposit. Even amounts of alloy much less than 1% will inhibit or totally prevent good welding or die bonding of semiconductor chips to a gold surface. Duplex coatings of a low-karat gold base overplated with a high-karat gold surface, although acceptable in some applications from an electrical point of view, have tended to lose their economic advantages as good engineering and new design have required less total gold.

ALKALINE CYANIDE BATHS (GROUP 1, CLASS D)

Table VI lists typical alkaline cyanide baths that are still used. Note that for mat-

te deposits, the higher the temperature the better the deposit and the higher the speed of plating; however, temperatures over 150°F result in a rapid breakdown of the free cyanide and a buildup of cyanide breakdown impurities.

The alkaline cyanide baths are particularly sensitive to organic impurities, both those introduced by drag-in and by the absence of general cleanliness, as well as those caused by cyanide breakdown. To maintain a deposit that has a good appearance and is structurally sound it is necessary to carbon treat and filter the solution periodically. The grade of carbon used must be pure enough not to introduce more impurities than it removes. Constant filtration through a filter packed with carbon is accepted practice but is not as efficient in removing impurities as a batch treatment. If the solution is quite contaminated before treatment it is important to save the used carbon and the used filter cartridge for refining to recover any gold lost in the treatment.

The best method to carbon treat a solution is as follows: (1) Heat the solution to 150 to 160°F. (2) Transfer the hot solution to an auxiliary tank. (3) Add 1/8 to 1/4 oz carbon per gallon of solution. (4) Mix for no longer than 20 to 30 min. (5) Filter the solution by decantation back into the original tank.

No general rule can be given for the frequency of carbon treatment. This will depend on general cleanliness and housekeeping as well as the work being processed; however, it will vary from once every two weeks to once every two months. The room temperature bright bath will require much less carbon treatment than the hot cyanide bath.

NEUTRAL CYANIDE SOLUTIONS (GROUP 2, CLASS D)

The neutral cyanide baths are primarily used by the semiconductor industry. Considerable care must be exercised to prevent contamination of the solution because even a few parts per million of undesirable inorganics can cause the deposit to fail in compression or die bonding.

Typical nonproprietary solutions are listed in Table VII. Pulse plating may be used to advantage with the high-speed formulation. Most effective is a 10% duty cycle. Proprietary baths add grain refiners that decrease porosity, increase the maximum allowable current density, decrease grain size, and generally improve the appearance of the deposit.

ACID CYANIDE PLATING SOLUTIONS (GROUP 3, CLASS E)

Table VIII lists typical acid cyanide plating solutions. Note that pulse plating can be applied with the high-speed bath, but is not widely used.

NICKEL PLATING

BY GEORGE A. DIBARI
INTERNATIONAL NICKEL INC., SADDLE BROOK, N.J.; www.inco.com

Nickel plating is the electrolytic deposition of a layer of nickel on a substrate. The process involves the dissolution of one electrode (the anode) and the deposition of metallic nickel on the other electrode (the cathode). Direct current is applied between the anode (positive) and the cathode (negative). Conductivity between the electrodes is provided by an aqueous solution of nickel salts.

When nickel salts are dissolved in water, the nickel is present in solution as divalent, positively charged ions (Ni^{2+}). When current flows, divalent nickel ions react with two electrons ($2e^-$) and are converted to metallic nickel (Ni^0) at the cathode. The reverse occurs at the anode where metallic nickel dissolves to form divalent ions.

The electrochemical reaction in its simplest form is:

$$Ni^{2+}+2e—=Ni0$$

Because the nickel ions discharged at the cathode are replenished by the nickel ions formed at the anode, the nickel plating process can be operated for long periods of time without interruption.

Estimating Nickel Thickness

The amount of nickel that is deposited at the cathode is determined by the product of the current (in amperes) and the time (in hours). Under ideal conditions, 26.8 A flowing for 1 hr will deposit 29.4 g of nickel (1.095 g/A-hr). If the area being plated is known, the average thickness of the nickel coating can be estimated. For example, if 29.4 g of nickel are deposited on 1 ft^2, the thickness of the deposit is 0.0014 in (Thickness equals the weight of nickel divided by the product of the area and the density of nickel. It is important to use consistent units. The density of nickel is 0.322 lb/in^3.)

Because a small percentage of the current is consumed at the cathode in discharging hydrogen ions, the efficiency of nickel deposition is less than 100%. This fact must be taken into account in estimating the weight and the thickness of nickel that will be deposited under practical plating conditions. Table I is a data sheet on depositing nickel based on 96.5% cathode efficiency. The table relates coating thickness, weight per unit area, current density, and time of plating. Some factors useful in making nickel-plating calculations are given in Table II.

Anode efficiency is normally 100%. Because anode efficiency exceeds cathode efficiency by a small percentage, nickel-ion concentration and pH will rise as the bath is used. Drag-out of nickel-plating solution may compensate for nickel metal buildup in solution to some extent, but at some point if may be necessary to remove a portion of solution from the plating tank and replace the solution removed with water and other constituents. The pH of the solution is normally maintained by adding acid.

Metal Distribution

It is desirable to apply uniform thicknesses of nickel on all significant surfaces to achieve predictable service life and to meet plating specifications that require min-

					Minutes for Obtaining Coating at Various Current Densities, A/ft²			
Thickness, in.	*Thickness μm*	*Oz/ft²*	*G/ft²*	*A-hr*	*10*	*20*	*50*	*100*
0.0001	2.5	0.0721	2.04	1.99	12	6	2.5	1.2
0.0002	5.1	0.144	4.08	3.98	24	12	5	2.4
0.0005	12.7	0.360	10.2	9.95	60	30	12	6
0.0008	20.3	0.578	16.3	15.9	96	48	19	9.6
0.0010	25.4	0.721	20.4	19.9	119	60	24	12
0.0015	38.1	1.082	30.6	29.8	179	89	36	18
0.0020	50.8	1.44	40.8	39.8	238	119	48	24

Table I. Data Sheet on Depositing Nickel (Based on 96.5% Cathode Efficiency)

imum coating thickness values at specified points on the surface. The amount of metal that deposits on the surface of any object being plated is proportional to the current that reaches the surface. Recessed areas on the surface receive less current. The current density and, consequently, the rate of metal deposition in the recessed area are lower than at points that project from the surface. The electrodeposited coating is relatively thin in recessed areas and relatively thick on projecting areas (Fig. 1).

The thickness of the deposit at the cathode and the distribution of the coating can be controlled by proper racking and placement of the parts in solution, and by the use of thieves, shields, and auxiliary anodes. Parts can be designed to minimize problems. It may be necessary to deposit more nickel than is specified to meet a minimum thickness requirement on a specific article.

The nickel processes used for decorative, engineering and electroforming purposes have the same electrochemical reaction. The weight of nickel deposited at the cathode is controlled by natural laws that make it possible to estimate the thickness of the nickel deposited. These estimates must be adjusted to account for variations in cathode efficiencies for specific processes. Normally, cathode efficiency values are between 93% and 97% for most nickel processes. Some of the so-called "fast" bright nickel-plating processes may have lower efficiencies. The actual thickness at any point on a shaped article depends on current flow. In practice, it is necessary to measure coating thickness on actual parts and make necessary adjustments to racks, thieves,

Multiply	*By*	*To Estimate*
Wt. of $NiSO_4 7H_2O$	21%	Wt. of nickel contained
Wt. of $NiSO_4 6H_2O$	22%	Wt. of nickel contained
Wt. of $NiCl_2 6H_2O$	25%	Wt. of nickel contained
Wt. of $NiCl_2 6H_2O$	30%	Wt. of chloride contained
Wt. of nickel carbonate	50%	Wt. of nickel contained
A-hr/ft² nickel plating	1.095	g nickel deposited
	0.0386	oz nickel deposited
	0.00086	mil. of nickel deposited
Mil thickness	19.19	A-hr/ft²
	1151	A-min/ft²
	0.0226	g/cm²
	0.742	oz/ft²

Table II. Factors Useful in Making Plating Calculations (Assumes 100% Cathode Efficiency)

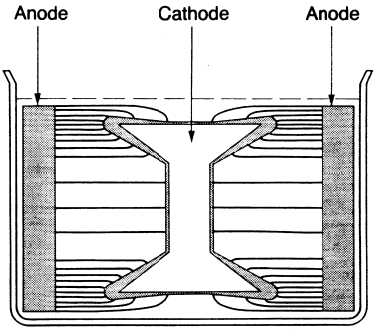


Fig. 1. Current distribution is not uniform over a shaped article. Areas remote from the anode receive a smaller share of the available current than areas near the anode.

and/or shields before thickness can be controlled within a specified range.

DECORATIVE NICKEL PLATING

The development of bright and semibright nickel-plating solutions, multilayer nickel coatings, and microporous and microcracked chromium have resulted in great improvements in the appearance and corrosion performance of decorative nickel coatings. Modern decorative nickel-chromium coatings are brilliant, highly leveled, and long-lasting.

Decorative Processes

The solutions used for decorative plating contain organic addition agents that modify the growth of the nickel deposit to produce fully bright, semibright, and satinlike surfaces. The basic constituents—nickel sulfate, nickel chloride, and boric acid—serve the same purposes as they do in the Watts solution (Table III).

Nickel sulfate is the principal source of nickel ions; nickel chloride improves anode dissolution and increases solution conductivity; boric acid helps to produce smoother, more ductile deposits. Anionic antipitting or wetting agents are required to reduce the pitting due to the clinging of hydrogen bubbles to the products being plated. Nonfoaming wetting agents that lower surface tension are available for air-agitated solutions.

The composition and operating conditions given in Table III for the Watts solution are typical of many decorative nickel-plating solutions, but wide variations in the concentrations of nickel sulfate and nickel chloride are possible. Since most decorative nickel-plating processes are proprietary, composition and operating conditions should be controlled within the limits recommended by the suppliers.

Bright Nickel Solutions

Bright nickel solutions contain at least two types of organic addition agents, which complement each other and yield fully bright nickel deposits.

One type produces deposits that are mirror-bright initially, but are unable to maintain the mirrorlike appearance of the deposit as its thickness is increased. This class includes compounds like benzene disulfonic acid, and benzene trisulfonic acid, benzene sulfonamide and sulfonimides such as saccharin. The presence of the sulfon group and an unsaturated bond adjacent to the sulfon are critical characteristics. Adsorption of the addition agent occurs by virtue of the unsaturated bond, onto growth sites, points or edges of crystals, and at dislocations. The organic compound is reduced electrochemically at the cathode, and this is accompanied by the reduction and incorporation of sulfur (as the sulfide) in the deposit. Fully bright nickel deposits typically contain 0.06% to 0.12% sulfur. These reactions control the structure and growth of the nickel as it is deposited.

The second type may be termed leveling agents because they make the surface smoother as the thickness of the deposit is increased. They are sulfur-free, bath-soluble organic compounds containing unsaturated groups and generally introduce small amounts of carbonaceous material into the deposit. Typical examples

	Watts Nickel	Conventional Sulfamate	Concentrated Sufamate
		Electro Composition, g/L	
$NiSO_4 6H_2O$	225 to 300		
$Ni(SO_3NH_2)_2 4H_2O$		315 to 450	500 to 650
$NiCl_2 6H_2O$	37 to 53	0 to 22	5 to 15
H_3BO_3	30 to 45	30 to 45	30 to 45
		Operating Conditions	
Temperature, °C	44 to 66	32 to 60	normally 60 or 70
Agitation	Air or mechanical	Air or mechanical	Air or mechanical
Current density, A/dm^2	3 to 11	0.5 to 32	Up to 90
Anodes	Nickel	Nickel	Nickel
pH	3.0 to 4.2	3.5 to 4.5	3.5 to 4.5
		Mechanical Properties	
Tensile strength, MPa	345 to 485	416 to 620	400to 600
Elongation, %	15 to 25	10 to 25	10 to 25
Vickers hardness, 100 g load	130 to 200	170 to 230	150 to 250
Internal stress MPa	125 to 185 (tensile)	0 to 55 (tensile)	see text

Table III. Nickel Electroplating Solutions and Typical Properties of the Deposits

of this second of class brighteners are formaldehyde, coumarin, ethylene cyanohydrin, and butynediol.

The combination of organic addition agents makes it possible to obtain smooth, brilliant, lustrous deposits over wide ranges of current density. The deposits have a banded structure consisting of closely spaced laminations believed to be related to the co-deposition of sulfur. Certain cations, for example. zinc, selenium, and cadmium, enhance the luster of electrodeposited nickel, and have been used in combination with the organic additives. Supply houses provide instructions for proprietary bright nickel processes that specify rates of replenishment and methods of analyses for specific addition agents.

Semibright Nickel

Semibright nickel solutions contain nickel sulfate, nickel chloride, boric acid, and a leveling agent. The original process used coumarin as the principal additive. Coumarin-free processes are now available. The process yields deposits that are semilustrous.

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The deposits are smooth and have a columnar structure unlike the banded structure characteristic of fully bright deposits.

The solution was developed to facilitate polishing and buffing; semibright nickel deposits are easily polished to a mirror finish. Efforts to eliminate polishing led to the combination of semibright and bright nickel deposits. Experience has shown that a multilayer nickel coating has greater resistance to corrosion than a single-layer coating of equivalent thickness.

Single Layer and Multilayer Nickel Coatings

Single and multilayer nickel coatings are used to produce decorative coatings that resist corrosion. Single-layer bright nickel deposits are specified for mildly corrosive service. Double-layer coatings are specified for use in severe and very severe service. In double-layer coatings, the first nickel layer is deposited from a semibright bath. The second layer is then deposited from a bright bath. Triple-layer coatings may also be specified for severe and very severe service. In this case, a special thin layer of bright, high-sulfur nickel is deposited between the initial layer of semibright nickel and the top layer of bright nickel. The very thin layer should comprise about 10% of the total nickel coating thickness and must contain greater than 0.15% sulfur (as compared with 0.06% to 0.10% normally found in fully bright deposits).

Multilayer nickel coatings provide improved protection because the active, sulfur-bearing bright nickel layer protects the underlying sulfur-free layer by sacrificial action. For optimum corrosion performance, it is critical that the semibright nickel layer contain no codeposited sulfur.

Microdiscontinuous Chromium

Electrodeposited chromium is applied on top of the decorative multilayer nickel coatings to prevent tarnishing of the nickel when exposed to the atmosphere. The chromium coating is relatively thin compared with the nickel, because electrodeposited chromium is not intrinsically bright and will become dull if thickness is increased beyond an acceptable level. Studies of the corrosion performance of multilayer nickel plus *conventional* chromium coatings revealed a tendency to form one or two relatively large corrosion pits that would rapidly penetrate to the basis metal. This was believed to be due to the relatively low porosity of the top layer of chromium. It was concluded by many investigators that a pore-free chromium electrodeposit should improve corrosion resistance. The pore-free chromium plating processes developed in the early 1960s were short-lived when it was observed that the chromium layer did not remain pore-free in use.

Other investigators concluded that chromium deposits with high porosity or crack densities on a microscopic scale would be preferable. This led to the development of microdiscontinuous chromium deposits of two types: microporous and microcracked. These deposits greatly improve corrosion performance by distributing the available corrosion current over a myriad number of tiny cells on the surface of the coating. Corrosion proceeds uniformly over the entire surface instead of concentrating at one or two pits and, as a result, the rate of pit penetration is slowed dramatically. Double-layer nickel coatings 40 μm thick (1.5 mils) electroplated with either microporous or microcracked chromium and applied uniformly resisted corrosion in severe service for more than 16 years.

Specifying Decorative Nickel Coatings

The specification of decorative nickel coatings is often misunderstood, despite

Layer (type of Nickel Coating)	Specific Elongation, (5)	Sulfur Content, (m/m)	Thickness (Percentage of Total Nickel Thickness) Double-Layer	Triple-Layer
Bottom (s)				
Middle (hgih-sulfur b)	—	Greater than 0.15	—	10
Top (b)	—	Greater than 0.04 and less than 0.15	Less than 40	Less than 40

Table IV. Requirements for Double - or Triple-Layer Coatings

the availability of good technical standards (ASTM Standard B 456 and ISO Standard 1456) that provide the necessary guidance. Some of the requirements for double- or triple-layer nickel coatings are summarized in Table IV. These requirements specify the ductility (percent elongation) of the underlying semibright nickel layer, the sulfur content of each layer, and the thickness of each layer as a percentage of the total nickel thickness. For example, for double-layer nickel coatings on steel, the semibright nickel layer should be 60% of the total nickel thickness. This ratio is important for controlling the corrosion performance, the ductility and the cost of the double-layer coating (the semibright nickel process is generally less expensive than the bright nickel one).

In addition to these general requirements, the standards give recommended thicknesses for nickel plus chromium coatings for various service conditions. The recommendations for coatings on steel from ASTM Standard B 456 are reproduced in Table V. The service condition number characterizes the severity of the corrosion environment: 5 being the most severe and 1 being the least severe. The classification numbers given in the second column of the table specify the coatings that are expected to meet the requirements of the condition of service.

For example, the classification number: *Fe/Ni35d Cr mp* indicates that the coating is suitable for very severe service; it is applied to steel (Fe); the double-layer (d) nickel coating is 35 μm thick and has a top layer of microporous (mp) chromium that is 0.3 μm thick. (The thickness of the chromium is not included unless

Service Conditon Number	Classification Number[a]	Nickel Thickness, Micrometers (mil)
SC 4 (extended time, very severe)	Fe/Ni35d Cr mc	35 (1.4)
	Fe/Ni35d Cr mp	35 (1.4)
SC 4 (very severe)	Fe/Ni40d Cr r	40 (1.6)
	Fe/Ni30d Cr mc	30 (1.2)
	Fe/Ni40d Cr mp	30 (1.2)
SC 3 (severe)	Fe/Ni30d Cr r	30 (1.2)
	Fe/Ni25d Cr mc	25 (1.0)
	Fe/Ni25d Cr mp	25 (1.0)
	Fe/Ni40p Cr r	40 (1.6)
	Fe/Ni30p Cr mc	30 (1.2)
	Fe/Ni30p Cr mp	30 (1.2)
SC 2 (moderate)	Fe/Ni40b Cr r	20 (0.8)
	Fe/Ni15b Cr mc	15 (0.6)
	Fe/Ni15b Cr mp	15 (0.6)
SC 1 (mild)	Fe/Ni10b Cr r	10 (0.4)

[a] See text for explanation of Classification Numbers.

Table V. Nickel Plus Chromium Coatings on Steel

it differs from 0.3 μm.)

The type of nickel is designated by the following symbols: b, for electrodeposited bright nickel (single-layer); d, for double or multilayer nickel coatings; p, for dull, satin, or semibright unpolished nickel deposits; s, for polished dull or semibright electrodeposited nickel. The type of chromium is given by the following symbols: r, for regular or conventional chromium; mp, for microporous chromium; mc, for microcracked chromium.

The standards provide additional information to assure the quality of electrodeposited decorative nickel-plus-chromium coatings. In essence, the available standards, which summarize many years of corrosion experience, show that multilayer nickel coatings are significantly more corrosion resistant than single-layer bright nickel coatings. Microdiscontinuous chromium coatings provide more protection than conventional chromium, and the corrosion protection afforded by the use of decorative electroplated nickel-plus-chromium coatings is directly proportional to the thickness of the nickel.

"Total quality improvement" goals cannot be achieved without understanding and complying with the requirements contained in technically valid standards.

ENGINEERING NICKEL PLATING

Engineering or industrial applications for electrodeposited nickel exist because of the useful properties of the metal. Nickel coatings are used in these applications to modify or improve surface properties, such as corrosion resistance, hardness, wear, and magnetic characteristics. Although the appearance of the coatings is important and the plated surface should be defect-free, the lustrous, mirrorlike deposits described in the preceding section are not required.

Engineering Plating Processes

Typical compositions and operating conditions for electrolytes suitable for engineering applications have been included in Table III. In addition, electrolytes for industrial plating, including all-chloride, sulfate-chloride, hard nickel, fluoborate, and nickel-cobalt alloy plating have been discussed by Brown and Knapp.[1]

Mechanical Properties

The mechanical properties are influenced by the chemical composition and the operation of the plating bath as indicated in Table III. The tensile strength of electrodeposited nickel can be varied from 410 to 1,170 MPa (60 to 170 psi) and the hardness from 150 to 470 DPN by varying the electrolyte and the operating conditions.

The operating conditions significantly influence the mechanical properties of electrodeposited nickel. Figures 2, 3, and 4 show the influence of pH, current density, and temperature on the properties of nickel deposited from a Watts bath. Additional information on how the properties of electrodeposited nickel are controlled is available.[2]

The mechanical properties of electrodeposited nickel vary with the temperature to which the coatings are exposed as shown in Figure 5. The tensile strength, yield strength and ductility of electrodeposited nickel reaches low values above 480°C (900°F). Nickel deposits from sulfamate solutions are stronger at cryogenic temperatures than deposits from the Watts bath.

Corrosion Resistance

Engineering nickel coatings are frequently applied in the chemical, petroleum, and food and beverage industries to prevent corrosion, maintain product purity, and prevent contamination. As a general rule, oxidizing conditions favor corrosion of

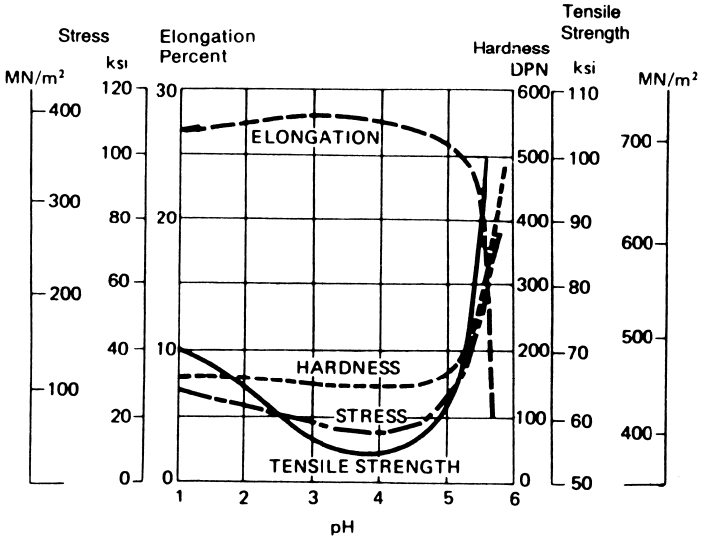


Fig. 2. Variation in internal stress, tensile strength, ductility, and hardness with pH. Watts bath 54°C (130°F) and 495 A/m² (46 A/ft²).

nickel in chemical solutions, whereas reducing conditions retard corrosion. Nickel also has the ability to protect itself against certain forms of attack by developing a passive oxide film. When an oxide film forms and is locally destroyed as in some hot chloride solutions, nickel may form pits. In general, nickel is

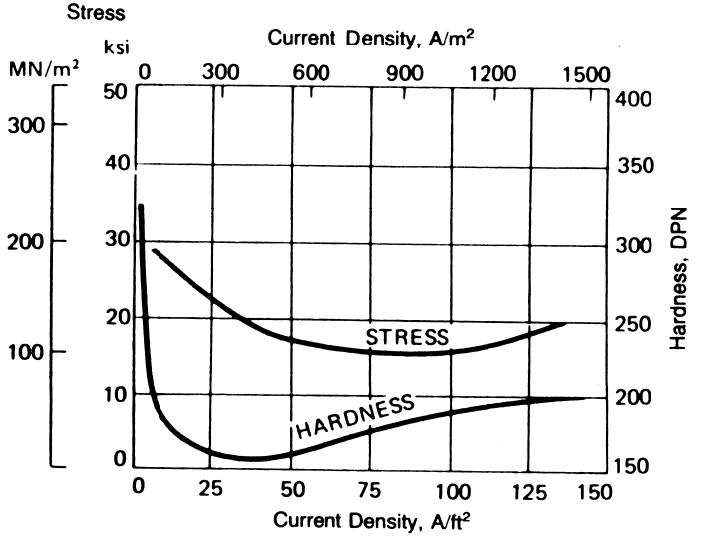


Fig. 3. Variation in internal stress and hardness with current density. Watts bath 54°C (130°F) and pH 3.

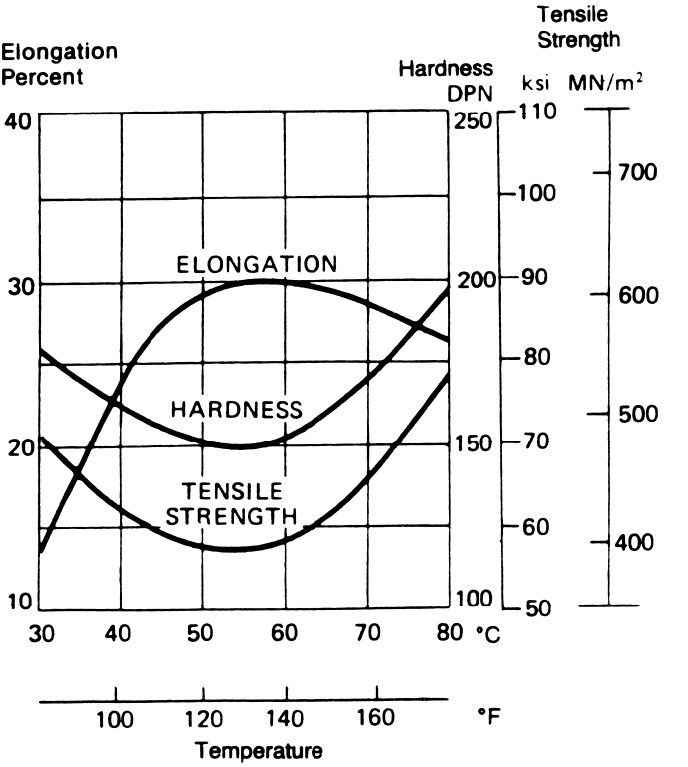


Fig. 4. Variation in elongation, tensile strength, and hardness with temperature. Watts bath pH 3 and 495 A/m² (46 A/ft²).

resistant to neutral and alkaline solutions, but not to most of the mineral acids.

Corrosion resistance in engineering applications is controlled by optimizing nickel thickness. The thickness of the nickel is dependent on the severity of the corrosive environment. The more corrosive the service conditions the greater the thickness of nickel required. Thickness generally exceeds 0.003 in. (75 μm) in engineering applications.

Nickel Plating and Fatigue Life

Thick nickel deposits applied to steel may cause significant reductions in the composite fatigue strength in cyclical stress loading. The reduction in fatigue strength is influenced by the hardness and strength of the steel and the thickness and internal stress of the deposits. Lowering the internal stress of the deposits lowers the degree of reduction in fatigue life; compressively stressed nickel deposits are beneficial. Fatigue life is enhanced by increasing the hardness and strength of the steel and by specifying the minimum deposit thickness consistent with design criteria. Shot peening the steel prior to plating helps minimize reduction in fatigue life upon cyclical stress loading.

Hydrogen Embrittlement

Highly stressed, high-strength steels are susceptible to hydrogen embrittlement

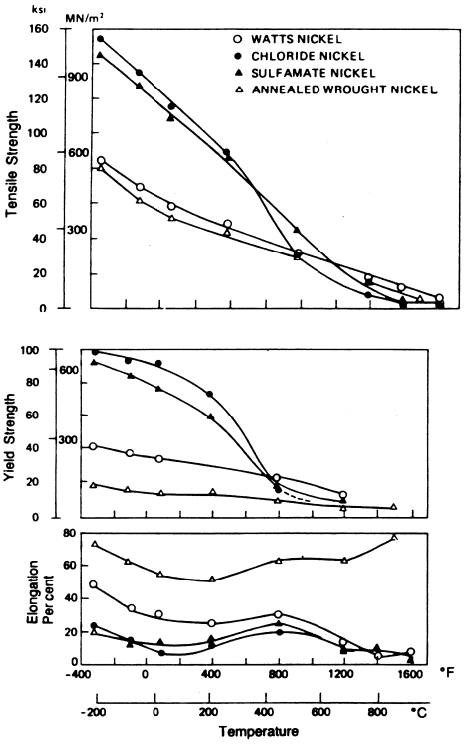


Fig. 5. Effect of temperature on the tensile strength, yield strength, and elongation of electrodeposited nickel.

during normal plating operations. Because nickel plating is highly efficient, hydrogen damage is unlikely to occur as a result of nickel plating *per se*. The pretreatment of steel prior to plating, however, may require exposing the steel to acids and alkalies. During these operations, excessive amounts of hydrogen may evolve which may damage steels susceptible to hydrogen embrittlement. Steels that are susceptible to hydrogen embrittlement should be heat treated to remove hydrogen. The time required may vary from 8 to 24 hr depending on the type of steel and the amount of hydrogen to be removed. The temperature is of the order of 205°C (400°F), and the exact temperature may be alloy dependent.

NICKEL ELECTROFORMING

Nickel electroforming is electrodeposition applied to the production of metal products. It involves the production or reproduction of products by electroplating onto a mandrel that is subsequently separated from the deposit. It is an extremely useful technology that continues to grow in importance.

Conventional Processes

The composition, operating conditions, and mechanical properties of deposits from the electrolytes most often used for electroforming (Watts nickel and conventional sulfamate) are given in Table III. Nickel sulfamate solutions are the most popular because the deposits are low in stress, high rates of deposition are possible, and the thickness of the deposit is less affected by variations in current densities than are deposits from Watts solutions. By maintaining the solution as pure as possible and the chloride as low as possible, the internal stress of the nickel sulfamate deposits can be kept close to zero. Watts solutions are very economical.

High-Speed, Low-Stress Process

A concentrated nickel sulfamate solution has been recommended for electroforming at high rates and at low stress levels in deposits that do not use organic stress reducers, which would introduce sulfur. The solution has a nickel sulfamate concentration of 550 to 650 g/L, a nickel chloride concentration of 5 to 15 g/L, and

a boric acid concentration of 30 to 40 g/L. It is operated at a pH of 4.0, a temperature of 140 to 160°F (60 to 71°C) and at current densities as high as 800 A/ft². The high rates of plating are made possible by the high nickel concentration. When the bath is properly conditioned and operated, it is possible to control internal stress at or close to zero because of the interrelations of stress, current density, and solution temperature (Table VI).

After purification with carbon to remove all organic contaminants, the concentrated solution is given a preliminary electrolytic conditioning treatment consisting of (1) electrolysis at 0.5 A/dm² on both anode and cathode for up to 10 A-hr/L; (2) electrolysis at 0.5 A/dm² on the anode and at 4.0 A/dm² on the cathode for up to 30 A-hr/L of solution. For this conditioning treatment, the anode must be nonactivated (sulfur-free). A corrugated steel sheet may be used as the cathode. When the solution has been conditioned, a deposit at a current density of 5 A/dm² and at 60°C should be lustrous and the internal stress as determined with a spiral contractometer or other device should be 48 ± 14 MPa (7,000 ± 2,000 psi) compressive.

To control the internal stress and other properties during operation, the solution is electrolyzed continuously at low current density by circulating through a small, separate conditioning tank. The conditioning tank should have 10 to 20% of the capacity of the main tank and the total solution should be circulated through it two to five times per hour. For this to work, the anodes in the conditioning tank must be nonactive, whereas the anode materials in the main tank must be fully active (containing sulfur). This is a means of controlling the anode potential in the conditioning tank so that only a stress reducer that does not increase the sulfur content of the nickel is produced. The use of an active anode material in the main tank prevents formation of sulfamate oxidation products in that part of the system.

Zero-stress conditions can be obtained at the temperature and current density values given in Table VI. The plating rate is also indicated in the table. For example, at 50°C, the stress is zero at approximately 8 A/dm², and will become compressive below and tensile above that value. To deposit nickel at 32 A/dm² at zero stress, the temperature must be raised to 70°C. Despite its seeming complexity, this process is being used successfully to electroform stampers for compact disc manufacture where flatness of the stamper is critical and to electroform ultrathin nickel foil continuously on rotating drums.

The internal stress in deposits from sulfamate solutions is influenced by reactions at the nickel anode. When a nickel anode dissolves at relatively high potentials, stress reducers are produced by anodic oxidation of the sulfamate anion. The use of pure nickel in the conditioning tank and active nickel in the main tank is designed to control the nature and amount of the stress reducer formed in this high-speed bath.

QUALITY CONTROL

Improvement in total quality is required by all industrial activity, including nickel plating. Quality assurance involves maintaining the purity of the nickel-plating solution and controlling the properties of the deposits. Some of the control procedures are summarized here.

Purification of Solutions

Nickel-plating baths freshly prepared from technical salts contain organic and inor-

Impurity	*Maximum Conc. (ppm)*	*Purification Treatment*
Iron	50	High pH and electrolysis
Copper	40	High pH and electrolysis
Zinc	50	High pH and electrolysis
Lead	2	Electrolysis
Chromium	10 (hexavalent)	High pH. It may be necessary to precede this with a potassium permanganate-lead carbonate treatment followed by lead removal.
Aluminum	60	High pH
Organic impurities	solution related	Activated carbon; activated carbon plus electrolysis

Table VI. Maximum Concentration of Impurities and Purification Treatments

ganic impurities that must be removed before the bath is operated. Older baths gradually become contaminated from drag-over from preceding treatments, from components that are allowed to fall off the rack and allowed to remain in the tank, from corrosion products from auxiliary equipment, from tools dropped into the tank, and from other sources. It is more effective to keep impurities out of the plating bath than to deal with rejects and production interruptions resulting from the use of impure solutions.

The maximum concentrations of impurities normally permissible in nickel plating solutions and recommended treatments for their removal are shown in Table VII. The electrolytic treatment referred to in the table, known as "dummying," involves placing a large corrugated cathode in the solution and plating at low current densities, 2 and 5 A/ft^2. Copper, lead, and certain sulfur-bearing organic addition agents are best removed at 2 A/ft^2, whereas iron and zinc are more effectively removed at 5 A/ft^2. A corrugated cathode is preferred because it gives a wider current density range. At 2 A/ft^2, impurities should be removed after the solution has been operated for 2 A-hr/gal; at 5 A/ft^2, 5 A-hr/gal should be sufficient.

The high pH treatment requires transferring the nickel solution to an auxiliary treatment tank. Sufficient nickel carbonate is added to bring the pH above 5.2. Approximately 0.5 to 1.0 ml/L of 30% hydrogen peroxide is added. The bath is agitated and kept warm for 2 hr. The pH is adjusted to the optimum level after the bath is filtered back into the main plating tank. The solution may then be electrolyzed at low current density until deposit quality is acceptable.

When organic impurities are to be removed, activated carbon is added prior to the high pH treatment described above. Approximately 0.13 to 0.4 oz/gal (1 to 3 g/L) of activated carbon is commonly added to the solution in the auxiliary treatment tank. The nickel carbonate and hydrogen peroxide are then added. The solution is then filtered. Electrolytic purification is often desirable at this point. After a new bath has been prepared, the high pH treatment, treatment with activated carbon, and electrolysis at low current densities are performed sequentially until the quality of the deposit as determined by the tests discussed in the next section is acceptable.

CONTROLLING THE PROPERTIES OF NICKEL DEPOSITS

Methods that measure thickness, adhesion, and corrosion resistance of nickel coatings are available as means of quality control. Properties such as porosity, ductility, tensile strength, internal stress, hardness, and wear resistance are important to control the quality of electroplated articles. Some of these properties may be measured by the following methods.

Thickness

Micrometer readings are often used to determine the thickness of a coating at a particular point when the deposit thickness exceeds 125 μm (0.005 in.). Other methods for determining the thickness of electrodeposited coatings can be found in ASTM standards. ASTM standard B 487 describes a method based on metallographic examination of cross-sections of the plated object. Alternate tests involve magnetic (ASTM B 530) and coulometric (ASTM B 504) measurements of thickness.

The STEP Test

The simultaneous thickness and electrochemical potential (STEP) test is similar to the coulometric method of determining thickness. By including a reference electrode in the circuit, however, it is possible to measure the electrochemical potential of the material being dissolved. The test was developed to control the quality of multilayer nickel coatings. For example, with double-layer nickel coatings, a large change in potential occurs when the bright nickel layer has dissolved and the underlying semibright nickel begins to be attacked. The potential difference is related to the overall corrosion resistance of the multilayer coating. The test has been standardized (ASTM B 764) and is specified for automotive plating.

Corrosion and Porosity Testing

Examination of the coated part after immersion in hot water for 2 to 5 hr for rust is one technique used in studying the corrosion resistance of plated steel. The number of rust spots in a given area is then used as the qualification for accepting or rejecting the piece. Modifications of this test include immersion for up to 5 hr in distilled water, in distilled water saturated with carbon dioxide, or in distilled water containing 0.5% by weight of sodium chloride at test temperatures of 82 to 85°C (180 to 185°F).

Several salt spray tests have been used to simulate marine environments. These tests are commonly used to evaluate nickel and nickel-plus-chromium coatings on ferrous and nonferrous substrates. The salt spray tests are also used as accelerated quality control tests and are described in the following standards: salt spray (ASTM B 117); acetic acid-salt spray (ASTM B 267); and copper-accelerated acetic acid-salt spray (CASS Test: ASTM B 368).

The ferroxyl test is another porosity test that is employed for coatings on ferrous metal substrates and involves the formation of Prussian blue color within exposed pits. The solution utilizes sodium chloride and potassium ferricyanide as reagents to develop the color.

The only truly satisfactory method of establishing the relative performance of various coating systems is by service testing. Therefore, care should be exercised in interpreting the results of accelerated corrosion tests. Once an acceptable service life has been determined for a specific thickness and type of coating, the performance of other candidate coatings may be compared against it.

	Conditioning Step One		*Conditioning Step Two*	
Basis Metal	*Solution*	*Operation*	*Solution*	*Operation*
Aluminum alloys	Zincate or stannate	Immersion	Coppy cyanide strike	Deposit copper at 2.5 A/dm^2 for 2 min; then at 1.3 A/dm^2 for 6 min
Copper Alloys	Sulfuric or hydrochloric acid	Immersion		
Iron castings	Sulfuric or hydrochloric acid	Immersion and water rinse	Alkaline clean	At 6.5 to 10 A/dm^2
Lead Alloys	10% Fluoborate	Immerse 10 to 15 sec		
Nickel	Acid nickel chloride	30 A/dm2; anodic for 2 min then cathodic for 6 min.		
Stainless steels	65% Sulfuric acid	Cathodic for 2 min	Acid nickel chloride	Cathoidc for 2 min at 16 A/dm^2
Low steel carbons	Alkaline cleaner	Anodic at 6 V for 1 to 2 min	10% Sulfuric acid	Immerse for 5 to 15 sec
High steel carbons	Sodium cyanide	Immerse or short anodic treatment	Sulfuric acid plus sodium sulfate solution	Anodic at 10 to 40 A/dm^2
Zinc	Copper cyanide	Cathodic strike	Cyanide copper	Cathodic

This table only gives the final conditioning steps. These steps are preceded by other critical steps. For complete details see the section on Chemical Surface Preparation in this *Guidebook and the Annual Book of ASTM Standards,* volume 02.05 published by American Society for Test and Materials, Philadelphia. Details are given in other handbooks including *Inco Guide to Nickel Plating*, available on request from Inco,Saddle Brook, NJ 07662. Rinsing steps have not been included; in general, rinsing or double rinsing is beneficial after each conditioning step.

Table VII. Summary of Conditioning Steps in the Preparation of Metals for Plating

Hardness
Hardness measurements involve making an indentation on the surface (or cross section for thin coatings) of the deposit. The indenter has a specified geometry and is applied with a specified load. In the case of industrial nickel coatings, the most common hardness determination is the Vickers method of forcing a diamond point into the surface under a predetermined load (normally 100 g). This provides a measure of that surface to permanent deformation under load. The figure obtained is not necessarily related to the frictional properties of the material nor to its resistance to wear or abrasion. The measurement of microhardness of plated coatings is discussed in ASTM B 578.

Internal Stress
The magnitude of internal stress obtained in deposits is determined by plating onto one side of a thin strip of basis metal and measuring the force causing the strip to bend. One method used in commercial practice involves plating the exterior surface of a helically wound strip and measuring the resultant change of curvature. Another method is based on the flexure of a thin metal disc. See ASTM B 636 for the method of measuring internal stress with the spiral contractometer.

Ductility
Most of the tests that have been used for evaluating the ductility of plated coatings are qualitative in nature. Two bend tests are described in ASTM B 489 and B 490. Both of these procedures require a minimum amount of equipment. Another method for measuring the ductility of thick deposits is to determine the elongation of a specimen in a tensile testing machine. This method is limited to relatively thick foils of controlled geometry and thickness. A method specifically designed for plated thin foils has been used and is known as the hydraulic bulge test. A mechanical bulge test is also available.

Adhesion
In general, the adhesion between a nickel coating and the basis material should exceed the tensile strength of the weaker material. As a result, when a force is applied to a test specimen, which tends to pull the coating away from the basis metal, separation occurs within the weaker material rather than at the boundary between the basis metal and the nickel coating. A number of qualitative tests have been used that utilize various forces applied in a multitude of directions to the composite basis metal and coating, such as hammering, filing, grinding, and deforming. Quantitative tests have also been described in the literature. Achieving good adhesion requires a sound bond between the substrate and the coating. A sound metallurgical bond may be achieved on most materials by proper surface preparation prior to plating. The selection of grinding, polishing, pickling and conditioning treatments for a variety of basis metals varies from one material to another, and depends on the initial surface condition of the metal. The activating treatments that follow polishing and cleaning operations are listed in Table VIII for the most commonly plated basis metals. ASTM standards provide additional information. Nonconductive plastics and other materials can be plated by metallizing the material, using etching and catalyzing techniques (ASTM B 727).

NICKEL ANODE MATERIALS
Important developments in nickel anode materials and their utilization have taken place. Of utmost significance was the introduction of titanium anode baskets in the 1960s. Today the use of expanded or perforated titanium anode bas-

kets filled with nickel of a selected size has become the preferred method of nickel plating. Titanium anode baskets are preferred because they offer the plater a number of advantages. Primary forms of nickel can be used that provide the least costly nickel ion source. Anode replenishment is simple and can be automated. The constant anode area achieved by keeping baskets filled improves current distribution and conserves nickel.

Several forms of primary nickel are currently being used in baskets. These include electrolytic nickel squares or rectangles and button-shaped material that contains a small, controlled amount of sulfur. Nickel pellets produced by a gas-refining process and similar pellets containing a controlled amount of sulfur are being utilized.

Prior to the introduction of titanium anode baskets, wrought and cast nickel anode materials were the norm. They are still used, but not to the extent they were before 1960. The wrought and cast anode materials comprise rolled bars containing approximately 0.15% oxygen; rolled nickel containing approximately 0.20% carbon and 0.25% silicon; and cast bars containing approximately 0.25% carbon and 0.25% silicon. Soluble auxiliary anodes are generally carbon- and silicon-bearing small-diameter rods.

With the exception of the sulfur-bearing materials, nickel anodes require the presence of chloride ion in the plating bath to dissolve efficiently. Rolled or cast carbon-bearing materials are used up to a pH of 4.5, and oxygen-bearing, rolled depolarized anode bars can be used above a pH of 4.5 when chlorides are present in solution.

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PALLADIUM AND PALLADIUM-NICKEL ALLOY PLATING

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Palladium has been electroplated from a wide variety of systems, which can be broadly characterized as ammoniacal, chelated, or acid processes. Of these, the most numerous are the ammoniacal systems, in which palladium is present as an ammine complex, such as palladosamine chloride, $Pd(NH_3)4Cl_2$, or diamino-dinitrite, $Pd(NH_3)_2(NO_2)_2$, which is known popularly as the P-salt. Some representative formulations are shown as follows:

P-SALT/SULFAMATE

Palladium as $Pd(NH_3)_2(NO_2)_2$, 10-20 g/L
Ammonium sulfamate, 100 g/L
Ammonium hydroxide to pH 7.5-8.5
Temperature, 25-35°C
Current density, 0.1-2.0 A/dm^2
Anodes, platinized

PALLADOSAMINE CHLORIDE

Palladium as $Pd(NH_3)_4Cl_2$, 10-20 gL
Ammonium chloride, 60-90 g/L
Ammonium hydroxide to pH 8.0-9.5
Temperature, 25-50°C
Current density, 0.1-2.5 A/dm^2

Palladium electrodeposits are notably susceptible to microcracking induced by codeposition of hydrogen. For this reason, it is important to plate at current efficiencies as high as possible. Proprietary brightening and surfactant systems are available, which increase the range of current densities over which sound deposits may be obtained. Ammoniacal electrolytes, particularly at higher temperature and pH, tend to tarnish copper and copper alloys. Proprietary palladium strike solutions have been developed. In most cases, however, a nickel strike is sufficient.

Chelated palladium plating solutions contain palladium in the form of an organometallic complex. These solutions operate in the pH range of 5 to 7 and are in almost all cases proprietary. Requisite details may be obtained from the manufacturers.

Acid palladium plating solutions have been used for producing heavy deposits of very low stress. Such systems are ordinarily based on the chloride, although a proprietary sulfate solution brightened with sulfite has been reported. A representative formulation for the chloride systems is as follows:

ACID CHLORIDE

Palladium as $PdCl_2$, 50 g/L

Ammonium chloride, 30 g/L
Hydrochloric acid to pH 0.1-0.5
Temperature, 40-50°C
Current density, 0.1-1.0 A/dm^2
Anodes, pure palladium

Deposits from the acid chloride system are dull to semibright. Current efficiency is 97 to 100%. The plating solution itself is notably sensitive to contamination by copper, which can displace palladium from solution. Work to be plated in this solution should thus be struck with palladium or with gold.

PALLADIUM-NICKEL PLATING

Palladium readily forms alloys with other metals and has been plated in numerous alloy formulations. Of these, the most important commercially has been palladium-nickel, which can be deposited as a homogeneous alloy over a composition range from approximately 30% to over 90% palladium by weight. Current practice favors an alloy composition from approximately 75 to 85% wt. palladium. A formulation suitable for alloys in this range is as follows:

Palladium as $Pd(NH_3)_4Cl_2$, 18-28 g/L (palladium metal, 8-12 g/L),
Ammonium chloride, 60 g/L
Nickel chloride concentrate, 45-70 ml/L (nickel metal 8-12 g/L)
Ammonium hydroxide to pH 7.5-9.0
Temperature, 30-45°C
Current density, 0.1-2.5 A/dm^2
Anodes, platinized

Palladium-nickel alloy electrodeposits are notably less sensitive to hydrogen-induced cracking than are pure palladium deposits. They are, however, somewhat more susceptible than pure palladium to stress cracking upon deformation. As with pure palladium plating systems, various proprietary additives are available for brightening and stress control.

SILVER PLATING

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It is not surprising that silver was one of the first metals to be deposited by electroplating during the early development of this manufacturing technique in the mid-19th century. Decorative application of a silver finish on hollowware and flatware fabricated from less-expensive metals was immediately a great commercial success.

The formulation of a typical, decorative silver-plating solution in use today is remarkably similar to that patented by the Elkington brothers in 1840. Despite the environmental, health, and safety issues associated with cyanide salts, cyanide-based silver-plating solutions offer the most consistent deposit quality at the lowest cost. This is particularly true for decorative applications. Although commercially viable, noncyanide processes have recently been made available to electroplaters.

Electroplated silver has many applications beyond decorative finishing. Its use on electronic components and assemblies has increased significantly during the past two decades. Recent application of silver to waveguides used in cellular telecommunications systems has added to its established use in packaging of integrated circuits.

CYANIDE SYSTEMS

A typical, traditional silver-plating solution suitable for rack work would be as follows:

Silver as $KAg(CN)_2$	15-40 g/L	(2.0-5.5 oz/gal)
Potassium cyanide (free)	12-120 g/L	(1.6-16 oz/gal)
Potassium carbonate (min)	15 g/L	(2 oz/gal)
Temperature	20-30°C	(70-85°F)
Current density	0.5-4.0 A/dm^2	(5-40 A/ft^2)

Barrel plating usually results in much greater drag-out losses and lower current density during operation so lower metal concentrations are desirable. A typical formula would be:

Silver as $KAg(CN)_2$	5-20 g/L	(0.7-2.5 oz/gal)
Potassium cyanide (free)	25-75 g/L	(3.3-10.0 oz/gal)
Potassium carbonate (min)	15 g/L	(2 oz/gal)
Temperature	15-25°C	(60-80°F)
Current density	0.1-0.7 A/dm^2	(1.0-7.5 A/ft^2)

The formulas above will produce dull, chalk-white deposits that are very soft (<100 Knoop). Additions of grain refiners or brighteners will modify deposits, causing them to become lustrous to fully bright.

Examples of these additives are certain organic compounds, which usually contain sulfur in their molecule, and complexed forms of a group V or VI element such as selenium, bismuth, or antimony. Deposits become harder as brightness increases; for fully bright deposits the usual hardness range will be between 100

and 200 Knoop. Antimony and selenium will produce harder deposits than most organic compounds, although the latter generally have better electrical properties.

Potassium carbonate is added to increase the solution conductivity and, since carbonate is an oxidation product of cyanide, additions are not needed after the initial solution makeup. This oxidation process occurs slowly even when the solution is not in use. When the potassium carbonate concentration has reached 120 g/L (16 oz/gal) it can cause deposits to become dull or rough. Removal of carbonate can be accomplished by crystallizing at low temperatures (known as "freezing-out") or precipitation with calcium or barium salts followed by careful and thorough filtration.

Anode purity is of paramount importance when using soluble silver anodes since typical impurities, such as copper, iron, bismuth, lead, antimony, sulfur, selenium, tellurium, and platinum-group metal, will cause solution contamination and may lead to anode filming, which inhibits proper dissolution of the silver. Silver anodes are produced by rolling, casting, or extruding the metal. Care should be taken to ensure adequate annealing has taken place after fabrication. The object of annealing is to obtain correct grain size so that the anodes do not shed during dissolution. (Shedding means that small particles break away from the anode and these can cause roughness in the silver deposit.)

Improper anode dissolution or shedding can also occur if the free cyanide concentration is too low or if there is insufficient anode area in use. Free cyanide concentration should be analyzed regularly, even when the bath is idle, and additions of potassium cyanide made as needed. Typical analysis frequency might be once daily for heavily used solutions. Optimum anode-to-cathode area ratio is 2:1; a maximum anode current density of 1.25 A/dm^2 (13.5 A/ft^2) is recommended.

Silver anodes should be removed from the solution if the process is to be idle for any extended period of time. Silver will continue to dissolve chemically into a cyanide solution and excessively high silver concentrations may result. Should this occur, mild steel anodes may be substituted for some of the silver anodes for a short period of operation until the silver concentration is brought back into its normal range.

Silver Strike

Silver is a relatively noble metal and as such will form immersion deposits on the surfaces of less noble metals that are immersed in its solution. This tends to happen even when the base metal enters the silver solution "hot" or "live," that is, with a voltage already applied. The inevitable result of this phenomenon is poor adhesion of subsequent deposits. To minimize this effect, it is essential to employ a silver-strike coating prior to plating the main deposit. A typical silver strike would be as follows:

Silver as $KAg(CN)_2$	3.5-5 g/L	(0.5-0.7 oz/gal)
Potassium cyanide (free)	80-100 g/L	(10-13 oz/gal)
Potassium carbonate (min)	15 g/L	(2 oz/gal)
Temperature	15-26°C	(60-80°F)
Current density	0.5-1.0 A/dm^2	(5-10 A/ft^2)

It is not necessary to rinse between such a strike and a cyanide-based silver-plating solution. Silver strike thickness is typically 0.05-0.25 μm (0.000002-0.000010 in.)

Table I. Comparison of Operating Conditions for Proprietary Noncyanide Silver Plating Processes

Parameter	*Process A*	*Process B*
Silver concentration, rack oz/gal)	21-24 g/L (2.8-3.2 oz/gal)	11.25-18.75 g/L (1.5-2.5
Silver concentration, barrel	21-24 g/L (2.8-3.2 oz/gal)	15-18.75 g/L (2-2.5 oz/gal)
Solution pH	8.0-9.0	8.5-9.5
Temperature range	16-29°C (60-85°F)	16-24°C (60-75°F)
Current density, rack	0.1-2.2 A/dm² (1-20 A/ft²)	0.5-2.2 A/dm² (5-20 A/ft²)
Current density, barrel	0.3-0.6 A/dm² (3-6 A/ft²)	0.5-1.6 A/dm² (5-15 A/ft²)
Anode material	Silver, stainless steel, or Pt/Ti	Silver
Anode to cathode area ratio	1:1-2:1	2:1
Agitation	Cathode rod + sparger	Cathode rod + air at anodes

Posttreatments

It is essential to employ proper rinsing procedures after silver plating. Inclusion of cyanide in the deposit during the plating process is unavoidable and results in discoloration of the deposit over time if it is not leached out of the deposit immediately after plating is complete. This discoloration of the deposit is referred to as "sweating out." Proper rinsing follows this sequence: silver plate, drag-out rinse, cold water rinse, cold water rinse, hot water soak (minimum temperature 90°C/195°F for 2 min), immediate cold water rinse (do not allow parts to dry in air before entering), (apply antitarnish coating if required), (cold water rinse), dry.

If desired, antitarnish coatings, such as those based on alkaline chromate, can be applied prior to final rinse and dry steps. Electrophoretic lacquers can also be applied before drying if desired. Solvent-based lacquers are rarely used today but if they are beware of their use on antimony-brightened silver deposits. Some traditional lacquers will react with the antimony in the silver surface, resulting in the formation of black spots. Unfortunately, these black spots usually develop during storage, making quality control difficult.

NON-CYANIDE SYSTEMS

Many compounds of silver have been investigated as potential metal sources for a noncyanide plating process. Several authors have subdivided these studies into three groups by compound type. These groups are (1) simple salts, e.g., nitrate, fluoborate, and fluosilicate; (2) inorganic complexes, e.g., iodide, thiocyanate thiosulfate, pyrophosphate, and trimetaphosphate; and (3) organic complexes, e.g., succinimide, lactate, and thiourea. The simple salts all appear to suffer from the same problem: sensitivity of the materials to visible and ultraviolet light. Although some smooth deposits have been obtained from such systems, they are not viable under normal production conditions.

Two noncyanide silver plating processes are currently being marketed. These are based on proprietary complexes of silver. Of the inorganic complexes considered, three are worth discussing further; these are the iodide, trimetaphosphate, and thiosulfate solutions. Silver succinimide complexes formed the basis of the first proprietary processes to be offered commercially. These are discussed here also.

Commercially Available Systems

The two proprietary systems currently being offered commercially are compared

here. The manufacturers-recommended operating conditions are compared in Table I.

Both processes will deposit silver directly onto copper alloys but both require a strike to promote adhesion to nickel, highly leaded brass, and other metals prone to passivity. Both suppliers recommend using a noncyanide-based copper strike where necessary.

Deposits are typically as bright as the substrate onto which they are plated. Brightening systems similar to those available for cyanide processes have not yet been developed. It is recommended that deposits from both these processes be dipped in 10 to 20% sulfuric acid before final rinsing and drying in order to whiten and stabilize the deposit color. It is possible to apply chromate passivation and electrophoretic lacquer coatings in a similar manner to silver deposits obtained from cyanide systems.

Careful maintenance of solution pH is very important with both these systems. If the solution pH is allowed to fall below 7.5 the complex degrades, resulting in precipitation of silver metal. This process is irreversible. Early processes lacked sufficient buffering and suffered short bath life due to low pH conditions at the anode. With better buffering and careful maintenance both suppliers claim multiple bath turnovers under production conditions. It is interesting to note that the process using agitation at the anode appears to last longer, again emphasizing the importance of pH at the anode. (Compare with high-speed processes below.)

Iodide Solutions

Several authors report some success with baths that are quite similar. A typical solution might be as follows:

Silver iodide	20-45 g/L	(2.5-6.0 oz/gal)
Potassium iodide	300-600 g/L	(40-80 oz/gal)
HI or HCl	5-15 g/L	(0.7-2 oz/gal)
Gelatin (optional)	1-4 g/L	(0.15-0.55 oz/gal)
Temperature	25-60°C	(80-l40°F)
Current density	0.1-15 A/dm^2	(1.0-150 A/ft^2)

Without exception these authors found iodine in deposits from their particular formula. This fact, and the relatively high price of the iodide salts, has prevented further use of this type of solution.

Trimetaphosphate Solution

A process was developed for silver plating magnesium and its alloys; its use on other metals is not reported.

Silver trimetaphosphate (monobasic), $Ag_2HP_3O_9$	3-45 g/L	(0.40-0.60 oz/gal)
Sodium trimetaphosphate (trimer), $Na_6P_6O_{18}$	100-160 g/L	(13.5-21.5 oz/gal)
Tetrasodium pyrophosphate, $Na_4P_2O_7$	50-175 g/L	(6.7-23.5 oz/gal)
Tetrasodium EDTA	35-45 g/L	(4.7-6.0 oz/gal)
Sodium fluoride	3-5 g/L	(0.40-0.70 oz/gal)
pH[a]	7.9-9.5	
Temperature	50-60°C	(120-140°F)
Current density	0.5-23 A/dm^2	(5-25 A/ft)

[a]Note: Adjust solution pH with triethanolamine or sodium bicarbonate.

Thiosulfate Solutions

Thiosulfate-based formulas have proven to be among the most successful of

inorganic complex-based silver-plating processes investigated. Early attempts to plate silver from such a solution resulted in rapid oxidation of the complex and precipitation of insoluble silver compounds. Additions of sodium metabisulfite were found to minimize this tendency and all thiosulfate-based processes now contain this ingredient. Solution composition can be expressed as follows:

Silver as thiosulfate	30 g/L	(4.0 oz/gal)
Sodium thiosulfate	300-500 g/L	(40-70 oz/gal)
Sodium metabisulfite	30-50 g/L	(4.0-6.7 oz/gal)
pH[a]	8-10	
Temperature	15-30°C	(60-85°F)
Current density	0.4-1.0 A/dm^2	(4-10 A/ft^2)

[a]Note: Adjust solution pH with sodium bisulfite or sodium hydroxide.

These electrolytes can be operated with stainless steel or silver anodes; however, the latter should be bagged. Problems of poor adhesion can be overcome by using a conventional silver strike or one in which there is no free cyanide. In either case, rinsing before entry into the thiosulfate solution is a good practice. A small amount of cyanide drag-in will react with thiosulfate in the solution to form thiocyanate:

$$CN^- + S_2O_3^{2-} \quad CNS^- + SO_3^{2-}$$

One reported advantage of thiosulfate over cyanide systems is that thickness distribution is better on complex-shaped objects; however, deposits seem to tarnish in air much quicker than cyanide-produced ones. Postplating passivation is recommended.

Succinimide Solutions

Several electrolytes based on this organic complex of silver have been patented, two of which are described below:

Silver (as potassium silver disuccinimide)	30 g/L	(4.0 oz/gal)
Succinimide	11.5-55 g/L	(1.5-7.4 oz/gal)
Potassium sulfate	45 g/L	(6.0 oz/gal)
pH	8.5	
Temperature	25°C	(77°F)
Current density	1 A/dm^2	(10 A/ft^2)

Potassium nitrite or nitrate can be substituted for the sulfate. The addition of amines, such as ethylene diamine or diethylenetriamine, and wetting agents produce bright, stress-free deposits.

Silver (as potassium silver disuccinimide)	24 g/L	(3.3 oz/gal)
Succinimide	25 g/L	(3.4 oz/gal)
Potassium citrate	50 g/L	(6.7 oz/gal)
pH	7.5-9.0	
Temperature	20-70°C	(70-160°F)
Current density	0.54 A/dm^2	(5.5 A/ft^2)

Potassium borate may be used in place of potassium citrate.

Tarnish resistance of deposits obtained from these processes is inferior to that of deposits produced from cyanide-based electrolytes unless they are dipped in dilute sulfuric acid immediately after plating is complete.

HIGH-SPEED SELECTIVE PLATING

Electronic components, such as leadframes, are usually plated with silver at high speed using selective plating methods. Silicon chips can be attached to the silver deposit using conductive, epoxy-based adhesives, and gold or aluminum wires are bonded to the silver by employing ultrasonic or thermosonic wirebonding techniques. The resultant assembly is referred to as an IC package (integrated circuit package). Silver thickness ranges from 1.875 μm (0.000075 in.) to 5.0 μm (0.000200 in.); deposition times are typically between 1 and 4 seconds.

The small areas to be plated demand the use of insoluble anodes. Platinum-clad niobium mesh and platinum wire are examples of anode materials in common use. Traditional cyanide-silver electrolytes suffer rapid degradation under these conditions, oxidation and polymerization of the cyanide at the inert anodes being the principal cause. Special solutions were developed to overcome this situation; these contain essentially no free cyanide but still depend on potassium silver cyanide as the source of silver. A typical formula is as follows:

Silver as $KAg(CN)_2$	40-75 g/L	(5-10 oz/gal)
Conducting/buffering salts	60-120 g/L	(8-16 oz/gal)
pH	8.0-9.5	
Temperature	60-70°C	(140-160°F)
Current density	30-380 A/dm^2	(300-3,500 A/ft^2)
Agitation	Jet plating	
Anodes	Pt or Pt/Nb	

Conducting salts can be orthophosphates, which are self-buffering, or nitrates, which require additional buffering from borates or similar compounds. Buffering is important in these solutions since there is a significant drop in pH at the inert anode during plating due to destruction of hydroxide ions. Insoluble silver cyanide forms on the anode surface as a result of cyanide depletion in this locally low pH. Plating current drops off rapidly due to polarization. The following equations summarize the reactions involved. (Compare with comments in Noncyanide Processes above where a similar breakdown of the complex occurs.)

$$4OH^- \quad 2H_2O + O_2 + 4e^-$$

$$Ag(CN)^- \quad AgCN + CN^-$$

Grain refiners are added to control deposit grain size. Because of the very high rate of deposition, little grain refining occurs without these additives. The type and concentration of grain refiner chosen depends on the desired current density and deposition speed. A typical grain refiner would be a Group VIb element, such as selenium, it would become more effective as current density increases. In other words, the concentration of grain refiner that gives a smooth, satin finish at 100 A/dm^2 will produce full bright deposits under similar conditions at 200 A/dm^2.

Pre- and Posttreatments

Since silver is being plated selectively the electrolyte is exposed to cleaned and activated substrate surfaces (typically copper-rich alloys or nickel-iron alloys) that are prone to forming immersion silver deposits. Any silver detected outside the package profile (i.e., on the outer leads) is cause for rejection of the leadframe due to fears that silver outside the package will migrate across the dielectric and cause short circuits. Hence, all traces of silver must be eliminated outside of the selectively plated spot itself. A typical process flow is degrease and rinse, electroclean and rinse, acid dip and rinse, anti-immersion predip, selective silver plate, silver

drag-out rinse, silver back-stripper, multiple rinses, dry.

The "anti-immersion predip" consists of a dilute solution of a mercaptan or similar compound, which will attach itself to active surface sites and minimize immersion deposition of silver without inhibiting adhesion of the desired electrodeposit. Since there is no rinse between the predip and the plating solution it is essential that the predip agent should not adversely affect the electrolyte performance. Most predip agents are actually added to the electrolyte during solution preparation so as to enhance the immersion deposition inhibiting effect. Some also act as an additional grain refiner.

Even with these precautions some silver can be detected outside the spot area and must be removed. This is usually achieved using a "back-stripper," which removes a small layer of silver from the entire surface. The most popular solutions are succinimide-based and many apply a reverse current in order to better control the amount of material stripped in this cell.

This plating technology has been fully developed and is projected to continue until the phasing-out of the lead frame itself.

SUMMARY

After more than 150 years, rack and barrel silver plating is still performed using a cyanide electrolyte that closely resembles the electrolyte in the original 1840 patent. After many years of R&D effort directed at finding an alternative to cyanide in silver plating, two processes are being offered commercially. Additional work is continuing with the objective of producing full-bright silver deposits from an electrolyte as robust as the traditional cyanide process.

The use of electroplated silver on electronic components is well established and continues to expand into new applications such as on waveguides for cellular telecommunications systems.

ZINC ALLOY PLATING

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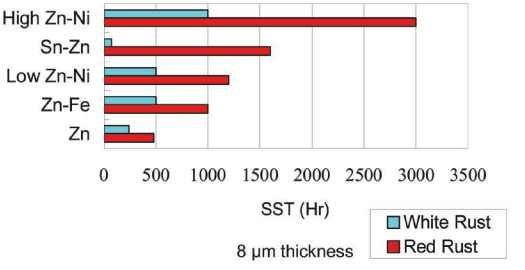
The application of sacrificial coatings onto steel and other ferrous substrates has long been established as an effective and reliable standard of the industry for corrosion protection. Due to its lower cost, zinc has been the predominant coating, although cadmium has also been widely used where zinc fails to provide the necessary corrosion protection for certain applications. Recent demands for higher quality finishes, and, more specifically, longer lasting finishes, have resulted in a move toward alloy zinc electrodeposits. This has been especially true in the automotive industry, but is also true in the aerospace, fastener, and electrical component fields, among others. Additionally, cadmium users are under increased pressure to stop using it due to its toxic nature.

Several different alloy zinc systems are available, giving deposits of somewhat different properties (Fig. 1). The differences come not only from the choice of alloying metal, but from the electrolyte system used as well. Much of the recent research work on alloy zinc electroplating processes was done in Europe and in Japan, where cadmium was effectively outlawed during the 1970s. The alloying elements successfully used with zinc have been iron, cobalt, nickel, and tin. Except for the tin, which is typically an alloy of 70% tin and 30% zinc alloy, zinc comprises from 83 to 99% of the alloy deposit. At these compositions, the deposit maintains an anodic potential to steel, yet remains less active than pure zinc. Analogous to conventional zinc, each of the alloys require a conversion coating to obtain improved corrosion resistance. Indeed, the passivate in this case is more effective on the alloy deposits than on the pure metal.

ZINC-NICKEL

Several electroplated processes have been invented since the zinc-copper alloy was developed in 1841. The merits of alloy plating are as follows:

1. New phases that did not exist on metallography phase diagrams can be achieved.
2. Homogeneous alloy compositions not attainable through standard melting methods, because low melting point metal vaporizes at the higher melting point temperature metal.
3. Thin film coating deposits can provide high performance



Features

- Corrodes sacrificially to steel
- Stability of corrosion by-products

Figure 1: Corrosion performance in neutral salt spray (NSS).

Table I. Bath Parameters for an Acid Zinc-Nickel Bath

Parameters	*Rack*	*Barrel*
Zinc chloride	130 g/L	120 g/L
Nickel chloride	130 g/L	110 g/L
Potassium chloride	230 g/L	—
Ammonium chloride	—	150 g/L
pH	5.0-6.0	5.0-6.0
Temperature	24-30°C	35-40°C
Cathode current density	0.1-4.0 A/dm²	0.5-3.0 A/dm²
Anodes	Zinc and nickel separately. In some cases, separate rectifiers and bussing are required.	

Table II. Bath Parameters for an Alkaline Zinc-Nickel Bath

Parameters	*High & Low Nickel*
Zinc metal	8.0 g/L
Nickel metal	1.6 g/L
Sodium hydroxide	130 g/L
Zinc/Nickel ratio	5.0:1
Temperature	23-26°C
Cathode current density	2-10 A/dm²
Anode current density	5-7 A/dm²
Anodes	Nickel-plated (25 microns) on steel anodes

- Adherent conversion coating
- Low dissolution rate of passivate film in neutral salt spray (NSS) testing

Corrosion of Steel Plated with Zinc and Zinc Alloy

Substrates are protected through the electrodeposition of zinc and zinc alloys. Due to their poor ionization tendency, zinc and zinc alloys sacrificially dissolve prior to the substrate. Corrosion by-products provide a very stable barrier film to protect the electrodeposited coating from the corrosive environment.

Zinc-nickel can be plated from acid or alkaline (cyanide free) solutions. The acid bath typically provides a nickel content of 10% to 14% as compared to alkaline formulations that will yield 5% to 8% nickel or 10% to 17% nickel. Corrosion protection increases with increasing nickel content approaching 17%. Beyond that level, the zinc-nickel deposit becomes more noble than the substrate, thus losing its corrosion protection properties (see Table I). Additionally, at a nickel content above 10%, the deposit has only one crystal structure, γ phase. The deposit from the acidic solution tends to have less uniform thickness distribution and a higher alloy composition variation from high to low current density areas than deposits from an alkaline electrolyte.

The alkaline bath produces a columnar structure with a lower tensile stress as compared to the laminar structure as deposited from the acidic electrolyte. Thus, the alkaline system maintains better deposit integrity when the part is formed, bent, or crimped after plating. The alkaline high zinc nickel process is non-embrittling to high-strength steels and can meet the requirements for a non-embrittling process per ASTM F 519 as a suitable replacement for cadmium.This bath is very simple to operate, being quite similar to conventional alkaline noncyanide zinc processes (Table II).

Table III. Bath Parameters for an Acid Zinc-Cobalt Bath

Parameters	*Rack*	*Barrel*
Zinc metal	30 g/L	30 g/L
Potassium chloride	180 g/L	225 g/L
Ammonium chloride	45 g/L	—
Cobalt (as metal)	1.9-3.8 g/L	1.9-3.8 g/L
Boric acid	15-25 g/L	15-25 g/L
pH	5.0-6.0	5.0-6.0
Temperature	21-38°C	21-38°C
Cathode current density	0.1-5.0 A/dm²	1-50 A/dm²
Anodes	Pure zinc	Pure zinc

High nickel (10-17%) alloy baths are in use and are specified in the European automotive industry, using alkaline noncyanide technology. Typically, these baths have a lower cathode efficiency than the low nickel baths. Some alkaline electrolytes compensate for this lower efficiency by plating at a slightly warmer temperature. Higher nickel content in the alloy composition will cause increased passivity and reduced chromium conversion film receptivity. One main reason for the success of zinc-nickel alloy electrodeposits with the major automobile makers is their requirement that neutral salt spray testing on plated parts be conducted after passivation and baking. Additionally, higher levels of nickel in the alloy may mean less ductility of the deposit; however, corrosion resistance may increase up to double that of the low nickel baths. Chromium passivation solutions for high zinc-nickel electrodeposits must be more aggressive in order to form a protective coating on the electrodeposit. Newly formulated passivates, with supplemental topcoats, have proven suitable on higher nickel content zinc-nickel electrodeposits, thus eliminating the need for hexavalent chromates.

Zinc-nickel has consistently achieved higher corrosion protection results as shown by accelerated corrosion testing (Erichsen and neutral salt spray), with the exception of the SO_2 (Kesternich) test, which favors tin-zinc (Fig. 2). Zinc-nickel at a thickness of 8 microns or less does, however, retain high corrosion resistance after the forming of parts, such as fuel lines, brake lines, hydraulic lines, and fasteners. The ability to continue to deliver good corrosion properties after heat treating has, in some cases, allowed parts to be baked after the application of a trivalent conversion coating, rather than before chromating, eliminating the need for double handling.

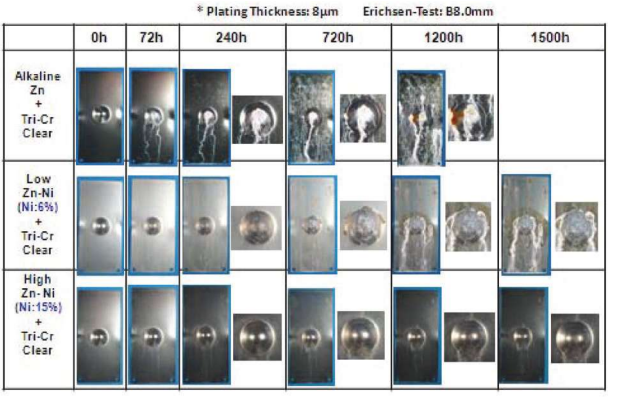


Figure 2: Corrosion performance test (NSS) with bending.

Table IV. Bath Parameters for an Alkaline Zinc-Cobalt Bath

Parameters	*Amounts*
Zinc metal	6-9 g/L
Sodium hydroxide	100-130 g/L
Cobalt metal	30-50 mg/L
Temperature	21-32°C
Cathode current density	2.0-4.0 A/dm²
Anodes	Steel

Table V. Bath Parameters for an Acid Zinc-Iron Bath

Parameters	*Amounts*
Ferric sulfate	200-300 g/L
Zinc sulfate	200-300 g/L
Sodium sulfate	30 g/L
Sodium acetate	20 g/L

Table VI. Bath Parameters for an Alkaline Zinc-Iron Bath

Parameters	*Amounts*
Zinc metal	8-15 g/L
Iron metal	0.05-0.1 g/L
Sodium hydroxide	120-140 g/L
Temperature	18-23°C
Cathode current density	1.5-3.0 A/dm²
Anodes	Steel

Table VII. Bath Parameters for a Neutral pH Tin-Zinc Bath

Parameters	*Rack*	*Barrel*
Tin (metal)	20 g/L	10 g/L
Zinc (metal)	8 g/L	10 g/L
Stabilizer	120 g/L	120 g/L
Antioxidant	80 g/L	80 g/L
Temperature	18-25°C	18-25°C
pH	6.0-7.0	6.0-7.0
Cathode current density	18.5 A/ft²	5.0 A/ft²
Anodes	Tin/zinc (65/35-75/25) mixed anodes	

Table VIII. Sulfur Dioxide Gas Corrosion Test

		Tin-Zinc Alloy Ratio	*Thickness (μm)*	*Hours to White Corrosion*	*Hours to Red Corrosion*
Tin-zinc alloy plating	Nonchromated	60/40	10	12	400
		60/40	5	12	210
		75/25	5	9	170
		85/15	5	12	185
	Chromated	60/40	5	20	250
		75/25	5	50	400
		85/15	5	50	250
Zinc plating	Yellow		5	12	200
	Iridescent Chromated		10	12	250

Sulfur dioxide gas concentration, 200-300 ppm; temperature, 40 ±2°C; humidity, >95%.

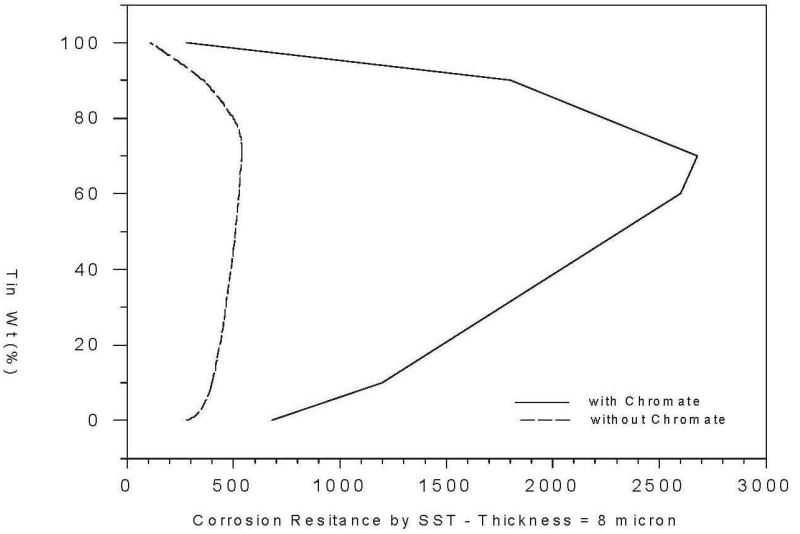


Figure 3: Corrosion resistance of tin-zinc alloys in salt spray in accordance with ASTM B117.

Adhesion of the conversion coating film onto zinc alloy electrodeposits is superior to zinc plating. This comes from an "anchor function" of the second metal. Tin, nickel, iron, and cobalt do not dissolve in the passivating solution.

Another application where zinc-nickel was found to offer excellent protection in combination with a topcoat is for the plating of fasteners that are to be used in contact with aluminum, safely replacing cadmium electrodeposits.

ZINC-COBALT

Commercial zinc-cobalt baths are essentially conventional low ammonium or ammonium-free acid chloride zinc baths, with the addition of a small amount of cobalt. The resulting deposit is generally up to about 1% cobalt, with the balance being zinc. This bath has a high cathode efficiency and high plating speed, with reduced hydrogen embrittlement compared with alkaline systems, but the thickness distribution of the deposit varies substantially with the current density. An alkaline bath comparison is provided (see Tables III and IV for acid and alkaline bath parameters).

Acid cobalt baths have many variables that can affect the cobalt codeposition percentage. These variables include cobalt concentration, zinc concentration, temperature, agitation, pH, current density, and chloride concentration.

Zinc-cobalt deposits will accept trivalent and hexavalent blue bright, yellow iridescent, and nonsilver black chromate conversion coatings. Higher corrosion performance with trivalent passivates is not achievable on zinc-cobalt electrodeposits.

ZINC-IRON

The primary advantages of zinc-iron are low cost and the ability to develop a deep uniform black conversion coating from a nonsilver passivate. Additionally, the alloy has good welding characteristics and workability, and can readily be used on

Table IX: Comparison of Zinc Alloy Plating Processes

Plating Bath			*Zn Alkaline*	*Sn-Zn Neutral*	*Zn-Ni Alkaline*	*Zn-Ni Acid*	*Zn-Co Acid*	*Zn-Fe Alkaline*
Appearance			B	C	B	B	B	B
Solderability			C	A	D	D	D	D
Wear-resistance			C	D	A	A	C	C
Whisker			D	B	B	B	D	D
Crimping, bending			B	A	B	D	C	C
Corrosion resistance	General	White	C	C	A	A	C	C
		Red	C	A	A	A	C	C
	After baking	White	D	C	A	B	D	D
		Red	C	C	A	C	D	D
	After crimping	White	C	C	A	C	D	D
		Red	C	A	A	C	D	D
Throwing power			A	C	A	D	A	A
Plating rate			C	B	C	A	C	C
Covering power			B	A	B	B	B	B
Bath control			A	B	B	D	C	C
Chromate availability			Blue Yellow Black	Clear	Clear Black	Clear Black	Clear	Yellow Black
Replatability			A	C	C	C	B	B
Anodes			Zinc/ steel	Tin/zinc alloy	Nickel plated	Zinc/ nickel	Zinc	Zinc
Auxiliary anode			A	C	A	D	A	A
Waste water			B	B	C	C	B	B
Thickness		X-ray	A	B	B	B	B	B
		Kocour	A	B	B	C	B	B
Composition		X-ray	-	B	B	C	D	D
		Analysis	-	B	B	B	C	D
Relative price			1.0	2.5–3.0	2.5–3.0	1.5	1.2	1.1
A: Excellent B: Good C: Fair D: Poor								

electroplated strip steel. It is also suitable as a base for paint. Of the alloys being considered, zinc-iron will generally give the least improvement in corrosion resistance compared with conventional zinc. If the iron content of the bath gets too high, blistering problems, including delayed blistering, may occur. Corrosion resistance of chromated zinc-iron plated parts drops drastically after exposure to temperatures over 250°F (see Tables V and VI for acid and alkaline bath parameters).

TIN-ZINC

A number of electrolytes are available for deposition of tin-zinc alloys. These

include acid, alkaline, and neutral formulations (see Table VII). In general, an alloy of 15% to 35% zinc with 65% to 85% tin is produced. This range of composition produces optimum corrosion resistance, especially in sulfur dioxide atmospheres, along with excellent solderability (see Table VIII and Fig. 3). As with the other zinc alloys, a conversion coating is required in order to achieve the optimum corrosion protection. In any event, the tin-zinc deposit has good frictional properties, and excellent ductility for use on parts that may be formed after plating; however, being very soft, it is also susceptible to mechanical damage. Electrical contact resistance of the tin-zinc alloy is low, and it is somewhat superior to pure tin for resistance welding of coated mild steel sheet. Additionally, tin-zinc coatings do not undergo bimetallic corrosion, and can be used, for example, on steel fasteners for aluminum alloy panels.

Tin-zinc deposits have good solderability during long periods of storage. This is superior to pure tin. The alloy also does not grow "whiskers" or dendritic crystals for periods up to 600 days. Cost factors previously made tin-zinc the least likely of the alloy deposits to be considered. Recently, this has changed to where it is in the same cost range as alkaline zinc-nickel.

HOW TO SELECT A FINISH

Unfortunately, there is no single answer as to the best substitute for zinc or cadmium. Each application must be examined to determine which parameters in the specification are most important. Compatibility of the process with existing equipment may also be a determining factor. For example, an existing acid chloride zinc line may be readily converted to acid zinc-cobalt, if that finish will meet the requirements of the part to be plated; however, if the part is to be heat treated after plating, zinc-cobalt is not indicated as the preferred deposit. An analysis must be made of cost versus quality, and a decision made based on a company's philosophy. Table IX presents data highlighting some of the areas of differences among the finishes described.

CURRENT APPLICATIONS

The United States automotive industry has led the way in the industrial use of zinc alloy plating processes. This mirrors past trends that were first seen in Japan and Europe. Many of the first acid baths have yielded to alkaline formulations, which give more uniform alloy deposition and thickness distribution. Some alloy zinc-plated parts processed include fuel rails and lines, injectors, climate control devices, cooling system pumps, coils, and couplers. Some non-automotive uses are electric metering parts, power transmission units, maritime, military, aerospace, bearings, and many more. Testing programs are lengthy, due to long-lived finishes. Specification changes are slow, largely due to the enormous cost of changes in rewrites. Zinc alloys have improved corrosion characteristics as compared to zinc and cadmium electrodeposits and have earned a well-deserved reputation for quality and performance.

ZINC PLATING

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The electroplater can achieve excellent results from bright zinc plating electrolytes when the baths are operated correctly. This article is designed to give quick reference to all vital data needed for optimum bath performance. Discussion has been kept to a minimum in favor of tables in an effort to convey more useful information in a simplified form. Present data concentrate on acid chloride zinc, alkaline non-cyanide zinc, and cyanide zinc baths. Typical bath compositions are given in Tables I and II.

PLATING TANK CONSTRUCTION

The choice of plating tank construction material should fit the type of bath. All types of tank linings have advantages and disadvantages ranging from length of wear to economy.

Acid Chloride Baths

Acid chloride zinc baths may use fiberglass tanks or polypropylene tanks, but steel tanks must be lined with any of the following: fiberglass, polyvinyl chloride (PVC), or polypropylene. Tanks for chloride zinc must not be constructed of unlined steel.

Alkaline Non-cyanide Baths

Alkaline non-cyanide zinc baths can use tanks constructed from steel, PVC, fiberglass lined with PVC, or polypropylene. Alkaline non-cyanide zinc systems cannot use unlined fiberglass tanks.

Cyanide Baths

Cyanide zinc baths can use tanks constructed of steel, fiberglass, PVC, or polypropylene.

TYPE OF SUBSTRATE TO BE PLATED

The selection of a bath to match the substrate characteristics is of major importance to the success of a zinc plating system. Regular steel substrates and leaded steel substrates both are compatible with acid chloride, alkaline non-cyanide, and cyanide zinc systems. In fact, these materials are the only two recommended for alkaline and cyanide plating.

Acid chloride zinc is more flexible in compatibility with other substrates. Successful use on malleable, high-carbon, heat-treated, and carburized substrates can be accomplished with acid chloride zinc systems.

AUTOMATIC CONTROL EQUIPMENT

Automatic control equipment can play an integral role in the operation of a consistent, high-quality plating line. Both acid chloride zinc and alkaline non-cyanide zinc systems can benefit from the use of starter, carrier, or refining agent automatic feeder systems. All three zinc baths are suited for the use of brightener feeders connected to rectifiers. An automatic pH controller can simplify and improve the operations of an acid chloride zinc bath.

Table I. Bath Composition

	Zinc Metal[1]	*Sodium Hydroxide*[2]	*Sodium Cyanide*	*Ammonium Chloride*[3]	*Potassium Chloride*[4]	*Boric Acid*[4]	*pH*
Acid Chloride Zinc:							
All ammonium chloride	2.0–4.0			16.0–20.0			5.0–6.0
Low ammonium potassium chloride	2.0–4.0			4.0–6.0	16.0–20.0		5.0–6.0
Nonammonium or all-potassium chloride	3.0–5.0				25.0–30.0	3.0–5.0	5.0–5.5
Alkaline Non-cyanide Zinc:							
Low chemistry	0.8–1.2	10.0–14.0					
High chemistry	1.8–3.0	16.0–20.0					
Cyanide Zinc:							
Low cyanide	1.0–1.5	10.0–12.0	1.5–2.5				
Mid cyanide	1.8–2.5	10.0–12.0	3.5–6.0				
High cyanide	3.5–4.5	10.0–12.0	11.0–14.0				

All figures in oz/gal. Conversion to metric: oz/gal 7.49 = g/L

[1]Zinc metal source:
Acid chloride zinc—zinc chloride.
Alkaline non-cyanide zinc—zinc oxide (preferably nonleaded).
Cyanide zinc—zinc oxide or zinc cyanide.

[2]Sodium hydroxide source: mercury cell grade or rayon grade.

[3]Ammonium and potassium chloride source: untreated is preferred.

[4]Boric acid source: granular preferred, as powdered form creates a dusting problem.

Table II. Bath Parameters

	Acid Chloride Zinc	Alkaline Non-cyanide Zinc	Cyanide Zinc
Wetting agents, refining agents or carrier	2.0–5.0% vol./vol.	1.0–3.0% vol./vol.	Not applicable
Brightener	0.05–0.2% vol./vol.	0.05–0.2% vol./vol.	0.2–0.5% vol./vol.
Temperature[a]	60–130°F (15–55°C)[1]	60–110°F (15–48°C)	60–110°F (15–43°C)

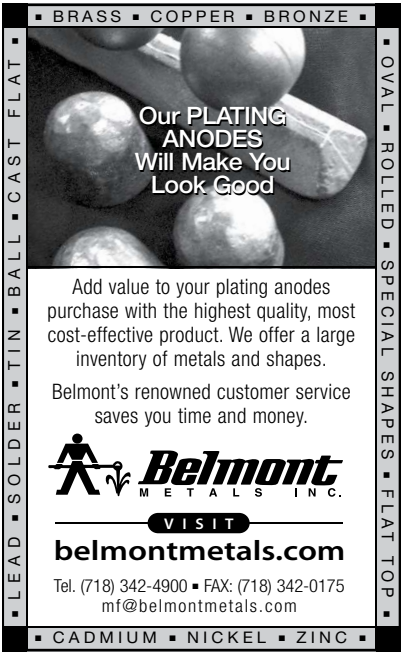
[a]Positive and negative effects are observed when a bath is operated above room temperature (75°F):
- Because of the solution evaporation, bath buildup problems can be minimized or eliminated.
- At higher temperatures, higher conductivity means less power consumption.
- Plating speed is increased at higher temperatures. This means less plating time is required.
- Operating at higher temperatures means savings in refrigeration cost.
- At elevated temperatures, brightener consumption may be higher than at room temperature.
- The solubility of organic additives can become a negative factor.

[1] New high-temperature chloride zinc systems for barrel work have reduced plating time 10–50% and increased production 30–100%.

SAFETY CONCERNS

The characteristics of zinc plating baths deserve consideration due to possible safety hazards. While acid chloride zinc and alkaline non-cyanide zinc result in no toxicity to humans, cyanide zinc is highly poisonous. Platers should remember that the formulations of acid chloride zinc baths make them corrosive to equipment. Alkaline non-cyanide and cyanide baths are noncorrosive to equipment.

Exposure to the chemicals in alkaline non-cyanide zinc and cyanide zinc baths can be corrosive to living tissue, whereas acid chloride zinc appears to have little



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Table III. Miscellaneous Requirements and Properties

	Acid Chloride Zinc	Alkaline Non-cyanide Zinc	Cyanide Zinc
Anode polarization	Seldom	Yes	Yes
Conductivity of the bath solution (higher conductivity lowers energy costs)	Excellent	LC-Poor, HC-Good	Fair
Agitation in rack operations	Required	Not required	Not required
Heating or cooling required	Yes	Yes	Yes
Filtration required	Yes	Yes	Not normally
pH adjustment required	Yes	No	No
Purifier needed to treat impurities	No	Yes	Yes
Chromate receptivity	Good	LC-fair, HC-excellent	Excellent
Waste treatment	Simple	Simple	Complex
Iron treatment by oxidation[1]	Yes	No	No

LC, low chloride; HC, high chloride.
[1] 30 - 35% Hydrogen peroxide is most commonly used. When necessary, 400 ml/1,000 gal (~100 ml/1,000L) of bath is a typical addition. The addition should be diluted with water to a 10% solution before adding. Potassium permanganate may also be used; however this generates a greater amount of sludge, possibly creating filtration problems and iron precipitation/filtration problems.

Table IV. Properties of Zinc Baths

	Acid Chloride	Alkaline Non-Cyanide Zinc		Cyanide Zinc		
		LC	HC	LCN	MCN	HCN
Ductility[1] at higher thicknesses	1 (>0.5 mil)	1	3–4	4	4	4
Bath efficiencies	95-97%	70-75%	70-95%	65-70%	70-75%	75-70%
Star-dusting	Yes[2]	No	No	No	No	No
Plate distribution[3]	1[4]	2–3	5	4–5[5]	4–5[5]	4–5[5]
Commercial plating thickness requirements	5	2	4	2	2–3	3–4

HC, high chloride; LC, low chloride; LCN, low cyanide; MCN, mid cyanide; HCN, high cyanide.
[1] Ductility is the ability of a materiality to be bent, molded, or formed without cracking, peeling, and/or chipping.
[2] Newer chloride zinc systems are available which minimize or eliminate star-dusting.
[3] Distribution or throwing power is the ratio of the amount of zinc deposited in the high current density to the amount of zinc deposited in the low current density.
[4] Newer systems are available in barrel applications that exhibit distribution properties equal to or better than that of Low Chemistry Alkaline Non-Cyanide Zinc plating.
[5] The plate distribution improves as the cyanide to zinc ratio increases.

corrosive effect on tissue. Remember to follow all OSHA requirements, checking appropriate material safety data sheets prior to the handling and/or use of all chemicals, whether general or proprietary in nature.

OTHER CONSIDERATIONS

Operational requirements for the three types of baths are presented in Table III. Table IV gives a comparison of deposit properties. Troubleshooting is addressed in Table V.

Table V. Troubleshooting for Zinc Plating

	Overall Dullness	*HCD Burning*	*Dull LCD*	*Mottled or Blotchy*	*Barrel Perfora- tion Spots*	*Rough- ness*	*Brittle Deposits*	*Pitting*	*Poor Efficiency*
Inadequate agitation	1								
Bath contamination	1,2,3	3,	2	3			2		2
High temperature	1,2,3		1,2,3				3	1	
Low temperature	2	1,2,3	2,3		1		3		1,2,3
High pH	1	1	1		1	1	1		
Low pH		1		1					1
Poor cleaning	1,2,3	1	1	1,2,3		1,3			1
High zinc	2	2	1,2						
Low zinc		1,2							1,2,3
High brightener			1	1			1,2,3,	1,2,3,	2
Low brightener	1,2,3	1,2,3	1,2,3						
Insufficient rinsing	3								
High carrier			1						2
Low carrier	1,2	1	1	1		1	1,2	1	1
High current		1,2,3			1	2,3			
Low current			1						1
Low ammonia		1				1			
Low boric acid		1			1				
Iron contamination		1			1				
Parts too close to anodes		1,2							
Low caustic		2,3	2,3						2,3
Arcing in barrels		3							
High cyanide									3
Low cyanide		3							
Parts burnt in electro		1,2,3							
Hig h chloride				1					
Low chloride			1					1	1
Metallic contamination			1,3					1	
Organic contamination			1,3	1				1,2,3	
Sulfide contamination			2						
Particulates in the bath			2			1,2,3	2,3		
Electrical problems			3						1,3
Chromium contamination				1					
Excessive water hardness				2					
Slow barrel rotation						1			
Magnetized particles						1,2,3			
Low anode area						1,2			1,2,3
Anode sludge						2,3			
Stray current						3			
High ratio							3		
Underpickling			2						1
Overpickling			2						1
Acid drag-in on parts						3			

1. chloride zinc; 2, alkaline noncyanide; 3, cyanide zinc.

(cont. on page 337)

Table V. Troubleshooting for Zinc Plating (con't)

	Poor Adhesion	*Poor Throw*	*No plate*	*Post-plate Staining*	*Post-storage Staining*	*Falling Zinc Level*	*Rising Zinc Level*	*High Additive Consumption*
Inadequate agitation		2						
Bath contamination		1						2
High temperature		2						1,2,3
Low temperature	2	2	1,2,3					
High pH	1	1				1		
Low pH							1	
Poor cleaning	1,2,3	1,2,3	1,2,3					
High zinc	2	1,2,3						
Low zinc	1							
High brightener	1,2,3	1		1				
Low brightener		2,3						
Insufficient rinsing				1,2,3	1,2,3			
Low carrier	1	1,2		1				
High current	1							
Low current		1,2,3						
Low ammonia	1							
Low boric acid	1							
High caustic							2,3	
Low caustic	2	2				2,3		
High cyanide							3	
Low cyanide		3				3		
Low chloride		1						
Metallic contamination	1			1,2,3	1,2,3			
Organic contamination	1,2							1,2
Electrical problems			1,2,3					
Chromium contamination	2,3		1,2,3					
Too much anode area							1,2,3	
Low anode area	2		1,2,3					
High ratio			3					
Underpickling	1,3	1,2	1,2,3					
Overpickling	1,3	1,2	1,2,3					
Copper in pickle	1,2							
Metallurgical characteristics	1,2,3	2,3	1,2,3					
Current interruptions	1,2							
Nitrate contamination	3							
Excess peroxide added		1	1					
Acid drag-in on parts		3						
Excessive dwell time				1,2				
Bright dip contaminated				1,2,3				
Rinses contaminated				1,2,3				
Improper passivation				1,2,3				
Corrosive environment				1,2,3				
Poor drying and handling				1,2,3				
Poor anode contacts						1		
High drag-in, drag-out						1		2
Anodes polarized						2,3		
Titanium baskets						2		
Low cathode efficiency							3	
Localized chemical adds								1
Improper bright-dip make-up			1,2,3					

1, chloride zinc; 2, alkaline noncyanide; 3, cyanide zinc.

ALTERNATIVES TO DICHROMATE SEALER IN ANODIZING OPERATIONS

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ABSTRACT

Ogden Air Logistics Center (OO-ALC) is the primary facility within the United States Air Force for maintaining and overhauling aircraft landing gear. Aluminum landing gear components are anodized at OO-ALC to provide enhanced corrosion resistance, paint adhesion, and wear resistance; a sodium dichromate sealing operation usually completes the anodizing process. During sealing, the pores of the anodized (oxide) layer are hydrated, which fills the pores and provides improved corrosion resistance. However, this sealer contains hexavalent chromium, which is listed on the Environmental Protection Agency's list of industrial toxic chemicals that are targeted for voluntary reduction or elimination. The specification that outlines the sodium dichromate sealing process delineates three alternative processes that are approved for use: 1) boiling de-ionized water, 2) cobalt acetate, and 3) nickel acetate. While some research to support the use of these and other sealing processes has been gathered under past efforts, additional work must be conducted to fully integrate non-chromate sealers into OO-ALC's anodizing operations. To meet this need, the Air Force Research Laboratory tasked Concurrent Technologies Corporation to identify viable alternatives to the sodium dichromate sealer, conduct testing on these alternatives, and recommend the most promising sealer(s) for implementation based on the test results. This paper will describe the requirements for anodizing and sealing operations within OO-ALC, as well as the sealing technologies that are available and a path forward to demonstrate/validate the most promising alternatives for the specific needs and applications of OO-ALC.

Anodizing is a mature and commonly used electrochemical process that controls and enhances the formation of protective oxide coatings on aluminum (Al) and Al alloys. The process is used for a wide variety of commercial and military applications. For example, anodizing operations are routinely performed at the Ogden Air Logistics Center (OO-ALC) at Hill Air Force Base, Utah, as part of the depot maintenance process, on numerous vehicles and weapon systems within the United States Air Force (USAF) inventory. Specifically, OO-ALC is the primary facility within the USAF for maintaining and overhauling aircraft landing gear. Al landing gear components are anodized at OO-ALC to provide wear- and corrosion-resistant surfaces. A photo of the C-5 Galaxy aircraft, as well as the main landing gear from this aircraft, is presented in Figure 1 [Refs. 1, 2, 3].

A sealing operation usually completes the anodizing process. During the seal-

REQUIREMENT	ACCEPTANCE CRITERIA		
	Type II	Type IIB	Type III
Coating Weight (milligram/square feet [mg/ft^2]), unsealed	1,000 minimum	200–1,000	4,320 minimum for every 0.001 inch of coating
Corrosion Resistance	Minimal corrosion after 336 hours		Not specified
Paint Adhesion	No intercoat separation between the paint system and the anodic coating or between the anodic coating and the base metal.		Not applicable
Coating Thickness (mils [0.001 in])	0.07–1.0	0.02–0.7	0.5–4.5

Table 1. MIL-A-8625F Performance Requirements for Anodic Coatings on Aluminum Alloy Components

ing process, the micropores of the anodized (oxide) layer are hydrated. Because the hydrated form of the oxide has a greater volume than the unhydrated form, this process fills the micropores and subsequently improves corrosion and staining resistance [Ref. 4]. The most commonly used sealing process, a sodium dichromate solution, has been used for many years and has proven to be both effective and robust. A standard dichromate sealer bath can last a year or longer with standard loading. However, this solution contains hexavalent chromium (Cr6+). Note: Cr6+ is a hazardous material that is listed on the Office of the Secretary of Defense (OSD) Emerging Contaminants Action List, the Environmental Protection Agency's (EPA's) list of toxic industrial chemicals to be voluntarily reduced or eliminated, and in Superfund Amendments and Reauthorization Act (SARA) Title 313 [Toxic Release Inventory (TRI)]. Additionally, the Department of Defense (DoD) issued a policy directive in April 2009 that restricts the use of Cr6+ compounds on military vehicles and weapon systems [Ref. 5]. Therefore, the DoD has an ongoing need to identify and validate a chromium-free sealer to reduce the use of Cr6+ in anodizing operations, thereby reducing associated environmental and compliance burdens.

MIL-A-8625F is the military specification that establishes the requirements for anodizing and sealing processes used for military components [Ref. 6]. This specification delineates three alternative sealing processes that are approved for use: boiling deionized (DI) water, solutions containing cobalt acetate, and solutions containing nickel acetate. However, sufficient data to promote the use of these and other chromium-free sealing processes do not exist.

To address these issues, the Air Force Research Laboratory (AFRL) Energy and Environment Team (RXSCP) tasked Concurrent Technologies Corporation (CTC) to identify and demonstrate/validate an alternative to sodium dichromate sealers used in anodizing operations at OO-ALC. The successful implementation of a chromium-free sealing technology will reduce environmental compliance bur-

TEST	TEST METHOD	ACCEPTANCE CRITERIA
Coating Weight (prior to sealing)	ASTM B137 [Ref. 9]	1,000 mg/ft^2 minimum for Type II; 200 mg/ft^2 minimum – 1,000 mg/ft^2 maximum for Type IIB
Corrosion Resistance	ASTM B117 [Ref. 7]	a. No more than a total of 15 isolated pits, none larger than 0.031 inch in diameter, in a total of 150 square inches of test area grouped from five or more test pieces (areas within 0.062 inch from identification markings, edges and electrode contact marks remaining after processing shall be excluded), and b. No more than 5 isolated pits, none larger than 0.031 inch in diameter, in a total of 30 square inches from one or more test pieces (areas within 0.062 inch from identification markings, edges and electrode contact marks remaining after processing excluded).
Wet Tape Adhesion	FED-STD-141, Method 6301 [Ref. 8]	No intercoat separation between the paint system and anodic coating or the anodic coating and the base metal.
Dry Tape Adhesion	ASTM D3359, Method B [Ref. 10]	No intercoat separation between the paint system and anodic coating or the anodic coating and the base metal.

Table 2. Acceptance Criteria for OO-ALC Anodized Parts Sealed with Sodium Dichromate



Figure 1. C-5 Galaxy, Aircraft



Figure 2. Main Landing Gear

dens and foster enhanced worker safety at OO-ALC. Under this effort, numerous interviews with OO-ALC personnel were conducted. The purpose of the interviews was to identify the technical requirements for the parts being processed and to capture the desired characteristics of an alternative sealer. CTC then identified relevant products by conducting Internet searches, vendor interviews, and literature reviews.

This article presents the findings from the interviews with ALC personnel (requirements analysis) and product search (technology assessment) conducted during this effort. Although this activity focused on the specific needs of OO-ALC (e.g., military components and applications), the information and methodology presented herein is useful for anyone interested in exploring alternatives to dichromate sealers for anodizing operations.

ANODIZING AND SEALING REQUIREMENTS

OO-ALC uses sulfuric acid (Type II and Type IIB) and hard coat (Type III) anodizing at its facility. Therefore, processing and coating requirements for Types II, IIB, and III anodizing at OO-ALC were determined. Based on interviews with OO-ALC personnel, anodizing processes at OO-ALC are used to treat components made from 2000, 6000, and 7000 series Al alloys. The performance requirements for the three types of anodizing conducted at OO-ALC must meet the requirements of MIL-A-8625F, which are summarized in Table 1 [Ref. 6].

The acceptance criteria recognize that corrosion resistance is determined using the standard salt spray test in accordance with ASTM B117 [Ref. 7], and that paint adhesion is determined in accordance with Federal Test Method Standard 141, Method 6301 [Ref. 8]. (1See Table 2: Acceptance Criteria for Corrosion Resistance.) .

SULFURIC ACID (TYPE II AND TYPE IIB) ANODIZING

OO-ALC uses sulfuric acid (Type II and Type IIB) anodizing to anodize the components of various aircraft landing gear. Current is applied when parts enter into the solution and is gradually increased to the desired current density

SEALER	ADDITIONAL INFORMATION
Sodium dichromate solution, 5-9 oz/gal	Baseline
Boiling deionized water	Baseline
Unsealed	Baseline
Sodium dichromate solution, 50 parts per million (ppm)	Benchmark
COTS permanganate solution	Candidate
COTS low nickel seal solution, with hot water seal	Candidate
COTS low nickel seal solution, without hot water seal	Candidate

Table 3. Test Matrix: Sodium Dichromate Sealers and Most Promising Seals to Evaluate for Replacement

(typically 12 to 22 volts). The coatings become harder and denser as the purity of the aluminum in the substrate increases [Ref. 4].

Parts that have been anodized with the Type II and IIB processes are sealed with the sodium dichromate sealer; therefore, these processes were the primary focus of this study. The main Environmental Health and Safety (EHS) concerns expressed by OO-ALC personnel for these processes are the corrosive nature of the sodium dichromate solution and the fact that it contains Cr+6.

HARD COAT (TYPE III) ANODIZING

OO-ALC performs the hard coat (Type III) anodizing process, after conducting Type II anodizing on a part, as part of their aircraft refurbishment processes. Because Type III anodized coatings are sealed in boiling DI water, the primary EHS concern is thermal exposure to the boiling water. Therefore, this process was not a focus of this study.

SEALING PROCESS AND ACCEPTANCE CRITERIA

OO-ALC personnel reported that OO-ALC has two sodium dichromate sealer tanks for sealing anodized parts. Both of these tanks contain solutions with concentration of 5 to 9 ounces per gallon (oz/gal) sodium dichromate. The pH is maintained between 5.0 and 6.3 with sodium hydroxide, and the temperature is maintained between 95–98 degrees Celsius (°C) (203–208 degrees Fahrenheit [°F]). Considering the requirements of MIL-A-8625F and the needs identified by OO-ALC, acceptance criteria for an alternative sealing process for Type II and Type IIB anodize were defined, as listed in Table 2 [Ref. 6].

OO-ALC personnel confirmed that the above tests would be sufficient to test alternatives for their acceptance as candidates to replace the sodium dichromate sealer.

TECHNOLOGY ASSESSMENT: AVAILABLE ALTERNATIVES TO SODIUM DICHROMATE SEALERS

To identify candidate technologies that meet the requirements described above

(technologies that may be promising for future study), a thorough technology assessment was conducted. The following activities were undertaken:

Review of past efforts that evaluated sealers for anodized coatings, specifically those focused on sodium dichromate replacement

Internet searches
Discussions with vendors
Literature search(es)

Processes undergoing research and development (R&D), as well as commercially available processes, were considered. For processes that were evaluated under past efforts, vendors were contacted to obtain the most recent information regarding their products. This assessment also identified recently developed or improved inorganic sealers that would require technology verification testing if found to be promising.

As expected, a number of technologies were identified for sealing anodized Al alloys. These alternatives are based on a variety of materials, such as nickel acetate, silicon, cobalt and molybdenum fluorides, and trivalent chromium, among others. Prior work in this field [Ref. 11] has classified the more prominent sealing processes into general categories that include:

Water-based sealing processes, such as boiling DI water and steam

Chromate sealing
Sodium silicate sealing
Nickel-based sealing technologies, such as nickel acetate and cold nickel fluoride

The additional category of cobalt-based sealers was identified during the current effort. A special assessment also was performed for emerging technologies. Each of these categories is briefly described in the following sections.

WATER-BASED SEALING TECHNOLOGIES

Water-based technologies have been a viable method for sealing anodized coatings for many years. The performance of the seal is dependent upon the pH, temperature, and purity of the water, as well as immersion time and current density used during anodizing [Refs. 4, 11]. DI water is commonly used for this reason. Past work has shown that hot water sealing may be the best sealing process for enhancing the dielectric strength of anodized coatings on Al [Ref. 12], which is essential for applications requiring electrical conductivity [Ref. 13].

Water-based sealing technologies work by converting aluminum oxide (anodic coating) to boehmite, which fills the micropores of the anodic coating. The mechanism is presented in Equation 1 [Ref. 11]:

$$Al_2O_3 + H_2O \quad 2AlO(OH) \qquad (1)$$

Steam sealing is a variation of boiling DI water sealing. This technique is used frequently in Japan and Europe and is generally more efficient than boiling DI water immersion, with a reported reaction rate increase of two to four times that of DI immersion [Ref. 11]. However, steam sealing requires specialized equipment, and it is rarely employed in the United States due to the high capital investment

and production costs.

Because boiling DI water is approved as a sealer in MIL-A-8625F and is already used at OO-ALC for Type III anodizing operations, it was a viable sealer for Types II and IIB anodizing. As such, it was considered to be a baseline process for future testing.

CHROMATE SEALING

Sodium dichromate solutions have been used as seals for anodized coatings for many years. The abilities of chromates to inhibit corrosion are well recognized and have been reported by Brooman [Ref. 14], Klingenberg [Ref. 15], and numerous others. Unlike water-based sealing technologies, chromate sealing technologies form either aluminum oxydichromate (lower pH ranges) or aluminum oxychromate (higher pH ranges) in the coating micropores [Ref. 11].

Cr+6 is used in most chromate sealing systems, especially those used for military applications, due to the enhanced corrosion protection that they impart. The Cr+6-containing sodium dichromate solution (5–9 oz/gal) being used at OO-ALC was identified as the baseline being targeted for replacement. The bath temperature for this seal is maintained at 90–100°C (194–212°F) and the pH is maintained between 5.0 and 6.0; immersion time is 15 minutes [Refs. 6, 11]. It is noted that, because OO-ALC is actively trying to reduce the use of or replace chromium-containing processes, even sealers based on trivalent chromium, which have been developed in recent years and are available and being used commercially, were not considered under this pollution prevention effort. However, it was determined that a sealing solution with a reduced sodium dichromate content (50 parts per million [ppm] as chromium) could be evaluated as a benchmark because successful results had been achieved in past work [Ref. 16] and reducing the Cr+6 content in the existing solution would be an interim contribution to OO-ALC's goal for chromium reduction.

SODIUM SILICATE SEALING TECHNOLOGIES

Sodium silicate sealing is a mature, effective sealing technique that is commonly used for Type III anodizing. The bath temperature is maintained at 85–95°C (185–203°F) and the pH is maintained at around 11.0; immersion time is 10-15 minutes [Ref. 11]. Like hot water sealing, silicate sealing converts aluminum oxide to boehmite (Eq. 1) [Ref. 11]. While promising for some applications, these processes are reported to be inferior with respect to corrosion resistance [Ref. 11] to other types of sealing processes, specifically hot water, dichromate, and nickel-based sealers. In addition, silicate sealers are not recommended for applications that require dielectric strength [Ref. 12]. Furthermore, silicate is recognized as being detrimental to conventional anodizing electrolytes, as contamination of the anodizing bath with silicates reduces the corrosion resistance of the resulting coating [Ref. 17]. Due to these limitations, as well as a lack of available information to justify the consideration of silicate sealing technologies, these types of sealers were not considered for further study.

NICKEL-BASED SEALING TECHNOLOGIES

A number of nickel-based sealing technologies are available. These are usually based on either nickel acetate (approved for use under MIL-A-8625F) or nickel fluoride. Nickel acetate sealing is one of the most predominant sealing

processes in U.S. anodizing operations due to the superior corrosion resistance it imparts [Refs. 4, 11]. Nickel fluoride sealing technologies have been adopted for some applications, but, reportedly, do not perform as well as nickel acetate sealers [Ref. 11].

The mechanism for nickel acetate sealing appears to be more complex than that of hot water or silicate sealing. Along with the aluminum oxide conversion to boehmite (Equation 1), the precipitation of nickel hydroxide also occurs, as described in Equation 2 [Ref. 11]:

$$Ni^{2+} + 2OH \quad Ni(OH)_2 \qquad (2)$$

These concurrent precipitation reactions (e.g., Equations 1 and 2) fill the micropores.

While nickel-based sealing processes are technically promising, nickel has also come under increased scrutiny from an EHS standpoint in recent years. Nickel is considered a carcinogen by the International Agency for Research on Cancer (IARC) and the National Toxicology Program (NTP), although it is not yet classifiable as a human carcinogen by the American Conference of Governmental Industrial Hygienists (ACGIH) [Ref. 18]. Nevertheless, the Occupational Safety and Health Administration (OSHA) maintains a long-standing permissible exposure limit (PEL) on the use of the soluble salts of nickel at one milligram per cubic meter (mg/m). Perhaps most importantly, nickel is on the OSD Emerging Contaminants Watch List [Ref. 19].

Despite these concerns, numerous nickel-based sealing technologies were identified under this activity, and at least three of these were found to be promising based on the review of the technical literature. Based on the maturity and availability of nickel-based sealers, as well as their approval under MIL-A-8625F, a commercial-off-the-shelf (COTS) nickel-based sealer product was selected as a candidate. This product operates at a lower temperature than the sodium dichromate sealer (29–35°C [85–95°F]), contains no chromates, and has low nickel content (5-10% by weight). Recommended immersion (sealing) time is between 4 and 15 minutes. It is noted that, as expected, the sealing reaction occurs much slower in lower temperature seals than in higher temperature seals. It has been found that a warm water rinse (71°C [160°F]) accelerates the sealing process [Ref. 4]. With this in mind, the COTS nickel-based seal was considered in two scenarios: with warm water rinse afterwards, and without the rinse.

COBALT-BASED SEALING TECHNOLOGIES

Cobalt-based sealers are also approved as a dichromate sealer replacement under MIL-A-8625F; however, these sealers appear to be a relatively new development, and sufficient data to support using cobalt as a sealer were not available. Even some process data, such as optimum immersion time and temperature, were not readily available. In addition, cobalt is on the OSD Emerging Contaminants Watch List [Ref. 19]. Based on these considerations, cobalt-based sealing technologies were not considered to be viable candidates for OO-ALC sealing requirements at this time. Therefore, they were not considered for further study.

EMERGING TECHNOLOGIES

Several additional technologies were found to be promising under this effort,

based on a review of past work [Refs. 20–23] as well as vendor surveys.

The Non-Chrome Post Treatment (NCP) process was found to be promising as a non-chromium seal for anodizing. NCP is a proprietary product of the United States Naval Air Systems Command (NAVAIR). Testing was conducted by NAVAIR under past work [Ref. 20], and the results demonstrated exceptional performance in corrosion-resistance testing and adhesion testing. While these results demonstrate that the NCP sealer might be viable for the needs of OO-ALC, the process was unavailable for demonstration at the time of testing; therefore, it could not be considered.

A COTS chromium- and nickel-free anodize sealer based on permanganate was identified that reportedly provides similar characteristics to those of the dichromate sealer. This solution was evaluated by the AFRL and CTC under past work [Ref. 20] and showed exceptional performance in corrosion resistance. This sealer also passed the dry tape adhesion test, but failed the wet tape adhesion test.

Sealing anodized coatings by using a liquid colloidal dispersion that solidifies (e.g., sol-gel) has been demonstrated. Specimens were anodized and then immersed in a working solution at 270°C for 15 minutes; the resulting specimens reportedly demonstrated comparable corrosion resistance to dichromate sealed specimens [Ref. 22]. However, this process is more expensive and decreases the abrasion resistance and hardness of the overall coating system. The incorporation of additional materials within the sealer, such as polytetrafluoroetheylene (PTFE) has also been explored [Ref. 23]. These technologies are typically used for low friction and/or "non-stick" applications; sufficient data that these sealers could meet the stringent needs of military specifications could not be obtained, and so they were not considered.

DEMONSTRATION/VALIDATION TESTING

Based on the findings of this activity, three candidates were selected for laboratory testing: the COTS permanganate solution, the COTS low-nickel sealing solution, and a 50 ppm sodium dichromate solution that will serve as a benchmark. As mentioned previously, the COTS low-nickel seal will be considered with and without a warm water rinse after the sealing process. The currently used sodium dichromate sealer, the boiling DI water seal, and unsealed options will be evaluated as baselines for all testing conducted for this effort. The candidate test matrix is summarized in Table 3.

Efforts to test aluminum alloy test panels that have been anodized and sealed with the above processes are in progress.

(2 The ideal processing temperature of the NCP process is 100°F and the optimum processing time is 10 minutes. 3 The solution was made up at 10% by volume. Temperature was maintained at 170-180°F, pH was maintained between 5.0 and 8.0, and seal time was 12 to 15 minutes.)

SUMMARY

The overall objective of this effort was to identify alternatives to the sodium dichromate sealer used in anodizing operations. To this end, the requirements for the sodium dichromate sealer currently in use at OO-ALC were determined. Furthermore, extensive literature and vendor searches identified promising can-

didates that may meet the requirements. The findings were then used to derive a path forward to demonstrate/validate the most-promising alternatives for the specific needs and applications of OO-ALC.

FUTURE WORK

Having established the test methods and acceptance criteria for replacing sodium dichromate sealers, as well as available candidates for testing, the effort will focus on testing and data evaluation. It is anticipated that this work will identify a candidate that can meet the needs of OO-ALC with respect to an anodizing seal. Once this candidate has been identified, thoroughly validated through testing, and recommended for use at OO-ALC, the process of modification of the relevant technical order (TO) for conducting anodizing and sealing operations at OO-ALC will be initiated accordingly. The replacement of sodium dichromate in this application will reduce the environmental burden and increase worker health and safety at OO-ALC.

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TRIVALENT PASSIVATES NEED TRIVALENT POST-DIPS

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The application of hexavalent chromium for conversion coatings reflects on a long and successful history in corrosion-resistant coatings starting in the early 1930s.1 Although chromium(III)-based conversion coatings date back as early as 1951,2 their industrial application was forced into practice by the European End-Of-Live-Vehicle (ELV) directive.3 In addition, the RoHS4 and WEEE5 directives preclude chromium(VI) from being used in metal coatings in electrical and electronic equipment. Therefore, the use of hexavalent chromium is actually limited to a rather small number of remaining applications.

In the years preceding the legal ban of chromium(VI), publications concerning trivalent alternatives grew dramatically. Most papers published during this pre-regulatory era discussed trivalent chromium–based systems, and rarely were they innovative in nature. These systems were quite often said to be at least as good as the good old hexavalent chromium systems but based on the environmentally sound chromium(III) compound. Trivalent chromates, often referred to as passivates, are less easily applied than chromates. Keeping the application parameters, such as concentration and particularly the solution's pH, within narrow upper and lower limits became much more important when switching from hexavalent to trivalent formulations.

Simultaneous with the introduction of the new chromium(VI)-free passivate technology, the needs of decorative and particularly corrosion protection properties have been revised in many specifications, leading to more stringent requirements for trivalent passivates. The use of sealers is often mandatory to achieve these elevated demands, especially on black passivated surfaces. Sealers, in general, mean polymer solutions or dispersions or silicate solutions that are dried on the surface, resulting in a film of either an organic or inorganic polymer on top of the conversion layer (Fig. 1). It is characteristic for a sealer layer to bear a completely different composition with regard to the underlying passivate layer. Together with the chromium(III)-based conversion layer, the sealer layer acts as a highly efficient bar-

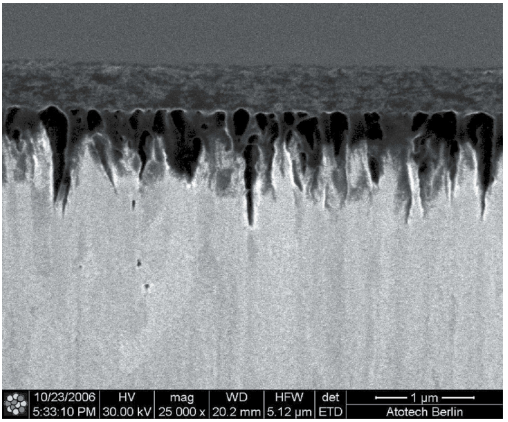


Figure 1: FIB cross section, SEM image of a sealer layer on top of a black passivated zinc layer (Protolux 3000 with Tridur Zn H1, Corrosil Plus 501).

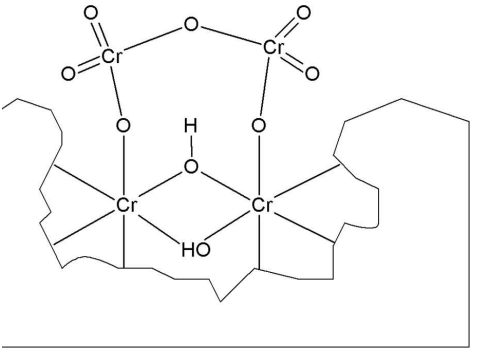


Figure 2: Structure of CCCs from hexavalent chromium solutions (the solid structure indicates further chromium-olate polymer).

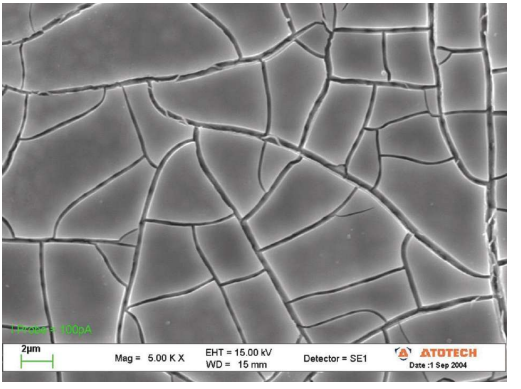


Figure 3: Surface SEM image of zinc–nickel with a black hexavalent chromate applied. Notice the typical "mud-crack" structure.

rier that effectively decelerates zinc corrosion.

Sealed conversion layers achieve the most stringent corrosion protection requirements and also bear excellent decorative properties. Furthermore, by using sealers, a broad range of friction coefficients can be precisely adjusted within narrow tolerances. Despite their assets, polymer-based sealers are specifically restricted from being used in some applications. To provide excellent corrosion protection as well as advanced decorative properties in those applications, an alternative approach to enhance the conversion layer is required. To date, black finishes, in particular, do not provide reliable and sufficient corrosion protection without the application of a final finish. This final finish is not allowed to introduce any components into the coating that are not already found in trivalent chromium conversion coatings. At the same time, it needs to fulfill the high decorative and functional demands required by the automotive industry. This approach leads to the obvious question: Why not just put more chromium into the layer?

This is not a cutting-edge idea. Post-dip solutions based on hexavalent chromium were already used on black chromium(VI)-based chromate conversion coatings, particularly on some black zinc–iron layers. These post-dip solutions mainly consisted of a chromium(VI) source such as sodium dichromate in a dilute acidic solution.

With the restrictions on hexavalent chromium use, the logical step from hexavalent chromium post-dips to trivalent chromium–based post-dips became obvious. Just changing from chromium(VI) chemistry to any chromium(III) compounds does not result in sufficient performance as a final finish. Surfaces achieved this way are noticeably inferior with regard to corrosion protection, as well as decorative properties. As with the change from chromates to passivates, R&D had to think about how the more difficult formulation and application of the new chromium(III)-based post-dip generation could be achieved, circum-

navigating the bluffs of trivalent chromium. Atotech has put quite a bit of effort into solving this problem. The outcome is Tridur Finish 300, a trivalent chromium–based post-dip solution, dedicated to passivated zinc, zinc–iron, and zinc–nickel alloys.

FORMATION MECHANISM, STRUCTURE, AND PROPERTIES OF CONVERSION LAYERS

Chromate conversion coatings. Chromate conversion coatings (CCCs) in general develop on zinc surfaces in acidic chromium(VI)-containing solutions by reduction of chromium(VI) to chromium(III). In the course of this reaction, oxonium ions are consumed:

$$Cr_2O_7^{2-} + 3Zn + 14H_3O^+ \rightleftarrows 2Cr^{3+} + 21H_2O + 3Zn^{2+}$$

$$2CrO_4^{2-} + 3Zn + 16H_3O^+ \rightleftarrows 2Cr^{3+} + 24H_2O + 3Zn^{2+}$$

Due to the consumption of oxonium ions, a pH-gradient toward more alkaline pH next to the zinciferous surface develops. In this zone of elevated pH the generated chromium(III) compounds hydrolyze, thereby generating the respective μ-oxo-bridged and μ-hydroxo-bridged polynuclear chromium(III) complexes.6 Chromium(VI) compounds from the solution are adsorbed on the surface of these polynuclear chromium-complex layers (Fig. 2) making up the chromate conversion coating.7

Investigation of the surface of a standard hexavalent chromate on zinc by means of SEM shows the typical fissured, "dry river bed-like" surface of the conversion layer (Fig. 3).

Black chromate conversion coatings can be categorized into zinc and zinc alloy processes. Black CCCs on non-alloy zinc use silver evenly spread in the conversion layer as a black pigment.

Yellow chromates on zinc usually show white corrosion products after 240–500 h in neutral salt spray testing according to ISO 9227.8 The corrosion protection of black chromates is found to be noticeably reduced compared to that of yellow chromates with a similar conversion layer thickness. This decreased corrosion resistance can be attributed to silver particles being abundantly present in the chromate layer and also in contact with the zinc surface. Consequently, the zinc in contact with the noble metal is forced to corrode by means of contact corrosion.

The other category of black chromates includes those being applied on zinc alloys like zinc–nickel, zinc–cobalt, or zinc–iron. The black pigment in the chromate layers on these alloys consists of iron, nickel, or cobalt, and their respective oxides, produced on dissolution of some zinc in the acidic process solution. Although these metals are nobler than zinc, the overall corrosion protection of the black CCCs achieved on these base metals is much better. Chromium(VI)-based post-dip solutions were commonly used on such chromates, giving about 240–360 h to white corrosion in neutral salt spray testing according to ISO 9227.

Passivate conversion coatings. Layer growth in hexavalent CCCs depends on the oxidizing effect of chromates on zinc, consuming acidity and increasing the pH on the zinc/solution interface.

In trivalent passivates, an alternative oxidant taking the role of the chromate is needed. The proper choice of oxidizing agents is crucial for the passivate's performance. A common, simple example being part of oxidant mixtures in passivates is nitrate. Zinc reduces nitrate according to the formulas given (Dikinis V,

et al. Trans Inst Metal Finishing 2004;82[3–4]:98):

$$NO_3^- + Zn + 2H_3O^+ \rightleftarrows NO_{2-} + Zn^{2+} + 3H_2O$$

$$2NO_{2-} + 4H_3O^+ + Zn \rightleftarrows 2NO\uparrow + 6H_2O + Zn^{2+}$$

$$2NO + 5Zn + 12H_3O^+ \rightleftarrows 2NH_4^+ + 5Zn^{2+} + 14H_2O$$

$$NO_3^- + 4Zn + 10H_3O^+ \rightleftarrows NH_4^+ + 4Zn^{2+} + 13H_2O$$

All these processes consume oxonium ions and, therefore, contribute to higher pH on the zinc surface compared with the bulk solution. Except for the kinetic properties of the individual reduction reactions, ligand exchange on the chromium(III) ion plays a crucial role in passivate as well as in chromate layer buildup. Lastly, the soluble chromium(III) compounds in passivates hydrolyze and build up a similar but usually thinner conversion layer on the zinc surface.

These passivate layers, not bearing adsorbed chromium(VI) on the surface, sometimes lead to inferior corrosion protection results compared to chromates.

Thick-film passivates can be used to generate transparent, iridescent layers with thicknesses of about 300 nm.9 The corrosion protection provided by these layers is similar to that of yellow chromates, although currently not achieved with black passivates.

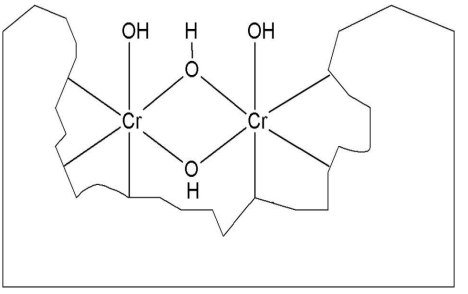


Figure 4: Model of chromium conversion layer from solutions of trivalent chromium. No hexavalent chromium is adsorbed to the surface.



Figure 5: Effect of fine tuning the solution's composition. Basic composition (left); advanced composition (middle); and composition fine-adjusted to final composition of Tridur Finish 300 (right).

Generating black finishes using trivalent chromium passivates is similar, in general, to black hexavalent chromates. On zinc, the black pigment may be generated from other transition metals from the process solution. Zinc–nickel or zinc–iron surfaces are usually rendered black by etching the surface, dissolving zinc, and leaving an iron- or nickel-based black pigment within the layer. Although a chromium(III)-conversion coating like the one previously described is also generated simultaneously with these black pigments, the layer's growth is commonly found to be limited, resulting in inferior corrosion protection results compared with black chromates. Without any further treatment, black trivalent passivates generally protect the respective zinc and zinc–alloy layers only for 24–48 h in neutral salt spray testing (ISO 9227). New developments in pigmenting a chromium conversion coating without using noble metals (with respect to zinc) at Atotech actually enable more stable results of 48 h to white corrosion. However, the current specifications of the automotive industry for unsealed black passivates require higher performance, which, to date, cannot be met without additional post-treatment.

Applying sealers that add an efficient layer to enhance corrosion protection and

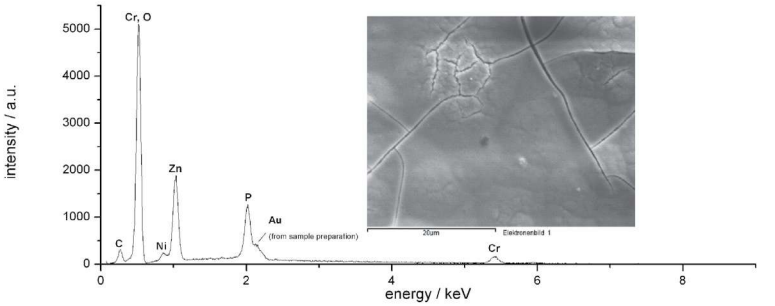


Figure 6: SEM/EDX (10 kV) of a black passivated zinc–nickel (Reflectalloy ZNA, Tridur ZnNi H1) surface with Tridur Finish 300 (20% v/v, pH 5.5, 45°C) applied. Only elements that are also commonly found in passivate layers are present with the post-dip applied. Gold is present due to sample preparation.

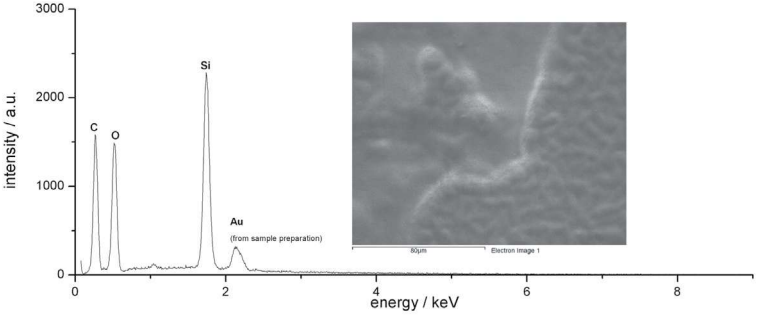


Figure 7: SEM/EDX (10 kV) of a black passivated zinc–nickel surface (Reflectalloy ZNA, Tridur ZnNi H1) with a polymer/silicate-based sealer applied (Corrosil Plus 501). Application of the sealer completely changes the surface's composition, which is now clearly dominated by silicon and carbon.

decorative appearance is precluded from some applications. Alternatively, virtually extending the conversion layer by adding chromium from a chromium(III)-based solution to the conversion layer is an option.

Consequently, with hexavalent chromium post-dip solutions in mind, the step to post-dip solutions resting on trivalent chromium is obvious.

TRIVALENT CHROMIUM APPROACHES IN POST-DIPS

Finding the proper coordination environment for Cr(III). Choosing the right coordination sphere for hexavalent chromium was not too difficult. The choice of ligands suitable for industrial use is almost completely limited to the oxygen moiety known from chromium trioxide (CrO_3), dichromates ($Cr_2O_7^{2-}$), or chromates (CrO_4^{2-}).

Upon switching from the 3d0 ion Cr(VI) to the 3d3 ion Cr(III), reactivity and toxicity changes completely. Contrary to chromium(VI), the chromium(III) ion bears exceptionally slow reaction rates with regard to ligand exchange. Also, contrary to chromium(VI), the trivalent ion does not act as an oxidizing agent in conversion coating process baths.

The primary criteria for evaluating appropriate ligands are the decorative (aspect)

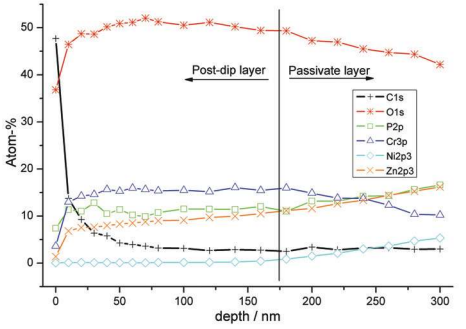


Figure 8: XPS profile of Tridur Finish 300 (20% v/v, pH 5.5, 45°C) on Tridur ZnNi H1. The vertical line indicates the sputter depth at which the change in composition, mainly nickel concentration, indicates the transition from post-dip to passivate at about 180 nm.

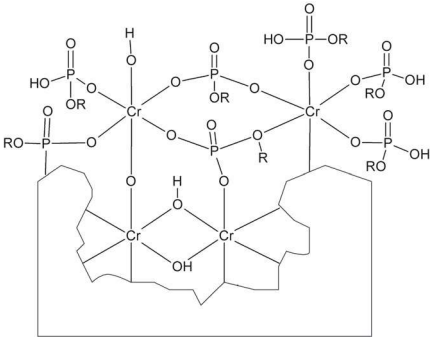


Figure 9: Structural proposal for the chromium(III) phosphate–based post-dip layer deposited on the trivalent chromium based passivate. R represents either hydrogen (H) or some organic rest, such as an alkyl or aryl-rest.

and functional (corrosion protection) properties of the coating.

Keeping the objective in mind that the final composition of the post-dip's layer should only bear components that are commonly found in passivate layers limits the range of eligible compounds. The formulation of the post-dip solution was adjusted until the best combination was found that achieved satisfactory appearance and corrosion protection performance. By fine adjusting an integrated additive system, the deposition of the post-dip could be attuned towards a highly uniform dispersal of the deposit while imparting a homogenous gloss with a minimized tendency to form drop marks (right panel in Fig. 5).

With the major component of the final composition being chromium(III) in a carefully adjusted coordination moiety, the surface layer from post-dip treatment does not bear any non-passivate like components.

Variations on the application parameters within reasonable limits around a set of initial figures were conducted in order to establish the final application parameters on black passivated zinc–nickel (Tridur ZnNi H1). Temperature, pH, make-up concentration, and dwell time, as well as drying temperature, have been changed individually, keeping the remaining parameters constant. Application at pH 5.5 (45 °C) in a 20% v/v solution has been elaborated to be the optimum set of parameters for the application on Tridur ZnNi H1. Dwell-time variations showed no visible difference within 10–40 s. Drying temperature has been shown to be best between 70–90 °C, for 10 min. The results were evaluated for both their decorative aspects and corrosion protection properties.

A semi-quantitative EDX analysis of the surface of black passivated zinc–nickel shows only elements, which are typically also found on zinciferous surfaces with trivalent chromium conversion coatings applied (Fig. 6). The deposit from the final formulation adds to the passivate layer. Upon application, the newly developed post-dip acts like a second conversion coating on the conversion layer.

For comparison, the EDX spectrum from black passivated zinc-nickel with an organic polymer/silicate-based sealer (Corrosil Plus 501) applied is shown in Figure 7. Obviously, the layer's composition is completely different from that of

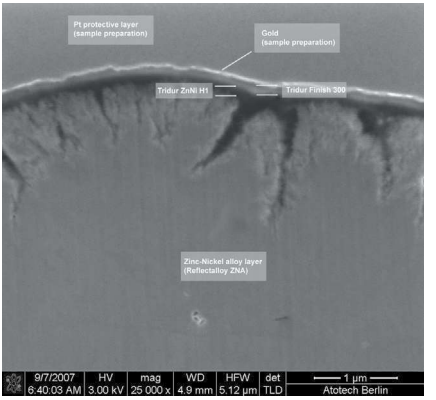


Figure 10: FIB cross section of black passivated zinc–nickel with the final formulation of the trivalent chromium post-dip solution (Tridur Finish 300 10% v/v, pH 5.5, 45°C).

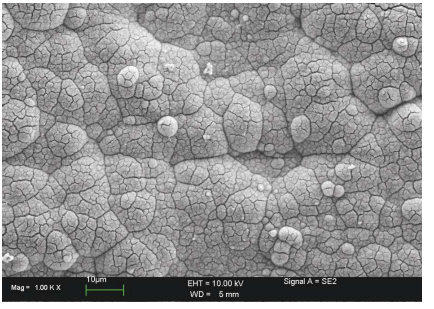


Figure 11: SEM micrograph of black passivated Zn/Ni alloy (Tridur ZnNi H1) without any further post-treatment.

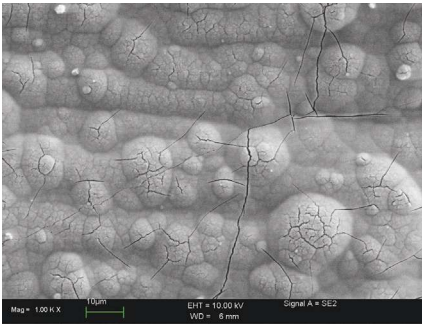


Figure 12: SEM micrograph of black passivated Zn/Ni alloy (Tridur ZnNi H1) with post-dip applied (Tridur Finish 300, 5% v/v, pH 5.5, 45°C, drying temperature of 80°C).

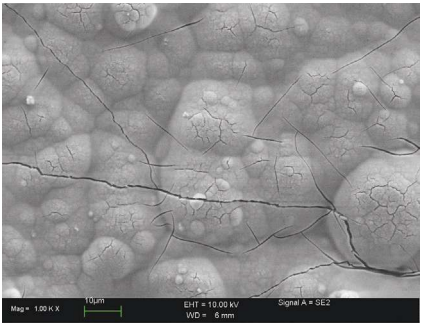


Figure 13: SEM micrograph of black passivated Zn/Ni alloy (Tridur ZnNi H1) with post-dip applied (Tridur Finish 300, 10% v/v, pH 5.5, 45°C, drying temperature of 80°C).

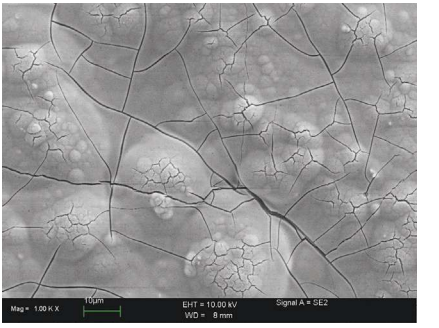


Figure 14: SEM micrograph of black passivated Zn/Ni alloy (Tridur ZnNi H1) with post-dip applied (Tridur Finish 300, 20% v/v, pH 5.5, 45°C, drying temperature of 80°C).

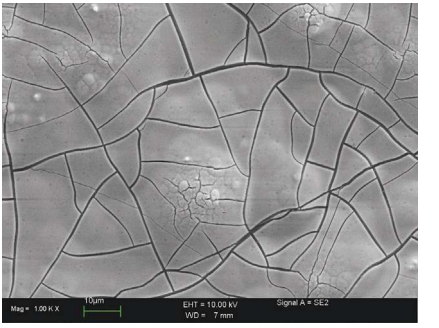


Figure 15: SEM micrograph of black passivated Zn/Ni alloy (Tridur ZnNi H1) with post-dip applied (Tridur Finish 300, 30% v/v, pH 5.5, 45°C, drying temperature of 80°C).

Base Layer/Passivate	Tridur Finish 300 Post-dip Solution			Corrosion Protection (ISO 9227)
	Concentration	Temperature	pH	
Zinc/Tridur Zn H1	100 ml/l	45°C (40–50°C)	pH 4.5 (4–5.5)	>72 h to wc
Zinc–iron/Tridur ZnFe H1	200 ml/l	45°C (40–50°C)	pH 5.5 (5–6.5)	>240 h to wc
Zinc–nickel/Tridur ZnNi H1	200 ml/l	45°C (40–50°C)	pH 5.5 (5–6.5)	>300 h to wc

Table 1: Application Parameters and Corrosion Results of the Post-dip (Tridur Finish 300)

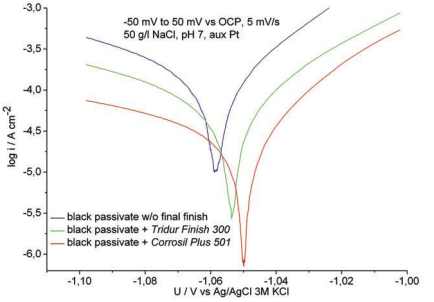


Figure 16: Log plot of polarization experiments of an experimental black zinc passivate formulation.

Sample	E_{corr}/mV	i_{corr}/µA/cm²
Experimental black zinc passivate without final finish	–1,059	89
Experimental black zinc passivate + Tridur Finish 300	–1,055	40
Experimental black passivate + Corrosil Plus 501	–1,050	16

Table 2: Corrosion Potential (E_{corr}) and Corrosion Current Densities (i_{corr}) from Tafel Analysis: Potentials vs. Ag/AgCl (3M KCl)

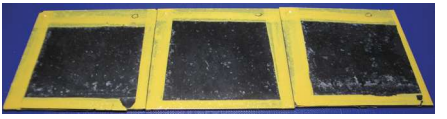


Figure 17: Tridur Finish 300 applied to Tridur ZnNi H1 on Zn/Ni (14% Ni, 8 µm) after 1,008 h in neutral salt spray testing according to DIN EN ISO 9227. No voluminous white corrosion products were produced.

the passivate or the passivate with post-dip system.

The conversion coating–like composition is confirmed by an XPS depth profile, recorded on a sample of Tridur ZnNi H1 with Tridur Finish 300 (20% v/v) applied (Fig. 8).

Significant carbon concentrations are only found on the surface, likely due to adsorption of CO2 from the air or surface contaminations. Within about 10 nm, the carbon concentration falls to a very low level, not changing significantly with increasing sputter depth. The composition of the post-dip layer and the passivate's conversion coating appear almost identical. A change in nickel concentration indicates a diffuse transition between the more post-dip-like and the more passivate-like layers. Therefore, the post-dip contributes to an increase in thickness of about 0.2 µm in this application.

However, the lack of sharp transitions is also due to the fact that the post-dip penetrates deeply into the passivate layer, effectively filling up micro cracks. Both the passivate layer and the post-dip layer bear reactive sites with regard to coordination chemistry. During the deposition at elevated temperature, and especially in the subsequent hot-air drying process, the chromium(III) present in the passivate layer reacts with the post-dip solution's components, finally building up the enhanced

Final Finish Applied	Hours to White Corrosion
None/passivate only	24–48 h
Tridur Finish 300 (20% v/v)	312 h
Corrosil Plus 501 BG*	432 h
*Organic polymer/silicate-based sealer.	

Table 3: Minimum Corrosion Resistance of Different Finishes Applied to Black Passivated Zinc-Nickel (Tridur ZnNi H1): Neutral Salt Spray Testing (ISO 9227).

conversion coating. Figure 9 shows a structural proposal for this layer's composition.

Polynuclear chromium(III) complexes bearing μ-phosphato bridges are described in literature10–12 and they most likely contribute to the post-dip layer's composition. Due to the very similar composition of Tridur Finish 300 layers and passivate

Conversion Coating	F/Nm	T/kN	K_{M10}	μ_{thread}	μ_{head}	μ_{tot}
Tridur Zn H1	120.3 ± 11.3	36.1 ± 0.01	0.33 ± 0.03	0.32 ± 0.04	0.22 ± 0.04	0.27 ± 0.03
Tridur ZnNi H1	150.9 ± 13.7	36.1 ± 0.02	0.42 ± 0.04	0.33 ± 0.07	0.35 ± 0.03	0.34 ± 0.03

Table 4: Friction Properties Determined on M10×50 Bolts (measurements ± standard deviation)

layers, it is very difficult to find some contrast between both layers by means of SEM imaging. However, Figure 10 shows an SEM image of a FIB cross section through a sample with Tridur Finish 300 applied to black passivated zinc–nickel (14% nickel). The image reveals a thickness of 100–200 nm for the passivate and the post-dip layer.

Layer morphology. The morphology of the post-dip layer was investigated using different concentrations of Tridur Finish 300 applied to a black passivated (Tridur ZnNi H1) zinc–nickel alloy surface. The morphology of the deposit in dependence of the concentration of the post-dip bath was studied by means of SEM micrographs on samples of black passivated zinc–nickel (Figs. 11–14).

The post-dip caulks the micro cracks of the black passivated zinc–nickel surface. The post-dip layer's appearance itself resembles that observed with a hexavalent black chromate on zinc–nickel with regard to the mud-crack-like surface observed. Above 200 ml/l the post-dip layer's cracks become larger in size (Fig. 15). This means that with excessive concentrations a lesser extent of the surface may be covered by the post-dip layer. No significant advantage concerning neither the aspect nor the corrosion protection could be determined with higher concentrations.

Corrosion-protection properties. Corrosion-protection properties were investigated with different concentrations of the post-dip solutions (Tridur Finish 300) applied to black passivated zinc–nickel. It was found that a high level of corrosion protection was already established with 50 ml/l of Tridur Finish 300, not increasing significantly with higher concentrations (100–300 ml/l). However, the aspect of the parts finished was found to be best at 200 ml/l (20% v/v). Evaluation on black passivated zinc–iron (Tridur ZnFe H1) produced similar results. On black passivated zinc (Tridur Zn H1), 100 ml/l was found to be a suitable concentration.

With regard to the decorative aspect of the finished surfaces as well as their corrosion-protection properties by means of neutral salt spray testing, the applica-

tion parameters shown in Table 1 have been proven in practice for application on some black passivates.

Tridur Finish 300 can be applied in both rack and barrel applications. The bath parameters are the same for both methods and depend only on the composition of the underlying conversion coating.

Tridur Finish 300 is no substitute for sealers in general. Usually the corrosion protection that can be expected from a chromium-based post-dip can be classified as slightly below that of a film-building sealer based on polymer dispersions or solutions (e.g., Corrosil Plus 501).

The corrosion behavior was analyzed by recording polarization curves ±50 mV around the open circuit potential in a three-electrode set-up, including a platinum counter electrode, a Ag/AgCl (3M KCl) reference electrode, and the sample as the working electrode. The samples were immersed in aerated solutions of 50 g/l sodium chloride adjusted to pH 7. After 3 min of equilibrium time the open circuit potentials (ocp) were measured and the sample was then polarized from –50 to 50 mV vs. ocp at a sweep rate of 5 mV/s. The data were then plotted on a graph (Fig. 12). The results of the Tafel analysis of the data are summarized in Table 2.

The registered corrosion currents correlate with corrosion rates. The surface with only the passivate and no post-treatment applied showed the highest corrosion rates. Reduced corrosion rates were observed on the surface with the post-dip applied to the black passivate, and even lower corrosion rates were found with the surface having the polymer-based sealer applied. Also, the sealed surface behaves in an electrochemical manner that is slightly nobler than the post-dipped surface, which itself appears nobler than the passivate surface.

This principal sequence in corrosion protection is confirmed by neutral salt spray testing on samples with Tridur ZnNi H1 with Tridur Finish 300 according to DIN EN ISO 9227 (Table 3). Fig. 17 shows three steel panels plated with a Zn/Ni-alloy (14% Ni, 8 µm), black passivated with Tridur ZnNi H1 and with Tridur Finish 300 applied as the final finish after 1,008 h in neutral salt spray testing (DIN EN ISO 9227). Only a small amount of non-voluminous zinc corrosion product formed on the rinsed and dried panels.

Torque and tension properties. The friction properties of the new surface were evaluated on M10×50 (thread pitch 1.50) hex head bolts of property class 10.9. The bolts were plated with 8–10 µm of zinc (Protolux 3000) as well as with zinc–nickel (14% Ni, Reflectalloy ZNA) and respectively passivated with a black zinc (Tridur Zn H1) or black zinc–nickel passivate (Tridur ZnNi H1). Tridur Finish 300 (10% v/v for zinc and 20% v/v for Zn/Ni) was applied as the final finish after the passivate treatments. Twelve samples (Zn), respectively 20 bolts (Zn/Ni), were tested on a Schatz Analyse 5413-4504 testing machine at a tightening speed of 30 min–1 according to DIN EN ISO 16047. The results are summarized in Table 4. Higher friction figures have been determined for the zinc–nickel surface compared with the zinc surface. With both surfaces the friction behavior is essentially the same as that found with hexavalent chromium–based conversion coatings (e.g., black or yellow chromates) without any sealer or lubricant applied.

CONCLUSIONS

The development of a trivalent chromium–based post-dip solution has been

demonstrated and its properties investigated. The post-dip solution does not act like a sealer but reinforces the trivalent chromium–based conversion coating. A μ-phosphate-bridged chromium(III) complex structure, bearing a similar constitution as that of the passivate layer, has been proposed.

In the course of the development of this additional step of substituting hexavalent with trivalent chromium, several efforts were necessary to adjust the formulation to achieve both the requirements for decorative appearance as well as those of corrosion protection. The objective was to develop a post-treatment process that acts as a second conversion coating and, therefore, can also easily be applied in normal plating equipment. This was successfully achieved with an elaborate new additive system.

This system governs the deposition process in the background without significantly contributing to the layer's composition. The corrosion-protection properties of surfaces with Tridur Finish 300 applied are found to be excellent but slightly lower than those of surfaces treated with film-building, polymer-based sealers. The tribological properties of the Tridur Finish 300-treated surfaces were essentially the same as those from hexavalent chromates. Although developed with black passivates in mind, the new Tridur Finish 300 final finish process can be applied to any trivalent chromium–based conversion coating in both rack and barrel applications.

While satisfying the high decorative demands issued when switching to trivalent conversion coatings, the new process achieves the corrosion-protection demands of the automotive industry, even with respect to non-sealed black passivated surfaces.

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TRIVALENT CHROMIUM FOR ENHANCED CORROSION PROTECTION ON ALUMINUM SURFACES

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Chromate conversion coatings have been routinely applied on aluminum-based surfaces in order to improve corrosion characteristics and adhesive properties. The conventional chromate conversion coating process uses highly oxidizing toxic hexavalent chromium (Cr+6) compounds and ferricyanide. The metal finishing industry has been developing less toxic alternative coatings in order to comply with environmental regulations and substance restriction legislation, such as the European Union's Restriction of Hazardous Substances (RoHS) directive.

One promising alternative is the trivalent chromium–based environmentally friendly conversion coating. This article will describe a new trivalent chromium process for chromate conversion on aluminum with high corrosion protection, good paint adhesion, low cost, quick and simple processing, and all while meeting the stringent requirements of military specifications. It is QPL (Qualified Product List) approved by the United States Navy–Defense Standardization Program under Governing Spec MIL-DTL-81706-B.

In addition, this article will outline various chromate conversion techniques for aluminum. It will address a new, environmentally friendly, cost-efficient, and performance-oriented chromate conversion coating with a unique and patented trivalent chromium pre- and post-treatment chemistry for aluminum.

CHROMATE CONVERSION OF ALUMINUM

Chromate conversion coatings have been used for several decades in the aerospace industry to improve the corrosion resistance of aluminum alloys. Chromate conversion coatings have also been used to passivate zinc, cadmium, copper, silver, magnesium, tin, and their alloys. Chromate coatings, similar to phosphate coatings, are processes of chemical conversion because they contain both substrate metal and depositing species. However, chromate coatings are formed by the reaction of chromic acid or chromium salt water solutions. Chromate conversion coatings usually exhibit good atmospheric corrosion resistance. These conversion coatings form an ideal substrate for paints by providing a clean, essentially inert surface, which provides optimum conditions for adhesion.

The application of chromated aluminum can cover a wide range of functions. Conversion coatings can provide mild wear resistance, better drawing or forming characteristics, and may be used to provide a decorative finish. In addition, they are also ideal for pretreatment prior to organic coating. Most organic coatings applied directly to aluminum surfaces will not adhere well, and if subjected to any deformation they will tend to flake off, exposing the bare aluminum. Scratching off the paint surface would also provide a nucleation site for aluminum corrosion and further undercutting of the coating.

DESIRABLE CHARACTERISTICS OF HEXAVALENT CHROMATE PASSIVATES

- Prevents oxide formation
- Provides color
- Slow corrosion in prototypic tests (e.g., salt spray, rooftop, etc.)
- Provides adhesion for organics (e.g. paint)
- Prevents corrosion of painted surfaces
- Conductive
- Thin
- Flexible
- Lubricious
- Easily applied
- Stable for weeks or months
- Durable
- Resilient (self healing)
- Coats in recesses
- Easy to strip
- Inexpensive equipment
- Single tank
- Inexpensive (charge-up cost)

The successful application of this conversion process requires the aluminum to be clean and free of organic soils, oxides, and corrosion products. Therefore, a pretreatment process is required that can be applied to aluminum and provides a suitable basis for subsequent coatings.

Conversion coatings that can be used on aluminum alloys and are compatible with most paint systems have been developed. The name "conversion coating" describes a process of chemical reaction that results in a surface film. As a result of this reaction and conversion, the film becomes an integral part of the metal surface, which exhibits excellent adhesion properties. Chromate conversion coatings are a thin chemical film, usually less than 0.25 microns in thickness and are electrically conductive.

HEXAVALENT CHROMATES

Historically, hexavalent chemistry has been used to process aluminum chromate conversion parts. Chromate passivation systems containing Cr+6 compounds are an extremely versatile group of aqueous chemistries that are extensively used in a diverse range of electroplating and metal treatment processes. They impart many beneficial and essential characteristics to metallic substrates and deposits obtained from a number of techniques, such as zinc electroplating. Chromate conversion coatings on alloys are formed by the reduction of chromate ions and the development of a hydrated Cr_2O_3 barrier layer, which provides corrosion resistance and further protection due to residual chromate ions.

Hexavalent-based passivation (Cr+6) exhibits a number of desirable characteristics. The process will passivate the surface of zinc and zinc alloy electrodeposits with a thin film that provides end-user benefits such as color, abrasion resistance, and increased corrosion protection. When damaged, these hexavalent chromates possess a unique "self-healing" property. This means that soluble Cr+6 compounds contained within the passivation films will re-passivate any exposed areas.

Hexavalent chromate has wet, gelatinous film drying at the surface. Subsurface moisture (dehydrating in approximately 48–72 hours) provides self-healing and lubricity characteristics. The deposits are harder than conventional trivalent chromate film, and they offer torque and tension to meet the finishing requirements of fasteners. Unfortunately, the Cr+6 used in generating cheap and very effective coatings poses serious health hazards as well as waste treatment prob-

Conversion Coating	Pretreatment	% Passed	% Failed
Enhanced	Etched	81	19
Standard	Etched	31	69
Enhanced	Non-etched	90	10
Standard	Non-etched	53	47

Table 1: Effect of an Additive on Corrosion Resistance

lems. Chrome sores, which are severe damage to mucous membranes and skin lesions, occur from exposure to the ever-present chrome-mists and aerosols in job shops. Environmental guidelines and regulations are in place that restrict and prohibit its usage.

The finishing industry is developing less toxic alternatives in order to comply with substance restriction legislation and directives from the European Union. The most significant directive is RoHS, signed on Jan. 27, 2003, which went into effect July 1, 2006. The restriction covers six hazardous substances: lead, mercury, cadmium, Cr+6, polybrominated biphenyls (PBB), and polybrominated diphenyl ether (PBDE).

Another European Union legislative action, the second edict that also contains Cr6+, is the End of Life Vehicle (ELV) directive, which went into effect on July 1, 2007. Four heavy metals included in ELV directive include: cadmium, lead, mercury, and Cr+6 (approximately 70% of total heavy metals is Cr+6).

Industry has been actively following any new development to replace Cr+6. The most common alternative is trivalent chromium, which is environmentally friendly. However, there are still some weaknesses with trivalent chromate coatings.

In order to achieve equal or better corrosion resistance compared with hexavalent chromate, in most cases a sealer or a topcoat is required. Some chemical manufacturers now offer better salt spray performance without any sealers or topcoats. Trivalent chromates do not have self-healing properties. Their bath life is shorter than a hexavalent chromate bath, they require a 140°F operating temperature, and they do not offer identical colors.

In recent years there have been new developments in trivalent chemistries. More colors are now available and coating performance has significantly improved, especially with respect to corrosion resistance. Typical trivalent chromate film has a pale greenish color. Trivalent chromate deposits are electrically non-conductive (unless applied over a zinc alloy or a metallic substrate).

The most significant development for the replacement of hexavalent chromates is the trivalent chromium pretreatment (or post-treatment), developed by the United States Navy, Naval Air Systems Command (NAVAIR). This is a unique chemistry, specially formulated and developed for aluminum. This formulation contains <1% trivalent chromium and operates at ambient temperatures (65–85°F). It does not contain any restricted or hazardous substances and, as a result, does not require any exhaust systems. Most importantly, it complies with all European Union edicts, including RoHS, ELV, and the Waste Electric and Electronic Equipment (WEEE) directives.

This novel chemistry has shown outstanding performance when compared with other conventional trivalent chromates. This trivalent chromate chem film is hard-

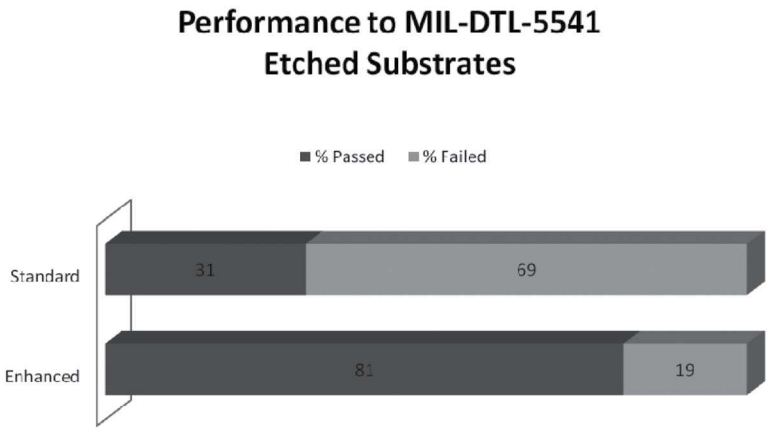


Figure 1

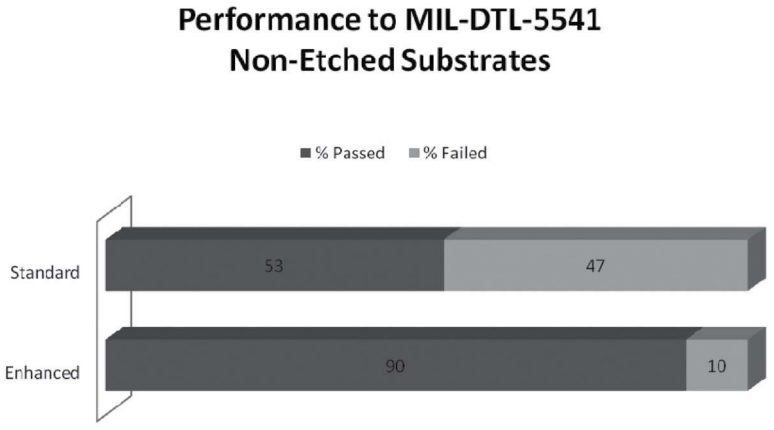


Figure 2

er than conventional trivalent chromate, is electrically conductive (low electrical resistance [LER]), and it meets or exceeds ASTM-D2559-9, MIL-DTL-5541F, and MIL-DTL-81706 for electrical resistance. Therefore, it is useful in electronic equipment where surface resistivity is critical and required. The trivalent chromium pretreatment has excellent adhesion and bonding properties and provides an undercoat for organic coatings, such as paints. It meets or exceeds dry tape adhesion requirements for ASTM-D3359 methods A & B.

This trivalent chromium pretreatment is an ideal undercoat for cured coatings and overcoat for plated materials that require subsequent hydrogen relief. This unique trivalent chromium pretreatment can be exposed to temperatures exceeding 800°F following a 24-hour cure period. It can be baked for hydrogen relief in excess of 500°F for more than 24 hours without loss of performance, whereas hexavalent chromates cannot be baked above 140°F without loss of performance.

Immersion Time (min)	Coating Weight (mg/ft²)
2	11.4
5	25.5
8	43.3

Table 2: Coating Weight of 2024 T-3 Alloy

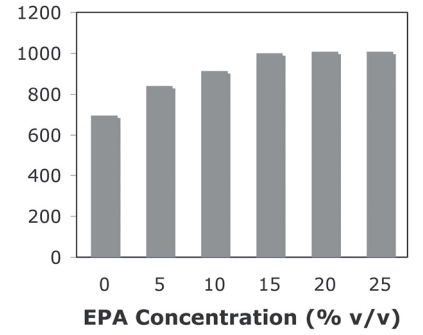


Figure 3: EPA = enhanced performance additive.

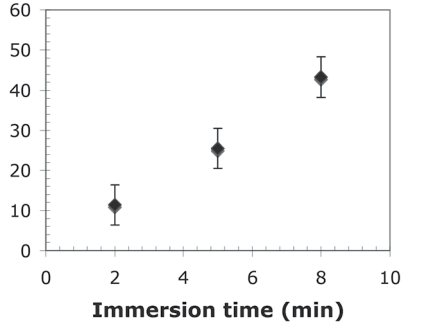


Figure 4

In most cases, corrosion-resistance performance of this trivalent chromium pretreatment is equal to or better than conventional trivalent chromates or hexavalent chromates. Results of 168 to 500 hours can be achieved in neutral salt spray testing (ASTM-B117), depending on the aluminum alloy tested. In short, this newly developed trivalent chromium chemistry offers an overall superior performance without any sealer or a topcoat.

This novel trivalent chromium treatment has also been used to replace high- and mid-temperature anodizing seals. It has proven to be an environmentally friendly and efficient anodizing seal without any hazardous chemicals.

RESULTS AND DISCUSSION

Most aluminum alloys were tested and able to achieve up to 500 hours of neutral salt spray (NSS) corrosion resistance. The concentration of trivalent chromium pretreatment material ranged from 15–25% by volume with various time cycles from 3–5 minutes at ambient temperatures. This new chemistry has been pursued due to its tremendous success in initial testing. It is a drop-in replacement for hexavalent chromate. As mentioned earlier, due to the low concentration and chemistry of non-hazardous substances, it can be operated in a manufacturing environment without any exhaust system requirements.

The pretreatment of aluminum is important to achieve desired specifications. Alloys such as 6061 and 7075 are relatively easy to process and can work with most available detergent and activation agents, acids, or deoxidizers. On the other hand, 2024 alloy (with up to 5% copper content) is very susceptible to localized corrosion due to segregation of intermetallic particles along the grain boundaries, and it requires specific pretreatment. The nature of this alloy makes it sensitive to some etching cleaners and may require certain acids to activate the part surface.

This patented trivalent chemistry by NAVAIR is simple to operate provided that

you pay attention to the pretreatment and pH of the bath. The normal operating pH range of this bath is 3.6–4.0. A pH that is lower than the operating range may cause early corrosion in salt spray testing as the bath becomes more aggressive. A combination of lower pH and slightly elevated temperature makes it extremely aggressive and supports a shorter time cycle.

Studies were performed by a licensee of NAVAIR's trivalent chromium conversion coating that examined test results of various aluminum alloys treated with different process cycles. It included various times, temperatures, and concentrations of more than one detergent. Special attention was given to the etching nature of some of the detergents. The objective was to achieve a clean surface without any modification or powdery film. After cleaning, the surface was activated by various chemical methods that were chosen based on the alloy. Also, important factors included concentration and cycle time in activation bath.

Rinsing was also given special attention. Tap water or deionized water was selected as required. Quality of rinse water, such as the levels of chlorides and total dissolved solids, were observed. The trivalent chromium pretreatment bath was operated at ambient temperatures as well as at elevated temperatures for evaluation purposes. Testing of different alloys included different concentrations of trivalent chromate in the bath. It also included different time cycles.

The results were based on the performance in a neutral salt spray chamber. We evaluated different test matrices and found that certain alloys required a specific overall treatment. Alloys, which had not been so difficult to process, offered us excellent results. Salt spray hours in neutral salt spray ranged from 168–800 hours. When a specific process cycle was followed, 2024 alloy also performed well in salt spray corrosion testing, with a range from 168 to more than 1,000 hours.

ENHANCED PERFORMANCE ADDITIVE

One of the most daunting aspects of trivalent conversion coatings as a drop in replacement for hexavalent chromium chemistries is the requirement of rigid pretreatment parameters in order to achieve maximum corrosion performance. Across the board, job shops and formulators alike go to great lengths to produce consistent results that pass requirements such as MIL-DTL-5541 and other corrosion specifications.

Application facilities not well equipped to perform experiments for pretreatment optimization are finding themselves making small beaker size batches of chemistry with the intention of scaling up to their production line. This is good practice when tight controls are met with proper standards, but the process can be convoluted for some and more work than what a typical job shop is used to when integrating a new product into their line.

The standard practice in industry is to purchase a material, follow the operating parameters, and, voilá, it works. Trivalent chromium conversion coatings are not, in general, that straightforward. The nature of the technology poses the burden of tailoring the facility's resources and equipment constraints to the product, which requires a slightly more sophisticated level of understanding. This may come as a shock to those transitioning to trivalent chromium chemistry and can often be discouraging.

There have been successful attempts in creating a more robust process to allow leeway in pretreatment parameters. Research institutions and private industry groups are looking for additives to put in trivalent chromium conversion coating baths. Anyone with experience using trivalent conversion coatings

knows that surface modification of a substrate, such as etching, can cause a drastic decrease in corrosion resistance. A study of one particular additive indicates an improvement rate for corrosion resistance of 50% on etched substrates and 38% on non-etched substrates when using an enhanced bath (see Table 1).

The study included 163 different processes that utilized several different cleaners, deoxidizers, and etchants at various temperatures, concentrations, and cycle times. All panels treated with an enhanced performance additive (EPA) were tested against a standard, non-enhanced (NAVAIR) trivalent chromium pretreatment bath. Test panels were sent to an outside party (a NADCAP-certified laboratory) for neutral salt spray testing (ASTM-B117) as well as undergoing inhouse inspection. Panels were examined at intervals of 96, 168, 212, 267, 336, and 407 hours and beyond. For the sake of brevity, only one parameter will be reported in this article: etched vs. non-etched. The total number of test panels was in the hundreds.

The data in Figure 1 indicates that, statistically, out of 100 different process variations, 81 of them will pass MIL-DTL-5541 on etched substrates using an enhanced version of a trivalent conversion coating, whereas only 31 process variations will pass using a standard, non-enhanced trivalent chromium chemistry.

Although the improvement on non-etched substrates is not quite as dramatic as it is for severely modified substrates, using an additive in a tri-chrome bath is still beneficial. The data in Figure 2 indicate that, statistically, out of 100 different process variations, 90 of them will pass using an enhanced version and only 53 will pass using a standard, non-enhanced bath.

Baths that include an EPA perform much better than standard trivalent chromate baths (NAVAIR). The addition of an EPA in a standard trivalent chromate pretreatment bath can vary from 15–30% by concentration. We used a 25% EPA concentration in a standard trivalent chromate bath for our test evaluation. The objective here was to study the influence of an EPA in a standard (NAVAIR) trivalent chromate pretreatment bath and to evaluate the difference in performance with the addition of the EPA.

In order to evaluate the effects, we set up a test plan and selected the appropriate chemistry. We chose the 2024 aluminum alloy as our baseline standard. The aluminum alloy 2024 contains up to 5% copper and a major fraction of the intermetallic inclusions are composed of Al_2MgCu (S-phase), which has cathodic potential relative to the aluminum alloy matrix. The intermetallic precipitates make the alloy very susceptible to localized corrosion. We assumed that if we could achieve superior results on this alloy, then the other alloys such as 5052, 6061, and 7075 would perform as well or better than 2024 alloy panels. We aimed to study whether the EPA helps enhance corrosion resistance performance of trivalent chromium pretreatment on aluminum.

Salt spray resistance: Figure 3 illustrates enhancement in salt spray resistance as the concentration of EPA increases.

Coating weight: Data in Table 2 list the coating weight of 2024 T-3 alloy. Coating weight of 11.4 mg/ft2 was achieved with only two minutes of immersion time, and this exceeds MIL-DTL-81706.

The detergents for this trial were selected based on some major customers' suggestions as well as our history of various testing with trivalent chromium pretreatment applications. The temperature was one of the important factors that

was controlled within a range of 120–125°F. As much as cleaning of a part surface is important, it is also important to clean the surface without drying out during the transfer stage. The concentration of these detergents was based on the lower end of chemical manufacturers' suggested operating range.

The results of NSS testing did not indicate any reason for a detergent to be responsible for failure. Therefore, we concluded that the process parameters for the various detergents were acceptable as tested for evaluation with the EPA in a standard trivalent chromium pretreatment bath.

The test panels were etched using a selected etchant as suggested by major customers. The study examined the difference in performance with and without the etchant for EPA performance. The results were favorable for the use of this etchant in a trivalent chromium pretreatment bath with the EPA additive. The process parameters were kept at the same level for etched and non-etched test panels for comparison.

Out of the 164 total test panels, 119 (73%) of the etched panels passed. There were fewer failures for the etched panels (22%) with the EPA than without it in a standard trivalent chromate pretreatment bath. On the other hand, there were fewer failures of non-etched panels (8%) when used with the EPA than when used in a standard trivalent chromium pretreatment bath. It was concluded from this study that the EPA increases corrosion resistance by 51% on etched panels. We also determined that EPA increases corrosion resistance by 39% on non-etched panels.

These data show that this extended protection additive helps to enhance corrosion resistance performance with or without the etchant when compared with a standard (NAVAIR) trivalent chromium pretreatment application. The results of NSS testing conducted by NADCAP-certified laboratory showed that standard trivalent chromium pretreatment (NAVAIR) performed from 96–768 hours with the etched panels. The non-etched panels in the same bath performed better in NSS, with a range of 168–2,786 hours.

The same process for evaluation of panels tested for EPA effectiveness showed that etched panels performed in NSS from 174–912 hours, whereas non-etched panels performed from 72 to more than 3,120 hours. To activate the part surface, an acid in combination with a deoxidizer was used. There were different mix ratios of acid and deoxidizer, as well as the process cycle time, for testing purposes. Results were based on various combinations of cycle time and concentration ratios.

NSS testing results indicated that lower concentrations of acid in a deoxidizer performed better than higher concentrations of acid/deoxidizer for the standard trivalent chromium pretreatment (NAVAIR) bath. However, acid concentration did not substantially influence the trivalent chromium pretreatment with EPA-treated substrates. Test panels processed with a low concentration of acid/deoxidizer in a trivalent chromium pretreatment (NAVAIR) bath failed at 168 hours, whereas test panels with an EPA passed 267 hours.

SUMMARY

The trivalent chromium pretreatment formulated and invented by NAVAIR performs very well for replacing hexavalent chromium on aluminum. Its performance varies depending on the type of detergent and its concentration, temperature, and cycle time. Also important is the surface activation and the type of acid and/or deoxidizer that is used for the application. However, the most

important factor is the type of aluminum alloy undergoing chromate conversion coating. It was concluded from the study that 2024 is the most difficult alloy due to its metallurgical content; if satisfactory results can be obtained for 2024, then it would not be so difficult to achieve successful results for other aluminum alloys .

The EPA, when added to a standard trivalent chromium pretreatment (NAVAIR) bath, exhibited outstanding performance in NSS testing. This additive is designed to enhance corrosion resistance of an aluminum alloy for trivalent chromium pretreatment performance. An EPA offers consistent corrosion resistance performance for difficult alloys, such as 2024. It is an additive that improves standard NAVAIR trivalent chromium application on aluminum for robust performance.

It is sufficient to say that the most important aspect of using this newly developed, patented additive for trivalent chromium pretreatment its effective and consistent corrosion- resistance performance.

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UPDATE ON ALTERNATIVES FOR CADMIUM COATINGS ON MILITARY ELECTRICAL CONNECTORS

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The metal finishing industry has been impacted by numerous regulatory actions related to the hazardous materials that are used in decorative and functional coating processes. These environmental regulations are applicable to both commercial and government facilities. In addition, Executive Order (EO) 13423, *Strengthening Federal Environmental, Energy, and Transportation Management, and EO 13514, Federal Leadership in Environmental, Energy, and Economic Performance,* were recently enacted. These EOs require government agencies to reduce the quantity of toxic and hazardous chemicals and materials acquired, used, or disposed.

Cadmium and hexavalent chromium are very toxic and carcinogenic materials heavily regulated by the Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA). In addition, hexavalent chromium is among the three hazardous materials that the Department of Defense (DoD) has targeted for reduction to meet the requirements of the EO 13423. Due to the toxicity and carcinogenicity, as well as the numerous regulatory actions related to these materials, the U.S. Army Tank-automotive Research Development and Engineering Center (TARDEC) has been working to eliminate or reduce the use of cadmium and hexavalent chromium in ground vehicles and related systems. The National Defense Center for Energy and Environment (NDCEE), operated by Concurrent Technologies Corporation (CTC), has been tasked to support TARDEC's activities in this area.

Specifically, the protective shells of electrical connectors currently used in military ground systems are cadmium plated and then chromated with chromate conversion coatings (CCCs) to provide additional corrosion protection. The aforementioned regulatory concerns underscore a need to find alternatives to the currently used coating processes to reduce environmental and safety risks.

However, the replacement of cadmium for any application is not a trivial task. Cadmium has been used as a protective coating for electrical connectors for many years because of the numerous properties that it imparts to the overall component. Key properties that cadmium coatings impart to electrical connector shells include: [1,2]

- **Ease of manufacturing**
- **Ease of repair**
- **Electrical conductivity**
- **Electromagnetic compatibility (EMC)/electromagnetic interference (EMI) effectiveness**

- **Environmental resistance, particularly corrosion resistance**
- **Galvanic coupling**
- **Inhibition of algae growth**
- **Low cost**
- **Lubricity (meets established torque/tension requirements)**
- **Shock resistance**
- **Solderability**
- **Temperature resistance**
- **Vibration resistance**

CCCs are applied over cadmium coatings to provide additional properties, the most important of which are:

- **Enhanced corrosion resistance**
- **Paintability (meets requirements for paint adhesion to coating)**
- **Color**

As seen above, the synergistic benefits provided by this coating system have made its replacement challenging. One example of the unique protective properties that are imparted by cadmium and hexavalent chromium is corrosion resistance. Cadmium coatings provide galvanic corrosion protection to electrical connector shells, and very few metals can provide a similar level of corrosion protection in this application. This is demonstrated by the position of cadmium in the galvanic series, shown in Figure 1. [1]

Figure 1 demonstrates that zinc and zinc alloys, beryllium, magnesium, and aluminum alloys are generally the most active metals in corrosive environments and, therefore, are the only materials that can provide sacrificial corrosion protection similar to cadmium in this application. However, beryllium is more hazardous than cadmium, and magnesium and pure zinc both corrode too rapidly for many engineering applications.

Other examples of the unique properties that are imparted by cadmium to connector shells involve electrical properties, specifically EMC and EMI effectiveness. Connector mating resistances must be kept to a minimum (e.g. less than 2.5 milliohms) for EMC, because greater mating resistances can lead to high voltages (and subsequent failures) when induced by sudden surge currents (such as a lightning strike). Cadmium-plated connectors meet this requirement throughout the life of the connector (i.e., the corrosion products of cadmium are generally non-insulating). Other plated coatings, such as electroless nickel (EN), meet this requirement initially, but lose effectiveness over time due to the resistances that are generated by corrosion products.

VIABLE ALTERNATIVES TO CADMIUM

The DoD has been interested in cadmium replacement for many years, and numerous potential replacements have been identified and explored in past work conducted by Brooman[2,3,4], Gaydos[5], Klingenberg[3, 4, 6], Legg[1]; and Shahin[7], among many others. It is the intent of this paper to summarize past work that has been accomplished in this area, with the intent of providing a rationale for the

selection of the most promising candidates for further study under future phases of this current effort.

Based on the many previous studies related to cadmium replacement, and the available data on candidate technologies, a number of promising candidates for cadmium replacement were identified. Due to the particular focus of this project, candidates were limited to commercially available or near-commercial technologies. These include:

- **Advanced materials**
- **Alloys deposited by chemical vapor deposition (CVD)**
- **Alloys deposited by molten salt bath processes**
- **Alloys deposited by ionic liquid processes**
- **Electrodeposited aluminum and alloys**
- **Electroless nickel technologies**
- **Electroplated tin alloys**
- **Electroplated zinc-cobalt**
- **Electroplated zinc-nickel**
- **Ion vapor deposited (IVD) aluminum and alloys**
- **Metal-filled paints and ceramics**
- **Sputtered aluminum and alloys**

The viability of each of these processes in the context of the specific application—electrical connector shells—is discussed herein. Where data is available, issues such as compatibility of the alternatives with existing cadmium-plated connectors will be addressed.

ADVANCED MATERIALS

The use of advanced materials as a replacement for cadmium-plated parts has been considered mostly for larger aerospace components. Stainless steel is the most likely candidate to replace cadmium on larger, non-electric components. A corrosion-resistant stainless steel, S53, was developed under a project funded by the Strategic Environment Research and Development Program (SERDP). This effort[1, 5, 8] focused on providing corrosion protection and resistance to stress corrosion cracking on aircraft landing gear. Stainless steel alloys would provide many of the necessary properties needed for electrical connector shells and may be acceptable for some applications. However, these materials generally exhibit a high mating resistance and also may not be cost-effective. Likewise, titanium alloys and Inconel® have been found to be adequate as substrate substitutes for cadmium plated fasteners5, but these may also be cost prohibitive for use in electrical connectors. Polymer composite materials (such as polyetheretherketone) are already in use in some commercial applications. However, military usage appears to be minimal (at least for ground vehicle applications), and consideration of this material introduces issues related to cost, conductivity, and mechanical wear for some applications. Overall, it is evident that additional research and development is required to use advanced materials to replace the standard shells in newer models of electrical connectors.

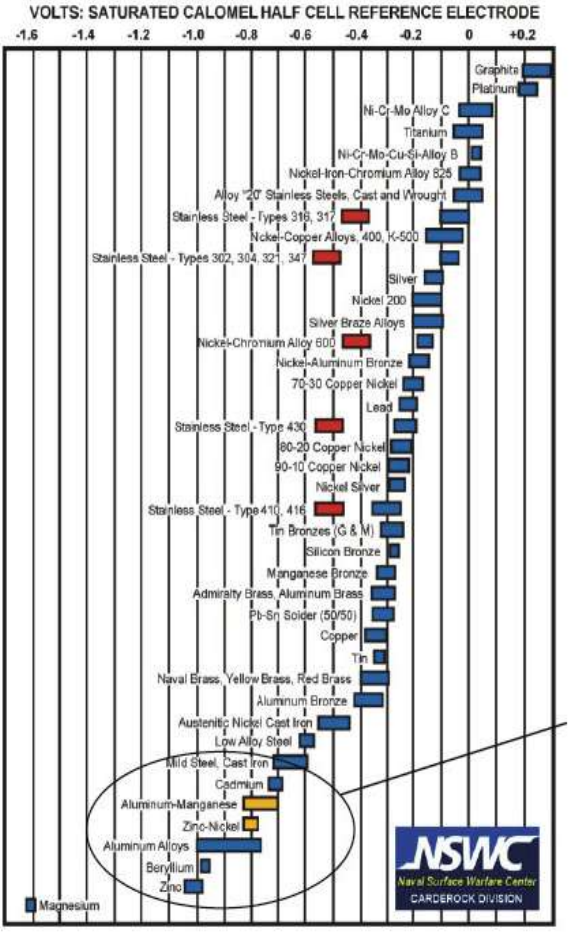


Figure 1. Galvanic series, showing position of cadmium and viable alternative metals. (Circled area: materials providing sacrificial protection.) 1

ALLOYS DEPOSITED BY CHEMICAL VAPOR DEPOSITION

The Air Force Research Laboratory (AFRL) evaluated aluminum coatings applied through Atmospheric Pressure Chemical Vapor Deposition (APCVD).9 Environmentally benign CVD processes using triethylaluminum as a precursor for producing high-quality aluminum coatings was explored. While promising, this process involves special high-cost, equipment. Considerable further development from a process standpoint would likely be necessary to implement this process for high-volume applications such as electrical connector shells.

ALLOYS DEPOSITED BY MOLTEN SALT BATH PROCESSES

An aluminum-manganese molten salt plating process was explored under funding from the Environmental Security Technology Certification Program (ESTCP), but the process was plagued by inconsistent bath composition, visible fumes, and excessive crust formation [Ref. 10]. In addition, this process operated at a very high temperature, which is likely to affect the properties of aluminum shells. While this technology is promising, considerable further development from a process standpoint would be necessary to implement this process for electrical connector shells.

ALLOYS DEPOSITED BY IONIC LIQUID PROCESSES

As an alternative to the molten salt bath process mentioned above, the use of ionic liquids as an electrolyte to plate aluminum is under investigation. [5,11] Ionic liq-

uids are salts with a low melting point, which originates in their chemical structure (a mix of anions and large organic cations). These liquid salts have unique properties that allow easy dissolution of normally insoluble chemicals, such as cellulose. Ionic liquids enable electrochemical plating of metals like aluminum; deposition rates of one micron per minute at low temperatures (60 to 100°C) have been reported.[11] These deposition rates are significantly superior to other low-temperature aluminum coating methods. While this process is not yet mature enough to enable the plating of commodity items such as electrical connector shells, work is progressing rapidly and promising results will be forthcoming.

ELECTRODEPOSITED ALUMINUM AND ALLOYS

AlumiPlate® is a proprietary process in which a pure aluminum coating is electrolytically deposited onto a substrate that has been immersed into a non-aqueous, fully enclosed solution in an inert atmosphere. The resulting coating is highly versatile. It can be anodized or topcoated with the standard CCC post treatment, trivalent chromium post-treatments (TCPs), or non-chrome post-treatments (NCPs). TCPs are much less hazardous than CCCs and meet requirements under the European Union's Reduction of Hazardous Substances (RoHS) Directive—although this substance is still regulated under U.S. requirements. Additionally, the AlumiPlate® process does not appear to impart hydrogen embrittlement—a concern with cadmium plating.[5]

AlumiPlate® is one of the more promising new processes for cadmium replacement on electrical connectors. Researchers at the Naval Air Systems Command (NAVAIR) conducted 2,000 hours of salt spray corrosion testing on electroplated aluminum electrical connectors with TCP[12,13], in accordance with ASTM B117.[14]. NAVAIR found that all connectors performed equal to or better than the cadmium-plated controls with respect to visual appearance of corrosion. A plated connector is shown after 2,000 hours of B117 exposure in Figure 2.[12].

From a functionality standpoint, all tested connectors met the requirement for shell-to-shell conductivity, with the exception of the AA6061 AlumiPlate® coating with TCP at 25% concentration (the most dilute). The AA6061 AlumiPlate® coating with Class III post-treatment was the top performer.

Other projects involving this process include a partnership between Lockheed, Alcoa, and the U.S. Air Force, which is evaluating several coatings, including AlumiPlate®, to replace cadmium for military and commercial fasteners.15 Based on the results from both the NAVAIR testing and this partnership, the AlumiPlate® coating is currently being qualified for electrical connectors under MIL-DTL-38999L as well as relevant internal manufacturers' specifications. Specifically, qualification and approval of the AlumiPlate® coating is anticipated for Model 38999 electrical connectors with spring fingers, which will be used on the Lockheed Martin F-35 Lightning II (also known as the Joint Strike Fighter) program.

Despite the good performance of this candidate and its recent qualification, several drawbacks remain with the use of AlumiPlate®. Due to the use of the non-aqueous electrolyte, it is unlikely that this process could meet the environmental requirements that would allow its use in a DoD facility.1 Furthermore, the process requires the use of highly specialized equipment (e.g. high start-up cost). Finally, there are questions regarding whether the plated coating can be repaired, although initial work has found that it may be possible to use brush-

Test Descriptions	Baseline Coatings						Alternative Coatings					
	LHE Cadmium	LHE Cadmium	Titanium Cadmium	Titanium Cadmium	IVD Aluminum	IVD Aluminum	Acid Zinc Nickel	Acid Zinc Nickel	Alkaline Zinc Nickel	Alkaline Zinc Nickel	Tin Zinc	Tin Zinc
Post Treatment →	None	CCC[1]	None	CCC	None	CCC	None	CCC	None	CCC	None	CCC
Thickness	P	P	P	P	P	P	P	P	P	P	P	P
Bend Adhesion	P	P	P	P	P	P	P	P	P	P	P	P
Paint, Adhesion, Wet Tape	P	P	P	P	F	P	F	P	F	P	P	P
Cyclic Corrosion Unscribed	P	P	P	P	F	F	F	F	F	F	F	F
Cyclic Corrosion Scribed	F	P	F	P	F	F	F	F	F	F	F	F
Hydrogen Embrittlement	P	P	P	P	P	P	P	P	P	P	P	P
EIC, Wet	P	P	P	F	F	F	F	P	F	F	F	F
EIC, Cooked	P	P	P	F	F	F	P	P	P	P	P	P

(1) CCC Chromate Conversion Coating
= PASSES OR FAILS WITH INCONSISTENT RESULTS
= FAIL PER ACCEPTANCE CRITERIA
= PASS PER ACCEPTANCE CRITERIA

Table 1: Summary of Coating Performance from NDCEE Study



Figure 2. AlumiPlate-coated electrical connector, After 2,000 hours B117exposure.[12]

plated tin-zinc to repair this coating.[1,5]

ELECTROLESS NICKEL TECHNOLOGIES

A number of new EN-based coating systems continue to be considered for electrical connector shells. However, as mentioned previously, the corrosion properties of nickel—and subsequent electrical properties—are considerably different than those of cadmium.2 Further testing would be required to fully assess this candidate for military electrical connector shells. Despite these concerns, at least one leading manufacturer of electrical connectors is investigating the use of EN with occluded particles (polytetrafluoroethylene, or PTFE) as a cadmium replacement.16 While the inclusion of these particles will provide lubricity, the corrosion characteristics and electrical properties imparted to the connector shell must be considered and are being evaluated.

ELECTROPLATED TIN ALLOYS

Among the most mature and promising tin alloy coatings for electrical connector shells are tin-zinc coatings. Tin-zinc electroplating processes are mature, commercially available systems that can deposit alloys of 20–30% zinc (balance tin) from an aqueous solution. Tin-zinc coatings have been considered promising for cadmium replacement 2,7,17, and this finish was found to be a top performer in past studies. 18 However, more recent studies have derived less positive results. An extensive study on potential cadmium replacements conducted by the NDCEE19 found that a proprietary tin-zinc coating failed both cyclic corrosion and wet notch environmentally influenced cracking (EIC) tests yet passed hydrogen embrittlement and cooked EIC. A summary of test results from this effort can be found in Table 1.[19]

In this study, it was noted that the deposited tin-zinc coating was found to have an insufficient amount of zinc in the deposit to provide adequate corrosion protection (less than 1% zinc, versus the anticipated >20% zinc concentration found in more corrosion-resistant coatings that had been tested under related projects). This implies that, while tin-zinc does show promise for some applications, some bath chemistries may not be robust enough to provide a consistent coating composition (and, hence, sufficient corrosion resistance) for the harsh environments to which military electrical connectors are routinely submitted. Promising results under past studies imply that this candidate could provide comparable performance to cadmium if the deposit composition could be made more consistent.

It is noted that other tin alloys, specifically tin-indium coatings, are being considered for both commercial and military applications, but these would take considerable development to be considered for electrical connector shells.

ELECTROPLATED ZINC-COBALT

Zinc-cobalt plating is typically used to finish relatively inexpensive parts that require a high level of abrasion and corrosion resistance. This coating is report-

ed to demonstrate particularly high resistance to corrosion in sulfur dioxide environments. Several suppliers of commercial electrical connectors offer connector shells coated with zinc-cobalt as a replacement for cadmium to meet RoHS criteria. Zinc-cobalt alloys are not commonly used in applications requiring heat treatment because these alloys have been reported to demonstrate reduced corrosion resistance when exposed to high temperatures. In one study[20], after salt spray corrosion testing in accordance with ASTM B117[14], zinc-cobalt-plated sleeves showed considerably less corrosion resistance after one hour heat treatment at 250°F as compared to the as-plated condition. While this process was initially considered as being a worthy cadmium replacement, the questionable characteristics under high-temperature environments excluded its consideration under further review.

ELECTROPLATED ZINC-NICKEL

Zinc-nickel electroplating processes are mature, commercially available systems that can deposit alloys of 5–15% nickel (balance zinc) from an aqueous solution. Zinc-nickel alloys can be deposited from both acid and alkaline processes. Boeing has found that the alkaline process is easier to maintain and provides a more consistent coating composition.[5] From a performance standpoint, the NDCEE found that a proprietary acid zinc-nickel coating with CCC passed bend adhesion, paint adhesion, and hydrogen embrittlement tests, but displayed only marginal EIC performance[19] (see Table 1). The corrosion resistance was significantly less than the cadmium baselines, but increased coating thickness and selecting a suitable conversion coating may improve those results—although the implications of these changes to the form, fit, and function of the electrical connector would need to be identified. The proprietary alkaline zinc-nickel coating with a CCC performed similarly to the acid zinc-nickel in this study19 (see Table 1). Previous TARDEC work also found alkaline zinc-nickel coatings with a CCC to be promising for some electrical connector designs, particularly on MIL-C-83513 microminiature D-subminiature connectors, but less promising on other connector designs.

Based on these promising results, zinc-nickel has seen implementation as a cadmium replacement process in several areas. The NDCEE work19 provided information that assisted Rolls Royce Defense Aerospace in qualifying zinc-nickel as an acceptable alternative to cadmium on the T56 engine system. Boeing also found that zinc-nickel plating is an acceptable coating to replace cadmium on component parts made of low strength steel (less than 200 ksi), stainless steel, aluminum, and copper alloys.[1]

Other ongoing projects involving this process include the aforementioned partnership between Lockheed-Martin, Alcoa, and the U.S. Air Force, which is evaluating several coatings, including both acid and alkaline zinc-nickel, to replace cadmium for military and commercial fasteners.[15]

It is recognized that both acid and alkaline zinc-nickel processes may provide an acceptable alternative coating for cadmium in many applications. Acid zinc-nickel processes have traditionally been used; however, some embrittlement issues have been related to this process.[1] For this reason, Boeing restricts the use of acid zinc-nickel to steels with ultimate tensile strength of 220 ksi or less. While these issues may not be relevant for electrical connectors, a post-process bake has been found to both relieve hydrogen embrittlement and enhance cor-

rosion properties.[2] In any case, alkaline zinc-nickel appears to be the stronger candidate for this application, due to the reduction in required maintenance of the bath and the aforementioned current interest in the properties of this coating.

ION VAPOR DEPOSITED ALUMINUM AND ALLOYS

Ion vapor deposited (IVD) aluminum is a physical vapor deposition (PVD) process in which a part is placed in a vacuum chamber and glow discharge cleaned. Pure aluminum is then melted in heated ceramic boats until it evaporates and condenses on the part to form a coating. Concurrently, ions from the discharge bombard the forming coating to enhance its density.

IVD aluminum is a mature process that has been used successfully to deposit a variety of coatings for many years, and has traditionally been one of the most promising technologies for cadmium replacement. It is non-embrittling and galvanically compatible with aluminum substrates. In addition, it has excellent high temperature properties and can be conversion coated. Corrosion resistance has been reported to be comparable to, or better than, cadmium in some environments.[2,21] Alloying the IVD aluminum coating is reported to provide even better corrosion protection; IVD aluminum-magnesium alloys with 10% magnesium have demonstrated significant pitting corrosion protection.[17] Past NDCEE work found that aluminum-tungsten and aluminum-molybdenum also demonstrated improved passivation over pure aluminum.[6]

As mentioned previously, Boeing has qualified IVD aluminum to replace cadmium on component parts made of low strength steel (less than 200 ksi), stainless steel, aluminum, and copper alloys. In a past TARDEC study, IVD aluminum demonstrated the best overall performance on aluminum connectors. Specifically, on MIL-C-38999 circular connectors, IVD aluminum performed similar to or better than cadmium, with lower shell-to-shell resistance, but slightly less corrosion resistance. It was noted that, on MIL-PRF-24308 D-subminiature connectors, cadmium demonstrated the best overall performance, with IVD aluminum being the best performing alternative. It was also noted that on MIL-C-83513 microminiature D-subminiature connectors, IVD aluminum was reported to have a significant drawback for use on these connectors. During the IVD process, aluminum coated the entire connector surface (including the phenolic material), causing the pins to be electrically continuous with each other and the connector shell, resulting in shorts and eventual connector failure.

As seen above, there are numerous drawbacks to using IVD aluminum for electrical connector shells. These include the aforementioned overcoating issues, as well as high start-up and operations costs because the equipment that is used to apply this finish is expensive. Also, while IVD aluminum is not completely limited to line-of-sight coverage, the conventional process cannot "throw" into deep recesses on some parts—particularly holes.[1, 5] There are some coating performance concerns as well. IVD aluminum coatings display a columnar structure with a high degree of porosity. As a result, the coatings must usually be glass-bead peened to densify the coating and alleviate porosity and corrosion concerns. The NDCEE found that IVD aluminum coatings, even with CCC, provide only marginal cyclic corrosion results[19] (see Table 1), underscoring the importance of a dense aluminum coating. Also, like many pure aluminum coatings, IVD aluminum has also been reported to have poor wear resistance, and has demonstrated galling issues. The latter is a particular concern for electrical connectors; an

aluminum-to-aluminum interface could result in excessive mating forces, or even unmateable connectors1 (the incorporation of dry film lubricants have been proposed to resolve this issue, but this would have an adverse effect on electrical connectivity).

In summary, while IVD aluminum may be viable to replace cadmium in many applications, it is not anticipated to be a direct replacement for electrical connectors. In fact, an Air Force study has recognized that IVD aluminum will not easily replace more than about 50% of cadmium plating requirements.[17]

METAL-FILLED PAINTS AND CERAMICS

Organic paint systems that are loaded with sacrificial metals (generally aluminum and zinc metal powders) have demonstrated significant corrosion resistance in several applications. However, they are generally not considered for cadmium replacement due to poor galvanic corrosion performance and poor adhesion (compared to electroplating).[5]

Metal-filled ceramic coatings are being considered for some cadmium-replacement efforts. One supplier offers a coating that incorporates aluminum flakes in a ceramic matrix. The coating can be applied via brush or spray. It is used primarily for larger components in aircraft such as landing gear (specifically the F-22), as well as for high-temperature applications. Drawbacks to this candidate include sole source (only one supplier provides the coating, and they only license to major users), high cost, limited available data, and the requirement to heat-treat the coating before use.[1,5] Also, coating conductivity has apparently not been determined. As such, this candidate is likely not feasible for electrical connectors.

SPUTTERED ALUMINUM AND ALLOYS

Sputtering, or magnetron sputtering, is another PVD process. In this process, a part is placed in a vacuum chamber, where it is glow discharge cleaned after the system is evacuated. The ionized gas (typically argon) is attracted to the biased aluminum target, and aluminum atoms are ejected from the target and condense on the substrate to form a coating. The "Plug and Coat" method of sputtering allows both inner diameters (IDs) and outer diameters (ODs) to be coated within the same chamber.

Recent work conducted by Boeing 1, 5 found that sputtering provides a better quality aluminum coating than IVD, with lower porosity. Through the "Plug and Coat" process, parts can be 100% PVD aluminum-coated (IVD Al on OD, sputter Al on ID). In addition, the process is non-hazardous as compared to cadmium plating (no air emissions, water emissions, or solid waste).

Sputtered aluminum alloys have also showed promise to replace cadmium. They include aluminum magnesium, aluminum-molybdenum, aluminum-tungsten, aluminum-manganese, aluminum-zinc, and aluminum-magnesium-zinc.[5, 6]

While promising, magnetron sputtered aluminum is still under development for coating aircraft parts. Susceptibility to environmental embrittlement has yet to be determined, and more recent work has generated mixed results.22 Also, while technically acceptable, this process involves high start-up and operational costs, and may not be cost-effective for smaller parts such as electrical connector shells.[5, 22]

OTHER DEPOSITION TECHNOLOGIES

Aluminum and its alloys can be readily deposited with thermal spray processes, such as flame spray, but these coatings are usually very thick—typically 76 to 127 microns (0.003'' to 0.005'')—and exhibit high roughness and porosity in the as-deposited state. The process also imparts a high degree of heat to the substrate. The latter issue can be partly alleviated by utilizing "cold spray" processes; however, the former issues restrict the use of this technology for electrical connectors.

As mentioned previously, the use of ionic liquids (salt mixtures that melt below room temperature) as an electrolyte to plate aluminum is currently under investigation. This technology is a relatively new development, and while some information is available[5,10], the ability to adapt this process to coat electrical connector shells in mass quantities has yet to be determined.

VIABLE ALTERNATIVES TO HEX CHROME TOPCOATS

The most promising alternatives to standard CCCs at this time are TCPs. Specific applicability for electrical connectors, when used in conjunction with the AlumiPlate® process, has been promising.[5,12,13] Further work is necessary to fully qualify TCPs as a replacement for CCCs.

NCPs are also becoming available, but these have been far less studied in this application. NAVAIR is currently continuing studies on the effectiveness of their NCPs, and AlumiPlate® offers a proprietary non-chromated topcoat over its coating system. An NDCEE Task is currently being conducted with the objective of evaluating NCPs for TARDEC.

SUMMARY

The most promising candidate coating processes to replace cadmium and hexavalent chromium in electrical connector applications are technologies that are already being used on electrical connectors to some extent, or demonstrate both considerable promise for the application and sufficient maturity. These include:

- **Electroplated aluminum (AlumiPlate®)**
- **Electroplated alkaline zinc-nickel (5-15% nickel in the deposit)**
- **Electroplated tin-zinc (at least 20% zinc in the deposit)**

Future efforts will focus on these three most promising candidates. In addition, to support efforts being undertaken by electrical connector manufacturers, two EN-based technologies, both incorporating occluded particles, will also be evaluated. Coatings with both CCCs and TCPs will be considered, as available, and cadmium with CCC will be used as the control.

The most promising candidate coating processes from emerging alternatives were also identified. These are technologies that show promise for electrical connector applications, but require further development for the electrical connectors employed by TARDEC. These include:

- **Alloys deposited from ionic liquids**
- **Magnetron sputtered aluminum alloys**
- **Tin-indium alloys**

Future efforts may consider these candidates as the technology matures and becomes more feasible for electrical connectors.

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BARREL PLATING

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Barrel plating typically involves a rotating vessel that tumbles a contained, bulk workload. The barrel is immersed, sequentially, in a series of chemical process tanks, including plating baths, while tumbling the workload. Utilizing interior cathode electrical contacts to polarize the workload, metals are attracted out of solution onto the individual workpieces. Effectively, the workload becomes part of the plating equipment during processing because the individual pieces function as bipolar electrical contacts to the other pieces in the workload. This bipolar contact is a significant contributor to the high efficiencies of barrel plating because the entire surface of the workload, in the current path at any time, is in cathode contact.

USES OF BARREL PLATING

Barrel plating is used most often for bulk finishing. It is the most efficient method for finishing bulk parts and any pieces that do not require individual handling. According to a Metal Finishing Industry Market Survey published a few years ago, there are approximately 6,750 plating facilities in the U.S. Of these, 37% exclusively provide barrel-plating services, and an additional 32% provide both barrel and rack plating; therefore, approximately 69% of all plating facilities employ the advantages of barrel plating in providing their services.

Plated finishes generally provide the following three functions (singly or in combination) for the plated article, or workpiece: (1) corrosion protection, (2) decoration/appearance, and (3) engineering finishes (for wear surfaces or dimensional tolerances). Barrel plating is used most often for corrosion protection of the workpiece. Because of the surface contact of the workpieces with each other inherent in the tumbling action during processing, barrels are not often used to produce decorative or engineering finishes.

Advantages

Along with the high efficiency already mentioned, in any event, the advantages of barrel plating are many and interrelated:

1. The relatively large cathode contact area yields faster, larger volume production, in the presence of ample current, when compared with rack-type plating.
2. A barrel-plating system occupies less floor space and requires a lower investment for equipment than a rack- or other-type plating line of similar capacity.
3. Barrel plating is labor efficient because it is not necessary to handle, rack, load, or unload individual workpieces.
4. The work usually remains in the same vessel for other operations, including: cleaning, electro-cleaning, rinsing, pickling, chromating and/or sealing. A more recent innovation in barrel plating/processing equipment is drying of the work while it remains in the barrel. This elimination of some

handling and some work transfer enhances the overall efficiency of the finishing operations.

5. Barrel plating is very versatile because of the variety of parts that can be processed in the same equipment. It is the predominant method for finishing fasteners, metal stampings, and similar bulk work. It has been said that "if a part can fit through the door of a barrel, it can be barrel plated." This is, of course, an oversimplification. Most often, the part configuration, end use, and finish type help determine the applicability of barrel plating.

6. Conversely to barrel operations, rack plating often requires special part carriers, or fixturing, and other purpose-built equipment. This can include special contacts, such as formed anodes, based on the individual part type and shape. Barrel plating does not usually require these items, although there are special-purpose contacts available for barrel plating when needed.

7. Barrel rotation causes the workload to tumble in a cascading action. This, in addition to the bipolar electrical activity from individually contacting parts, usually produces a more uniform plated finish than rack plating.

8. Agitation of the tank solutions by barrel rotation inherently eliminates stratification and produces homogeneous baths. Additional agitation equipment is usually not required, although certain tanks and operations are equipped with spargers (air agitation manifolds) when needed.

Origins

Barrel-plating methods originated in the post-Civil War era, with equipment readily adapted from available wooden barrels, kegs, or baskets. Equipment was constructed of wood because it was probably the most economical and available material that was not a conductor of electricity.

Subsequent advances in the knowledge of chemistry, electricity, and material sciences enabled the evolution of barrel-type metal-finishing equipment for bulk finishing. This evolution culminated in the third or fourth decade of the 20th century with now-familiar basic designs.

Today, the submerged portions of barrel-plating equipment are constructed, as much as possible, of nonconductive, chemically-inert materials that can be utilized in various acid and alkaline solutions. Great advances in plating-barrel performance, capability, and longevity were possible largely as the result of plastic materials newly available after World War II. Prior to that time, plating barrels were known to be constructed of more primitive plastic or phenolic materials and wood.

EQUIPMENT TYPES

Available barrel equipment varies widely but generally conforms to two major configurations: (1) horizontal barrels and (2) oblique barrels. Horizontal units are the most common, being adaptable to a greater variety and capacity of work (see Fig. 1).

Horizontal barrels also vary by size and are grouped into three major categories: (1) production barrels, (2) portable barrels, and (3) miniature barrels.

Production barrels, the largest units, usually have a capacity in the range of 1.5 to 17 cubic feet. They handle the majority range of the work.

Portable barrel units are so named because of their generally smaller size (capacities range from 0.1 to 1.5 cubic feet) and their ability to be transferred from

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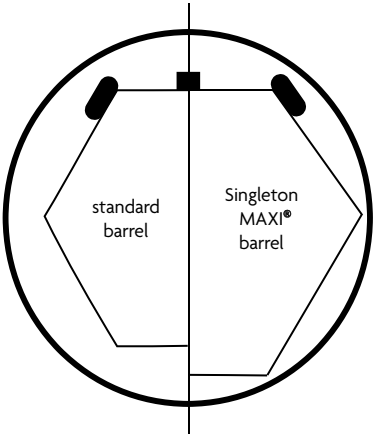
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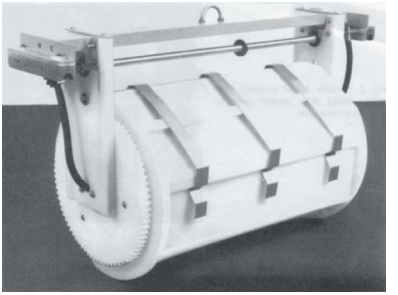


Fig. 1. Typical horizontal barrel and superstructure assembly showing inverted V-type contacts.

one operation to the next, sometimes manually, without the aid of an overhead hoist. Portable barrel units are used for plating smaller parts, smaller lots, delicate parts, and "precious-metals" work (see Fig. 2).

Miniature, or mini-barrel, units are used for many of the same reasons as portable barrels. Mini-barrels range in capacity from 6 to 48 cubic inches. Mini-barrels are used to process the smallest and most fragile loads and work. Also, miniature barrels are often used for lab work such as product or process development (see Fig. 3).

Whereas rotation about a horizontal or inclined axis is common to different types and styles of barrel-plating equipment, there are many diverse construction features and components available that enhance capabilities and improve versatility. Examples of these barrel features are as follows:

1. Cylinders with maximized load volumes (see Fig. 1.) within the dimensional clearance limits of associated equipment
2. Special-diameter and/or special-length barrel assemblies for use in nonstandardized installations such as rack tanks
3. High-capacity electrical contacts (allowing plating operations with individual barrel assemblies handling as much as 1,400 A per station)
4. Automatic operation of the barrels for handling, loading, and unloading to reduce labor requirements (see Fig. 4)
5. "In-the-barrel" drying equipment to dry the work while it remains in the barrel, which reduces, or eliminates, some parts transfer and handling operations
6. "Up-rotation" apparatus to minimize contamination and carryover ("drag-out") of solution to adjacent process tank stations
7. Special apparatus to spray/rinse work while it remains inside the barrel to reduce water usage and ensuing treatment costs.

The previous examples are representative. There are other barrel and system enhancements that increase production and reduce cycle times, drag-out, and maintenance requirements. Optional equipment types are many, including the examples of barrel assemblies spe-

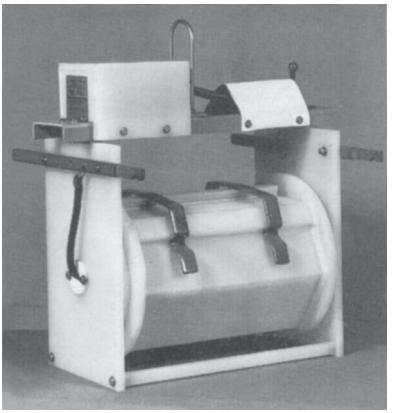


Fig. 2. Portable barrel assembly with self-contained drive, dangler contacts, and clamp-style door.

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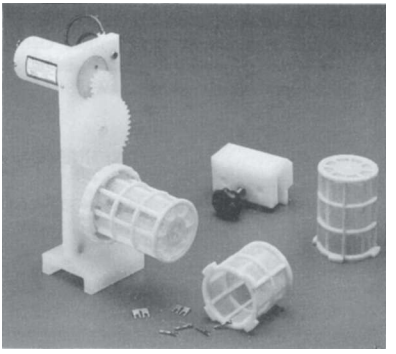


Fig. 3. Ministyle barrel assembly with self-contained drive and integral-mesh, molded baskets.

cially manufactured to operate in existing rack-plating installations shown in Figs. 5 and 6.

Another type of production barrel is the horizontal oscillating barrel. These often utilize barrels that are open on top and have no doors or clamps. The technique is to limit barrel motion to a back-and-forth (usually less than 180° of arc) rocking action about the horizontal axis, rather than 360° full rotation. The motion is more gentle for very delicate parts and can be a plus when treating parts that tend to nest, tangle, or "bridge" badly inside the barrel. Because agitation and tumbling are not as vigorous as full rotation, the operator/plater must take care to avoid possible non-uniform plating (particularly for parts that tend to nest). Processing is generally limited to smaller loads with these type barrels to avoid spillage and part loss because of the continuously open door.

Oscillating barrels are not utilized as much as they were in the past. This is because operators/platers can use variable-speed drives to produce slower rotational speeds on full-rotation barrels to obtain equivalent results. Many older oscillating barrel installations have been converted to full-rotation operation.

The second major barrel equipment style is the oblique barrel. It can be pictured as an open-top basket that rotates around an axis tilted to a maximum 45° from the vertical. Work capacity diminishes beyond a 45°-axis tilt.

The major feature of oblique barrels is the elimination of doors or other closure devices. Because the top is open, unloading consists of raising the barrel about a pivot at the top of its rotational axis shaft to a position that dumps the workload. Similar to 180° horizontal oscillating barrels, this results in relatively small workloads and reduced tumbling action. Today, operators/platers can take advantage of fully automatic doors on full-rotation horizontal barrels to achieve the same advantage with greater ease and higher production.



Fig. 4. Fully automatic load/unload system with integral door barrel assembly for hands-off operation.

FINISH TYPES

All common types of plating are done in barrels, including zinc (alkaline and acid in various chemical systems), cadmium, tin, copper, "precious-metals" (such as silver and gold), and nickel (both electrolytic and electroless).

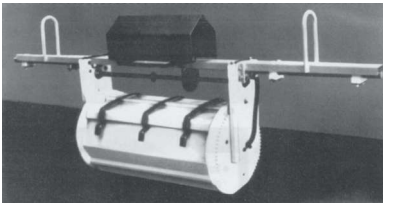


Fig. 5. Barrel assembly equipped for use in a rack plating line.

Barrels are used to plate chrome where ample current and continuous-contact are available (when gentle abrasion of the part surface is not a problem). One can infer from the previous example that a barrel's value and versatility depend on its capability to (1) plate a particular finish and (2) function properly in system solutions and temperatures. This capability is determined by the materials, construction, and detail features incorporated into the barrel unit.

Some barrel equipment lines have the capability to produce more than one plated metal or finish type; however, most plating lines are dedicated to one finish type. Elimination of "drag-out" in a plating line that produces more than one finish type is a primary concern. Drag-out, or cross-contamination, of the different plated metals in stations used for: rinsing, sealing, chromating and cleaning can be minimized by incorporating an "up-rotation" sequence in the barrel operation. Up-rotation is discussed in the section "Hoist Systems, Tanks, and Ancillary Equipment."

WORKLOAD

The barrel plater needs to evaluate each of the following items to decide if the desired finish on a particular part can be barrel plated: finish function (relative to use of the part), part configuration, part size, part weight, calculated part surface area, and total workload volume and square foot surface area.

The workload capacity is usually 40 to 60% of the total interior barrel volume. The maximum workload volume is usually determined based on total square foot surface area of the load and the capacity of the bath chemistry and electrical equipment to plate. Other factors are the weight of the individual workpieces and their propensity to damage the finish or serviceability of other parts in the load. Damage of this type is usually the result of the weight, configuration, or edge characteristics of the parts as they tumble against each other in the barrel.

As designated in the section about the uses of barrel plating, plated-finish functions are of three basic types: corrosion protection to increase the useful service life beyond performance of the un-plated base material; decoration for appearance, which also enhances the value of the base material; and engineering applications to attain (add material) or maintain a dimensional requirement and/or as a bearing surface.

There are requirements for plated finishes that need to perform more than one of the previously mentioned three basic functions. Barrel plating is most commonly used to finish parts for corrosion protection. Decorative finishes are successfully barrel plated when surface effects from part contact are controlled to an acceptable level. Engineering finishes are not usually applied by barrel plating.

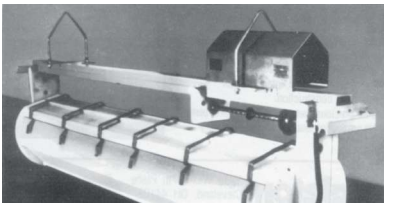


Fig. 6. Special-length barrel assembly for plating elongated parts or for use in a rack plating line.

Configuration of the workpieces affects the ability of work to be suc-

cessfully barrel plated. Generally, parts that weigh less than 1 lb each and are each less than 25 cubic inches in volume can be barrel plated successfully. A simple shape is obviously easiest to barrel plate. Barrel plating is usually the most successful, cost-effective way to plate threaded parts and fasteners properly. The tumbling action of the barrel makes and breaks the electrical contact throughout the workload, yielding the most even coverage on the root, mean diameter, and crest of the threads.

Part material must not be adversely affected by any baths required in the total plating-process cycle. A trial load is a useful tool for evaluating which type of barrel equipment and technique can be utilized for plating a particular part.

Long workpieces and entangling parts, such as rods, bars, or tubes, can be successfully barrel plated. Methods used to plate these parts include long barrels; longitudinal and radial compartments; rocking motion; and various, special stationary contacts (see Fig. 4). Special extra-length barrels allow long parts to fit, whereas compartmented barrels confine movement of long parts and entangling parts, helping to eliminate bridging or entanglement. Limited barrel oscillation or rocking motion (usually 180° of rotation or less) accomplishes the same task by minimizing part movement. To do this, a reversing switch, or contactor, along with an adjustable control timer can be installed on the barrel drive to rotate the cylinder alternately in each direction.

The barrel interior can be equipped with stationary cathode contacts to plate small, delicate, or nesting parts (for example, small electronic components with projecting fingers). Stationary contacts rotate with the cylinder so that there is little relative movement between the workpieces and the contacts. As a result, the work cascades over or around the stationary contacts, and less abrasion or edge contact takes place, minimizing the potential for damage to the work (see Fig. 7). Disk, center-bar, cup, strip, button, hairpin, and chain are some types of stationary contact. Certain types of stationary contacts, such as strip contacts, assist tumbling of the work.

Parts that are flat or lightweight should be plated in barrels with uneven interior surfaces that are not flat and smooth. A convoluted or uneven barrel interior surface, such as grooved, ribbed, or dimpled, promotes tumbling and eliminates much of the sticking of flat workpieces.

When finishing recessed or cupped parts, other smaller parts, which are to be plated to the same specification, may be mixed in with the load to provide contact into recessed areas; however, the cost of the time spent to separate the smaller parts from the others after plating/processing must be acceptable.

BARREL EQUIPMENT DESIGN

All designs of barrel equipment, including horizontal and oblique, should include features to optimize productivity. Reduction of labor requirements and improved ease-of-maintenance are important factors for well-designed components and systems. Some of these important features are discussed in the following sections.

Barrel Construction

Barrels should be made of materials that are chemically and physically inert to use in each bath or piece of equipment in the plating line. It is important that the barrels be capable of operation in excess of maximum bath temperatures in the entire system.

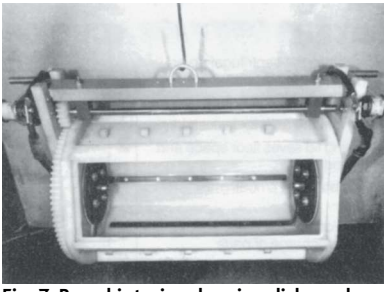


Fig. 7. Barrel interior showing disk- and strip-type contacts.

A plating barrel may expand and contract as much as 3/8 in. in total length due to the different bath temperatures in a plating line. Changes in temperature cause stresses that can "work" a barrel to pieces. This is particularly critical for barrels constructed of materials with different coefficients of expansion. The effects of the temperature changes can be minimized with good design and quality construction. When barrels are fabricated of a single type of plastic and joined by a plastic weld or fusion process, stress points are eliminated. Barrels made this way can expand and contract at a uniform rate, which greatly extends their useful service life. The use of metal fasteners for barrel assembly is a less desirable method because it results in stress points and the possibility of loosening. Minimizing the effects of temperature changes promotes barrel integrity and long service life. The capability of a barrel to be used in higher temperature baths can, as an added benefit, aid faster plating.

Good equipment design will reduce maintenance and replacement part costs. Costs are reduced significantly when it is possible to replace individual wear parts and components. Wear parts that are manufactured as an integral piece of a larger component to reduce manufacturing costs should be avoided. Examples are: (1) trunnion hub-bearing surfaces molded integrally as a component of hanger-arm supports and (2) cylinder "ring", or "bull", gears that are also the barrel head. These perform the same as other equivalent parts when new, but when the wear part needs to be replaced, the larger piece, of which the wear part is a component, must be replaced. This can sometimes require the replacement of the entire plating barrel and can be very costly for the user.

Detail Features

For the majority of plating, flat-sided barrels are best. Flat-sided barrels produce "pumping-action" as a benefit of rotation. Pumping action is the inherent agitation of the bath caused by rotation of the flat-sided barrel. Round barrels do not produce pumping action as efficiently. Pumping action helps constantly replace metal-depleted solution from inside the barrel with fresh solution from the rest of



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the bath. It also helps maintain a uniform, homogeneous solution throughout the process tanks.

Flat-sided barrels tumble parts more effectively. This tumbling is optimized when the flat interior surfaces of the barrel are not smooth. They can be ribbed, grooved, or dimpled. The various types of uneven surfaces also minimize sticking of parts to the panel surfaces, as mentioned previously. Additional tumbling ribs, cross bars, or load breakers of various types are usually needed only for round-plating barrels. They can be added to flat-sided barrels for specific applications. Most oblique-type barrels incorporate uneven, stepped bottoms to attempt to produce these same effects.

Perforations

The type of work being processed in a barrel must be considered when specifying the perforation shapes and sizes. Barrels are available with round, slotted, tapered, and mesh perforations. Job shops generally use barrels with smaller perforations to accommodate the widest range of potential workpiece sizes. Captive shops often have the luxury of using barrels with larger holes because they can more easily predict their minimum part size. Larger perforations usually exhibit faster drainage, more efficient exchange of metal-depleted solution, and less drag-out (carry-over) contamination of adjacent tank solutions. This is because larger perforations minimize the negative effects of liquid surface tension.

Many shops maintain extra barrel assemblies that have the smallest perforation sizes that will be needed. In this way, the line can be operated the majority of the time using larger-hole barrels. The smaller-hole barrels are used only when necessary.

It is very important that all barrels used in a single production line have the same open-area ratio, regardless of perforation size. The open area ratio is defined as the total number of holes in a barrel panel multiplied by the individual open area of each hole and divided by the total area that contains the included perforations.

Open Area Ratio = (Number of Holes x Open Area of Each Hole)/(Total Area of Included Perforations)

For example, if you count 133 holes, 3/32″ in diameter (0.0069 square inch open area for each hole), in a 4 square inch perforated area, the calculation would be as follows:

$$\text{Open Area} = 133 \times 0.0069/4 = 0.23 \text{ or } 23\%$$

Interestingly, there is a convenient geometric relationship between hole-size, center-distance from hole-to-hole, and open area. When the distance between centers, of given diameter holes, is twice the diameter of the holes (in a staggered-center pattern that has six holes equi-distant all the way around), the open area ratio is 23%. Consequently, 1/8″ diameter holes on 1/4″ centers, 3/16″ diameter holes on 3/8″ centers, and 1/16″ diameter holes on 1/8″ centers and 1/4″ diameter holes on 1/2″ centers are all 23% open area ratio patterns. Experience indicates the 23% open area ratio optimizes barrel strength relative to plating performance.

Because the open area of any barrel determines the access of the plating current to the work, the plating performance is directly related to the percentage of open area; therefore, barrels with the same open-area ratio can be used in the same plating line regardless of hole size. Because the access of the plating current to the work will be the same, there is no need to adjust rectifier settings or current density. It

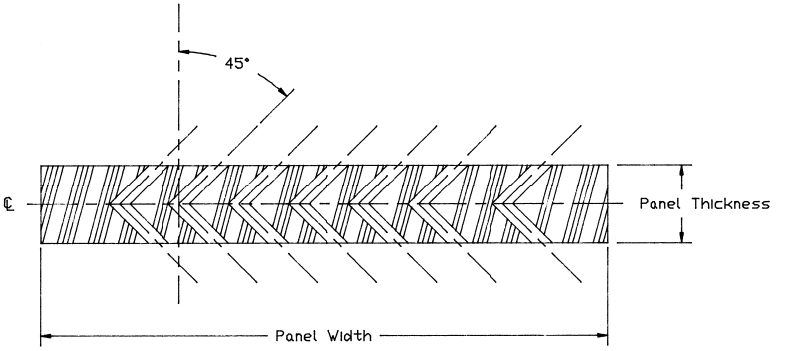


Fig. 8. Cross-section of herringbone-style perforations to keep small-diameter, straight parts inside barrel.

is very apparent from this that for operational convenience and optimization of operations most barrels utilized should be manufactured with a 23% open area.

As mentioned above, there are other types of barrel perforations available to the plater. These include herringbone, screen, fine mesh, and slots. To produce herringbone perforations, the barrel panels are drilled halfway through each panel at a 45° angle relative to the inside and outside panel faces (see Fig. 8). In this way, the holes intersect at the middle of the panel in a 90° angle. Small-diameter, straight workpieces, such as nails, pins, etc., cannot pass through the perforations because the holes are not straight. Plating solution and current can pass through the perforations, although at a reduced rate.

Barrels with fine-mesh panels with very small openings are generally made of polypropylene and are used to plate very small or delicate work. Larger workpieces will tear, gouge, or wear through the mesh in an unusually short period of time.

Some barrels are manufactured with thinner panels in perforated areas to aid drainage. Consideration must be made that this may come at the expense of barrel integrity and service life.

Cathode Electrical Contacts

The type of interior cathode electrical contacts in a barrel significantly determines the variety of work the barrel can process. Flexible-cable dangler-type contacts are the most common in barrel plating (see Fig. 9). Dangler contacts are dynamic relative to the workload because the workload rotates with the barrel and tumbles over the danglers. The danglers remain fixed to the barrel support assembly as this occurs. Other types of dynamic cathode contacts are "hairpin" and chain. These are uncoated metal, usually steel, contacts that extend into the workload to enhance cathode contact for specialized workpiece types.

The best barrel plating results are achieved when the end contact surface, or "knob", of the danglers remain "submerged" in the workload as a result of optimum equipment design. This configuration causes danglers to maximize electrical contact and minimize, or eliminate: arcing, sparking, or burning of the work that could otherwise result from inconsistent/intermittent contact which is "making" and "breaking" contact. The contact knob end of each dangler should touch the bottom of the barrel one-fourth to one-third of the inside barrel length from each barrel end. To determine proper dangler length, measure the total distance

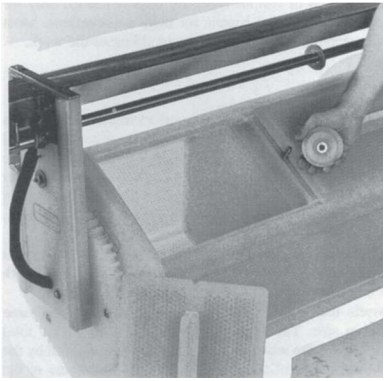


Fig. 9. Knob-style, two-section door with center bar and partition.

from the point that the dangler contact knob should touch the inside bottom of the barrel, continuing through the barrel hub (trunion) to the outside mounting point of the danglers. For short barrels or stiff dangler cable, the danglers can be extended beyond the midpoint of the barrel to provide contact at the opposite end of the barrel to insure that they remain submerged in the load.

Special dangler contact knobs have been developed to help maximize performance when a standard configuration is not totally adequate. Custom knobs that are heavier can be specified to help ensure they remain submerged in the workload. Also, special knobs with larger contact surface area are available where improved conductivity is important.

Special dangler contacts can be ordered with the knobs made of stainless steel, titanium, or other materials. This is important when the mild steel knobs of standard danglers would be negatively affected by the type of plating chemistry used. Be aware that the alternate materials will probably exhibit lower conductivity.

Other stationary cathode contact types, such as disk, cone, center-bar, strip, and button contacts, will usually do a better job of plating rods, long parts, and delicate parts. These types of cathode contacts are referred to as stationary because they are affixed to the barrel itself and rotate with the load. They are, therefore, stationary relative to the load. Stationary contacts are less abrasive to the work and generally exhibit fewer problems with entanglement. A plate-style contact is usually utilized in oblique-style barrel equipment.

Barrel Doors

There are several available styles and fastening methods for plating-barrel doors. Clamp-style doors have predominated over the years. This is because they are both quick and easy to operate. Knob-style doors are also greatly utilized (see Fig. 10). The threaded components of knob doors must be designed for efficient operation and durability to extend useful service life to minimize replacement. Divided doors can be furnished for ease of handling because they are smaller, being one half of the total barrel length each. Divided doors are used with partitioned barrels that have a transverse divider in the middle of the barrel for compartmentalization when necessary to plate/process different types of parts in the same barrel at the same time.

There is, as in all things, diversity in barrel equipment and door operations. Most shops use and prefer clamp-style doors. Clamps are efficient because of quick installation and removal. Others operate successfully with knob-style doors. Many shops use more than one style barrel and door retainers.

Because barrel-door security for part retention and efficient mounting, fastening, and opening of barrel doors is critical to operation of the entire line, much attention is given to this area. Some other door designs secure the workload within capturing edges of the door opening, rather than from the outside. With this type of design, the door carries the weight of the workload on the capturing edges,



Fig. 10. Dangler-style interior barrel cathode contacts.

rather than the retaining clamps or knobs. This type of design is good for very small parts or workpieces that cumulatively pry and wedge into crevices.

Other modern innovations to automate operation of plating barrel doors are sometimes utilized to eliminate manual labor for opening, loading, and closing. In equipment systems of this type the barrel door usually remains an integral functional component of the barrel assembly rather than a separate item to be manually manipulated. In addition to the inherent labor savings, the safety of the overall finishing operation is increased because significant labor interaction with the equipment is eliminated. Automatic barrel operation translates into system automation, which can greatly enhance efficiency and eliminate costs. Other additional automated aspects of barrels, hoist systems, and related material handling equipment can be configured in which the equipment automatically sizes and weighs workloads, loads the barrels, closes the barrels for processing, opens the barrels, and unloads the finished work to conveying equipment for further processing or drying (see Fig. 4). This is the ultimate evolution of a barrel-finishing system.

Detail Components

There are important equipment features that substantially affect plating system performance and serviceability. It is very important to consider these items and their benefits when selecting barrel-plating equipment.

Horizontal barrel assemblies equipped with an idler gear will result in fully submerged operation of the barrel, ensuring maximum current and solution access to the work. Fully submerged barrel plating also minimizes any potential for problems with accumulated or trapped hydrogen.

Barrel rotation causes a cascading action of the workload inside the barrel. Because of this, the center of gravity of the workload is shifted to one side of the barrel assembly. Tank-driven, horizontal barrel assemblies equipped with an idler gear offset the center of gravity of the cascading workload to the proper side to best resist the tendency of the rotating tank drive gear to lift the barrel contacts from the tank contact points; therefore, use of an idler gear on the barrel assembly helps maintain, and optimizes, good electrical contact between the barrel assembly contacts and the cathode contact saddles of the tank. Conversely, a barrel assembly without an idler gear promotes poor electrical contact because the center of gravity of the workload is shifted to the opposite side and works against maintaining good, positive, constant contact.

Another positive feature is hanger arms made of non-conducting materials such as plastic. Non-conducting hanger arms eliminate “treeing”, stray currents, and possible loss of plating-current efficiency. (Treeing is the accumulation of deposited metal on the plating barrel or any components of the barrel assembly because of stray currents.)

Design simplicity and efficiency of barrel equipment are important for ease of maintenance, particularly for components operating below the solution level. The use of alloy fasteners that are nonreactive to the chemical system in use is especially important for acid-based plating systems such as chloride zinc.

HOIST SYSTEMS, TANKS, AND ANCILLARY EQUIPMENT

It is important to the performance capabilities of a barrel hoist and tank system to review the following items and include the advantageous features where possible.

Most barrel-plating tanks are designed to maintain the solution level approximately 5 in. below the top rim of each tank. At this level, the plating barrels should run fully submerged, eliminating the potential for excess hydrogen accumulation. Operating with a solution level higher than 5 in. below the top rim of a tank can cause the solution to be splashed out during barrel entry or exit, resulting in wasted solution, treatment issues, and, possibly, environmental problems.

Solution loss and adjacent tank drag-out contamination can also be minimized by equipping the barrel hoist system with "up-barrel rotation". A drive mechanism on the hoist rotates the barrel and load in the overhead, above-tank position, facilitating better drainage before moving to the next process station. This is especially helpful when finishing cupped, or complex-shaped, parts.

Locating the plating-tank anodes (including anode baskets or holders) in the closest proximity to the barrel exteriors, without allowing mechanical interference, ensures greatest current densities for the workload. Anodes that are contour curved to just clear the outside rotational diameter of the barrels can result in 10 to 20% increase in current density.

For horizontal barrels, vertical adjustment capability of tank-mounted barrel drives should optimize engagement of the gears. Drives that are adjusted too high will carry the weight of the loaded barrel assembly on the drive gear, resulting in excessive stress on the gear, drive shaft, and bearings. This causes premature wear and failure of these components. Reducer oil leakage is also a potential resulting problem. In addition, when the weight of the barrel unit is concentrated on the drive gear and drive shaft rather than on the plating or electro-clean tank saddles, proper contact is not possible. If the drive gear carries the barrel assembly, the contacts are most often lifted out of position.

When a tank drive unit is adjusted too low, poor drive-gear engagement results. Sometimes the driven barrel gear hops across the tank drive gear and the unit does not turn. This situation not only results in premature gear wear because of abrasion but also in poor plating because of poor electrical contact.

It is best to alternate tank drive rotation in a barrel plating line in each subsequent/following process station. The advantage of having approximately an equal number of drives rotating the barrels in the opposite direction is to ensure even wear on all drive components (bearings, gears, etc.) and greatly extending service life. Alternate rotation of drives certainly minimizes replacement requirements and downtime.

The teeth of the steel gears on barrel assemblies and tank drives should be greased to enhance service life and fully engaged performance. Displaced grease will not negatively affect the tank baths because the gears are normally located beyond and below the tank end wall.

Barrel drives, whether tank or barrel mounted, can have provision to change barrel rotation speed. This is to allow for change of workload type or plating finish. For example, a lower rotation speed is often better for very delicate or heavy parts to minimize abrasion. A faster rotation speed may be used to produce a more uniform plated finish or more readily break up loads of nesting or sticking parts. Allowing for change of barrel rotation speed maximizes the capability to produce the greatest variety of finishes on a larger variety of parts.

Certain tank drives provide for speed change by using multiple-sheave belt pul-

leys on the output shaft of the drive motor and the input shaft of the speed reducer. Moving the belt onto other steps in the pulley yields a different speed for each step. Many present-day systems use directly coupled C-flange motors bolted directly to the reducer. The speed-change adjustment capability for these is achieved electrically through the control panel by using adjustable drive controls.

For a long time, it was thought that process tanks with more than three to five stations should be avoided. This is because smaller duplicate tanks, doing the same process, will allow the plating line to continue in operation if a bath needs to be replaced or one of the tanks requires maintenance. Separate tanks for the same process can be plumbed to each other for uniformity of the baths. Each tank can be isolated with valves, when necessary, for maintenance. Experience has shown, however, that many platers prefer to use single-unit, multi-station tanks because the bath is more homogeneous and the temperature more uniform. They schedule maintenance at downtimes and have been able to make emergency repairs in a short time, when necessary, in order not to interrupt production.

NEW DEVELOPMENTS

There have been some notable developments in barrel plating systems in recent years. As the industry moves toward increasing efficiencies and decreasing waste, rinsing and drying are receiving attention as operations that can be modified, or automated, to provide savings. "In-the-barrel" drying eliminates labor needed for transfer of the work from the barrel to the dryer basket, and the loading and unloading of the dryer. When equipment is provided to dry the work in the barrel, workflow is more efficient. The plater must, however, consider the type of workpieces because some do not lend themselves well to in-the-barrel drying. Adequate airflow through the load may not be possible for some types of work. This is particularly true for workpieces that tend to nest together, reducing air circulation. Also, some parts and finish types can be negatively affected when they are tumbled in the dry condition.

Benefits from minimizing water usage and wastewater-treatment costs have caused equipment suppliers to develop equipment to use less water during the plating process. Some are trying to do this by reducing the amount of drag-out or carryover contamination between solution tanks in a plating line. Barrel manufacturers have approached this problem with a number of different solutions; however, most focus on the same basic property of barrel design, the perforations. Different hole geometries, mesh screen, thin-wall construction, and greater percentage of open area are all available today on just about any size plating barrel. While some of these designs may demonstrate a noticeable reduction of drag-out, it can come at the expense of reduced workload capacity and equipment service life.

Another development is to connect separate rinse tanks from different parts of the line together, in sequence of descending water quality, to optimize the use of the water before it is sent through the filtration and treatment process. In other words, the water is taken advantage of for more turns and less water is added to the rinse tanks, in total. Of course, not all rinse tanks can be handled together this way because cross-contamination could negatively affect some steps in the finishing process. For where it is practicable, the water savings can be significant. For example, acid rinse baths can be further utilized for the cleaning rinses, as the next step after the cleaning stations is normally the acid dipping or pickling. Also, the acid rinses can have a neutralizing effect on the cleaning rinses.

Another approach to minimizing water usage is the application of spray rins-

ing equipment rather than an immersion rinse. Water manifolds with spray nozzles directed on the outside of the barrel wash the barrel and contained workload. Sometimes the barrel is rotated, tumbling the work, while being sprayed. It is expected that water usage is reduced. This method is not effective for all types of work, an example being cupped parts or convoluted workpieces. A variation on this is to actually spray or rinse down the entire plating assembly. This not only rinses the workload but prolongs the service life of the equipment by rinsing away any solution that may attack the barrel assembly support superstructure and components. Another type of spray rinsing equipment incorporates an interior manifold in the barrel and water connection equipment on the outside of the barrel to spray directly onto the work inside the barrel for rinsing. Again, water conservation is the goal for which this equipment has been designed.

RATE OF PRODUCTION

Reasonable production may be maintained with total workload surface area ranging between 60 and 100 ft^2 per single barrel. Amperage settings can vary substantially with the type of plating. Most production barrel platers operate in the 15 to 40 Amps/ft^2 range. Nickel plating can vary to 50 Amps/ft^2. Take note that actual current density is higher because only the exposed surface of the workload in the direct path of the current at any time is plating. The exposed surface is much less than the total calculated surface of the entire load. All surfaces eventually receive the same relative exposure due to the tumbling action in barrel plating.

Barrel tanks generally draw higher currents than still (rack) tanks of the same capacity; therefore, it is important to equip barrel tanks with greater anode area, usually in a 2 to 1 ratio to the total surface area of the workload. Barrel anodes corrode faster than rack-type plating anodes; however, the production is much greater than for a rack-type line.

There are references located elsewhere in the *Metal Finishing Guidebook* that permit estimating the time required to deposit a given thickness for many types of plating. There is also information for selecting proper current densities and total cycle times.

RECORDS

Proper operation of a barrel-plating line requires the maintenance of records for each part and plating specification done in the shop. The data is generally entered in a computer database or on file cards and used to construct graphs and/or tables for thickness, time, area, and current relationships. Using the graphs or tables, a plater can make reasonably accurate initial judgments for processing new or unfamiliar work. Suggested items to record for each job include material, part surface areas, part weight, finish type, thickness required, current, and voltage used, as well as load size and plating time.

SUMMARY

Barrel plating has distinct advantages: the ability to finish a larger variety of work and producing a greater volume of work for a specified time period over what is generally possible from a rack-type finishing line. By incorporating as many aspects of the previously mentioned information as possible, the capacity and capability of a barrel finishing production line can be optimized.

SELECTIVE PLATING PROCESSES (BRUSH PLATING, ANODIZING, AND ELECTROPOLISHING)

SIFCO APPLIED SURFACE CONCEPTS, INDEPENDENCE, OH

WHAT IS SELECTIVE PLATING?

The term "Selective Plating" includes three different processes

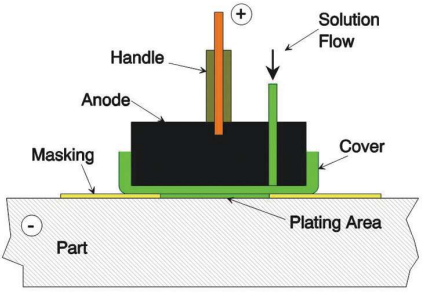
- **Selective (Brush) Electroplating**
- **Selective Anodizing**
- **Selective Electropolishing and Weld Cleanup**

These processes differ from traditional tank finishing processes because the plating, anodizing, or electropolishing is done out of tank, focusing the operation onto a localized area of a part. Additionally, the processes are portable. They can be carried out in the shop or in the field. Selective plating is a very flexible process. Operations can be carried out manually, they can be mechanized, or they can be automated.

HOW IT WORKS

The plating tools, typically graphite, are wrapped with an absorbent material that both holds and distributes the solutions uniformly over the work area. Solution is supplied to the work area by either dipping the tool into a container, or by pumping the it through the tool and recirculating. The plating tool is then moved over the work area. In the selective plating process there must be movement between the plating tool and the part – move the tool over the part, move the part and hold the tool stationary, or move both the tool and the part.

A portable power pack (rectifier) provides a source of direct current for all the processes. The power pack has at least two leads. One lead is connected to the tool and the other is connected to the part being finished. Direct current supplied by the power pack is used in a circuit that is completed when the tool is touching the work surface. The tool is always kept in motion whenever it is in contact with the work surface. Movement is required to ensure a quality finish.



Preparation of the area to be processed is accomplished through a series of electrochemical operations. These preparatory steps are performed with the same equipment and tool types that are used for the final finishing operation. Good preparation of the work area is as important as movement of the tools to produce an adherent, quality deposit or coating.

DEVELOPMENT

Selective plating systems evolved from traditional tank plating processes. Some of the equipment and terms used in these portable processes still resemble their counterparts in tank processes. However, tools, equipment and solutions cannot be used interchangeably between portable and tank systems.

Since it is more difficult to control temperature and current density in portable plating processes than in tank processes, there is a need for complete, integrated portable systems for commercial applications. These systems have been developed so they can be used by operators who are not familiar with tank finishing techniques.

Today, selective plating systems are available for electroplating, anodizing, and electropolishing. They are used to provide deposits and coatings for corrosion protection, hardness, wear resistance, conductivity, lubricity, anti-galling, salvage, and decorative applications. These systems vary in degree of sophistication and capability and are available worldwide.

Small pencil-type systems apply only flash deposits on small areas. Sophisticated systems use power packs with outputs up to 500 A and are capable of producing excellent quality finishes over a wide range of thicknesses and characteristics on large surface areas.

INDUSTRY ACCEPTANCE

Selective plating processes have gained widespread acceptance, with well over 100 commercial specifications now written. Specifications have been prepared by companies in the key industries that include aerospace, oil & gas, power generation, automotive, marine, military, railroad, pulp & paper, and many others.

The following specifications are representative of the current acceptance of selective plating processes:

MIL-STD 865	Selective (Brush Plating) Electrodeposition
MIL-STD 2197(SH)	Brush Electroplating On Marine Machinery
AMS 2451	Plating, Brush, General Requirements
	/1 General Purpose Nickel
	/2a Low Stress Hard Nickel
	/3a Low Stress Low Hardness Nickel
	/4 Cadmium LHE
	/5a Chromium Hard Deposit
	/6a Copper
	/7a Low Stress Medium Hard Nickel
	/8a Non-Cyanide Silver
	/9a Zinc-Nickel LHE
	/10a Tin-Zinc LHE
	/11a Cobalt
	/12 Tin
	/13 Silver

EQUIPMENT AND MATERIALS

Selective plating equipment includes power packs, preparatory and plating solutions, plating tools, anode covers and auxiliary equipment. The proper selection of each item is important in achieving optimum finishing results.



POWER PACKS:

Power packs, also known as rectifiers, change alternating current into the direct current that is used for the plating operation. Power packs are durable and portable. These attributes are necessary because the power packs are routinely transported to the work site. This may be from plant to plant or to various locations within the same plant. Power packs specifically designed for selective plating have several features that set them apart from rectifiers used in tank finishing operations.

Typical Features on a Selective Plating Power Pack:

- **Voltmeter**
- **Ammeter**
- **Ampere-Hour Meter**
- **Pole Changer**
- **Audible Reverse Current Alarm**
- **Overload Protection**
- **Twistlock Connections for Output Leads**
- **Constant Current and Constant Voltage Operation**



Power packs have forward-reverse current switches. These switches allow the direction of direct current flow (polarity) to be changed quickly. This is necessary because the combination of preparatory steps and a final finishing step usually requires several rapid changes in the direction of current flow.

These power packs incorporate several safety devices such as fast acting circuit breakers which minimize damage, in case the anode, handle or lead accidentally come in contact with the work surface, causing a short circuit and arcing.

A voltmeter displays the voltage setting for each step in a finishing procedure. An ammeter displays the amperage for each step as it is being carried out. This allows the operator to make adjustments to the current density during the preparatory or plating operation. A precision ampere-hour meter provides data to accurately control the thickness of an electroplated deposit or anodized coating.

SOLUTIONS:

Selective Plating solutions can be divided into three groups according to their use. Refer to Table I, which lists commonly used solutions.

The first group contains solutions that are used to prepare various types of base materials for finishing. As the name suggests, preparatory solutions are used to prepare the surface so that the final step, whether it is brush plating, anodizing or electropolishing, will produce a quality end product. A quality end product will

have a finish which is evenly colored and distributed on the work surface, and in the case of brush plating will have good adhesion and cohesion.

The selective plating process referred to as brush plating has preparatory procedures which have been developed for all of the base materials commonly encountered in industry These include steel, cast iron, stainless steel, aluminum, copper-base alloys and nickel-base alloys, and titanium. When recommended procedures are followed, the strength of the bond between the brush plated deposit and the base material is equivalent to the weaker of the cohesive strength of the deposit or the base material itself. Typically, the bond strength of a brush plated deposit is > 11,000 psi.

Preparation of a base material usually begins with mechanical and/or chemical precleaning. This is followed by electrocleaning and then etching. Depending on the base material, a desmutting, activating and/or preplating step may be required. For instance, the procedure for brush plating a copper deposit on to 400 series stainless steel requires all of the steps previously mentioned .

Brush plating solutions are quite different from tank plating solutions. Brush plating solutions have a higher metal content, are less likely to utilize a toxic material such as cyanide, are more likely to use metal-organic salts rather than metal-inorganic salts and are more likely to be complexed and/or buffered with special chemicals than are tank plating solutions.

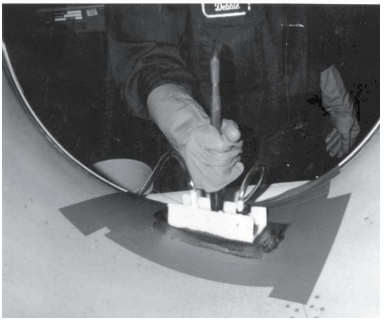
Solutions used for brush plating must produce a good quality deposit over a wider range of current densities and temperatures than tank plating solutions. They must plate rapidly, operate with insoluble anodes, and produce a good deposit under variable conditions for a prolonged period of time. In addition, the solutions should be as nontoxic as possible, and they should not require chemical control by the operator. Formulations that are different from those used in tank plating obviously are required to achieve these objectives.

The third group of solutions have been developed to meet the specific application requirements of portable processes such as selective anodizing, specialized black optical coatings, and electropolishing.

SELECTIVE ANODIZING:

Anodizing is a widely used electrochemical surface treatment process for aluminum and its alloys. Depending on the particular type of anodizing process used, the resulting anodic coatings provide improved wear resistance, corrosion protection, and/or improved adhesive properties for subsequent painting or adhesive repair.

Selective anodizing is used when limited, selective areas of large or complex aluminum assemblies need anodizing to either restore a previously anodized surface or to meet a specification requirement. The SIFCO Process of selective anodizing is a versatile tool which can be used for many different, demanding OEM and repair applications. This portable process can be used both in the shop and in the field.



Anodizing is the formation of an oxide film or coating on an aluminum surface using reverse current (part is positive) and a suitable electrolyte.

Principal types of anodized coatings are chromic, sulfuric, hard coat, phosphoric and boric-sulfuric. The SIFCO Process of selective electroplating has been expanded to provide a portable method of selectively applying these anodized coatings for a variety of localized-area applications.

The five types of anodizing film differ markedly in the electrolytes used, the typical thickness of the coating formed, and in the purpose of the coating. Also, the five types of anodized coatings are formed under distinctively different operating conditions.

The electrolytes used for selective anodizing are available in water based solutions, or may be in the form of anodizing gels. Solutions are available for all five types of anodizing and gels are available for chromic acid, phosphoric acid and boric-sulfuric acid anodizing. The operating conditions for the gels are the same as for their respective solutions, and they apply coatings of the same quality.

The gel is used when anodizing near critical components that may be damaged by splashed or running anodizing solutions. The gel stays over the work area and does not stray into inappropriate places such as aircraft instrumentation, equipment and crevices where corrosion would start. The gels produce coatings comparable to solution electrolytes and have the advantage of staying on the selected work surface. The gels are ideally suited for work in confined areas where it would be difficult to clean up.

In military and commercial applications, anodized coatings are usually applied for dimensional reasons (salvage), corrosion protection and/or wear resistance purposes. Selective anodizing meets the performance requirements of MIL-A-8625 for type I, II and III anodized coatings. In the consumer marketplace, anodizing is often utilized for cosmetic appearance reasons.

SELECTIVE PLATING TOOLS:

Tools used in Selective Plating processes are known as plating tools, stylus or styli. They are used to prepare, as well as brush plate, anodize and electropolish work surfaces. The tools consist of the following elements: a handle with electrical input connectors, an anode, an anode cover, and in some cases, a means of solution flow. Additionally, the tool must have a high current carrying capability and must not contaminate the solution.

Only insoluble anodes are used in selective plating. The reason for this is simple. Products of the anodic reaction would build up on a soluble anode when subjected to the high current densities necessary for selective plating applications. The reaction products would be contained by the anode cover resulting in a decrease in current to unacceptable levels. For this reason, soluble anodes are not used.



Graphite and platinum are excellent materials for selective plating anodes. The purer grades of graphite are economical, thermally and electrically conductive, noncontaminating, easily machined and resistant to electrochemical attack.

Platinum anodes, although more expensive, are used in some cases. These anodes may be made from pure platinum or from either niobium or columbium

clad with platinum. The use of platinum anodes is generally reserved for brush plating applications that are long term, repetitive or that require thick brush plated deposits.

Platinum anodes are also an excellent choice when brush plating bores as small as one-sixteenth of an inch diameter. Graphite anodes this small in diameter are brittle and are easily broken.

Since selective plating occurs only where the tool touches the part, it is best to select a tool that covers the largest practical surface area of the part. Selecting the correct tool also ensures uniformity of the finish.

Manufacturers offer a wide selection of standard selective plating tools. These tools are available in a variety of sizes and shapes to accommodate different surface shapes. However, special tools are frequently made to accommodate special shapes or large areas. Proper design of these tools is critical to successful finishing operations.

An equally important aspect of selective plating processes is the selection of an anode cover. Anode covers perform several important functions. They form an insulated barrier between the anode and the part being finished. This prevents a short circuit, which might damage the work surface. Absorbent anode covers also hold and uniformly distribute a supply of finishing solution across the work surface. The solution held in the anode covers provides a path for the direct current supplied by the power pack. This is required for all selective plating processes. Anode covers also mechanically scrub the surface being finished.

All anode cover materials sold by manufacturers are screened for possible contaminants. Many materials, that seem similar, contain binders, stiffening agents and lubricants that will contaminate finishing solutions. Testing has shown that these contaminants have a significant impact on finish quality and adhesion of deposited materials. Anode covers suitable for selective plating should be obtained from solution manufacturers to avoid contamination.

AUXILIARY EQUIPMENT:

When a finishing operation is required on a large work surface or a deposit is applied in a high thickness, best results are obtained by continuously recirculating the finishing solution with a simple pump or a flow system. This method will reduce the time required for the finishing process by eliminating lost time from dipping the anode and by supplying fresh solution to cool the work surface so that higher current densities can be used.

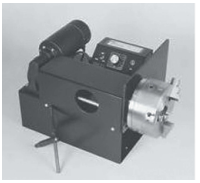
Submersible and peristaltic pumps are used when operating in the 1 to 100 A range, and when the finishing solution does not have to be preheated. Flow systems, which include specially fabricated tanks ranging in size from 1 to 10 gallons and heavy duty magnetic drive pumps and a filter, are used when operating in the 100 to 500 A range, and when the solution has to be preheated.

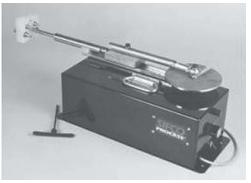




The most sophisticated flow systems are used with nickel sulfamate brush plating solutions because they require preheating and constant filtering. These units have reservoirs of several sizes,

pumps designed for high temperature operation, provision for filtering and the capability of changing filters while plating. In addition, they include a heater and heater control that preheats and maintains the solution at the proper temperature. Flow systems also can be equipped with cooling units for anodizing and high current brush plating operations.





Turning equipment is frequently used to speed up and simplify finishing operations. Specially designed turning heads are used for small parts, i.e. a diameter less than approximately 6″, a length less than 2 ft, and a weight less than 50 lb. Lathes are often used to rotate large parts while brush plating inside or outside diameters.

When a part cannot be rotated, special equipment can be used to rotate anodes. For bores up to 1 1/2″ in diameter, small rotary units are used. These units have a variable speed motor, flexible cable and a special handle with rotating anode and stationary hand-held housing. For bores in the 1″ to 6″ diameter range, larger rotary units are required. These units are similar to the smaller ones but include heavy duty components, and they have provisions for pumping solution through the anode.

The largest turning units are used for bore sizes in the 4″ to 36″ diameter range. These units have two opposing solution-fed anodes which are rotated by a variable speed motor. The anodes are mounted on leaf springs which apply the correct amount of pressure and also compensate for cover wear. These devices are used at up to 150 A. They are not hand-held, but mounted on a supporting table instead.

Traversing Arms are used to supply either a mechanical oscillation or a back and forth "traversing" motion for an otherwise manual selective plating operation.

ADVANTAGES AND DISADVANTAGES

Selective plating processes are used approximately 50% of the time because they offer a superior alternative to tank finishing processes and 50% of the time because they are, in general, better repair methods for worn, mismachined or damaged parts.

For example, the decision to use brush plating rather than tank plating, welding or metal spraying, depends on the specific application. There are distinct advantages and disadvantages that should be considered.

Some advantages of brush plating over other repair methods are:

- **The equipment is compact and portable. It can be taken to the work site so that large or complicated equipment does not have to be disassembled or moved.**
- **No special surface preparation such as knurling, grit blasting or undercutting is required. The only requirement is that the surface be reasonably clean. Often solvent cleaning or sanding the work surface is sufficient.**
- **Brush plating does not significantly heat the part or work surface. Only occasionally is the part heated to approximately 130°F, and**

never does the temperature of the part exceed 212°F. Hence, distortion of the part does not occur.

- **The process can be used on most metals and alloys. Excellent adhesion is obtained on all of the commonly used metals including steel, cast iron, aluminum, copper, nickel & nickel alloys, stainless steels,zinc, chromium and titanium.**
- **Thickness of the plated deposit can be closely controlled. Frequently, mismachined parts can be plated to size without remachining.**
- **Parts having a wide variety of sizes and shapes can be easily brush plated.**

Some disadvantages of brush plating compared to other repair processes are:

- **Brush plated deposits are applied at a rate that is at least 10 times faster than tank plating. However the rate of deposition is considered to be moderate when compared to welding or metal spraying. A fair comparison is not complete unless consideration is given to the quality of a brush plated deposit and the fact that brush plating often eliminates the need for pre or post machining and grinding, which is required with other repair processes. Because parts often can be plated to size, brush plating provides a finished product in a shorter period of time.**
- **In practice, the hardest deposit that can be applied in a high thickness with the brush plating process is 54 Rc. This is not as hard as the hardest deposits produced by some other processes. However, the other processes do not offer the range of hardnesses or deposit types that can be applied with the brush plating process.**
- **Brush plating is usually a superior approach to plating a selected area on a complex part. However, it usually is not suitable for plating an entire part that has a complex shape, such as a coffee pot.**

QUALITY OF BRUSH PLATED DEPOSITS

Brush plated deposits meet the performance requirements of their tank plated counterparts. Manufacturers of brush plating products are continuously improving their solutions and well as developing new solutions, procedures, and equipment to meet today's demanding applications. Some examples include the development of a Chromium Carbide Metal Matrix Composite Coating for high temperature oxidation protection and special process for preparing titanium alloys to receive adherent brush plated deposits for OEM or salvage applications.

The manufacturers of brush plating equipment generally offer a number of plating solutions for each of the more important metals. One reason for this is to offer a choice in properties. For example, one user may want a hard, wear resistant nickel while another wants an impact resistant, ductile coating. Since the ductility of metals, whether wrought, cast or plated, generally decreases with increasing hard-

ness, it is impossible to meet both requirements with a single solution.

Brush plating manufacturers are keeping up with the movement toward green solutions, offering alternatives to cadmium, such as zinc-nickel and tin-zinc. Additionally they are offering trivalent chromium conversion coatings for zinc-nickel, and anodized coatings.

ADHESION:

The adhesion of brush electroplates is excellent and comparable to that of good tank plating on a wide variety of materials including steel, cast iron, stainless steel, copper, high temperature nickel-base materials, etc. When plating on these materials, the adhesion requirements of federal and military specifications are easily met. Limited, but occasionally useful, adhesion is obtained on metals that are difficult to plate such as tungsten, and tantalum. There is now a process available for achieving very good adhesion on common titanium alloys.

Most adhesion evaluations have been made using destructive qualitative tests such as chisel or bend tests. These tests indicate that the adhesion and cohesion of brush plated deposits is about the same as the cohesive strength of the base material.

Quantitative tests have been run using ASTM Test Procedure C-653-79 "Standard Test Method for Adhesion or Cohesive Strength of Flame Sprayed Coating." As an example four samples were plated using a nickel neutral solution. The cement used to bond the nickel plated sample to the testing apparatus failed during the test. Since the adhesive had a bond strength rated at approximately 11,300 psi, it was shown that the bond strength of the plated deposit to the substrate is at least 11,300 psi. Even brush plated deposits with a fair adhesive rating survived this test and, therefore, have an adhesive bond and cohesive strength of at least 11,300 psi. Therefore, brush plated bonds are stronger than the bonds found with flame sprayed coatings.

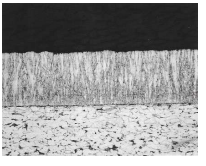
METALLOGRAPHIC STRUCTURE:

The metallographic structure of an electroplate can be examined in an etched or unetched condition. In the unetched condition, most brush plated deposits are metallurgically dense and free of defects. Some of the harder deposits, such as chromium, cobalt-tungsten, and the hardest nickel, are microcracked much like hard tank chromium. A few deposits are deliberately microporous, such as some of the cadmium and zinc deposits. Microporosity does not affect the corrosion protection of these deposits, since they are intended to be sacrificial coatings. The microporous structure offers an advantage over a dense deposit because it permits hydrogen to be released out naturally at ambient temperatures or in a baking operation. Etched brush plated deposits show grain structures that vary, but parallel those of tank deposits. However, brush plated deposits tend to be more fine grained. Coarse grained, columnar structures, such as those found in Watts nickel tank deposits, have not been seen in brush plated deposits.

HARDNESS:

The hardness of brush plated deposits lies within the broad range of the hardnesses obtained with tank deposits. Brush plated cobalt and gold, however, are harder than tank plated deposits. Brush plated





chromium is softer, since tank plated chromium is generally in the 750 to 1100 D.P.H. range.

CORROSION PROTECTION:

Brush plated cadmium, lead, nickel, tin, zinc, and zinc-nickel deposits on steel have been salt spray tested per ASTM B-117. When the results were compared with AMS and military specification requirements, the brush plated deposits met or exceeded the requirements for tank electroplates.

ELECTRICAL CONTACT RESISTANCE:

Brush electroplates are often used to ensure good electrical contact between mating components on printed circuit boards, bus bars and circuit breakers. A low contact resistance is the desired characteristic in these applications.

HYDROGEN EMBRITTLEMENT:

Cadmium and zinc-nickel plating solutions have been specifically developed for plating or touching up high-strength steel parts without the need for a post-plate hydrogen embrittlement relief bake. Additional testing has shown that brush plated Nickel High Speed likewise shows favorable HE performance.

Hydrogen embrittlement testing over the past 20 years has become progressively more stringent. A no-bake, alkaline, brush plating cadmium deposit has passed an aircraft manufacturer's test, which is perhaps the toughest imaginable. The test consisted of the following steps:

1. Prepare six notched tensile samples from SAE 4340, heat-treated to 260-280 Ksi with 0.010″ radius notch.
2. Plate samples with 0.5 to 0.7 mil cadmium
3. Load the bars to 75% of ultimate notched tensile strength.
4. Maintain the load for 200 hours.

The evidence acquired to date suggests that brush plating offers low levels of hydrogen contamination of base metals.

A REPRESENTATIVE JOB

To illustrate how brush plating is performed, consider, as an example, building up a 6″ diameter by 2″ long bore in a housing which is oversized 0.002″ on the radius.

The part is too large to be mechanically turned so the operation will be done manually. The part is set up in a position that will be convenient for the operator and permit solutions and rinse to be controlled during processing.

The area to be plated is precleaned to remove visible films of oil, grease, dirt and rust. Adjacent areas are solvent cleaned to assure that masking will stick. Areas next to the bore are masked for about two inches.

The base material is identified and the supplier's manual is examined to determine the preparatory procedure. If the base material is cast iron, for example, three steps are involved: electroclean, etch and desmut.

Several nickel and copper plating solutions are suitable for this application. If an alkaline copper solution is selected, a nickel preplate or "strike" is required to ensure adequate adhesion; therefore, a five-step preparatory and plating proce-

dure is required.

Tools of suitable size and shape are selected for each step. Tools that cover about 10% of the total area are appropriate for preparing the base material. The plating tools should contact more surface area so plating will proceed faster; consequently, the tool used for plating is selected more carefully. It is larger than the preparatory tools, and it covers the full length of the bore. The anode portions of the tools are covered with appropriate covers.

Once the tools are selected, suitable amounts of solutions are poured into containers. There is enough plating solution to soak the anode covers and to complete the plating operation without stopping.

The power pack is then connected as follows: the negative (black) lead to the part (cathode) and the positive (red) lead to the tool (anode).

Prior to starting the job, the operator completes the calculation of a set of formulas that will help assure the job is carried out properly. Some of the commonly used symbols and definitions used in these formulas are listed in Table V. The formulas used and sample calculations for this job are shown below.

1. Calculate the area to be plated (A)
   A = 3.14 x diameter x length
   A = 3.14 x 6 x 2
   A = 37.7 in sq.

2. Calculate the ampere-hours required.
   Amp-hr = F x A x T
   Amp-hr = 150 x 37.7 x 0.002
   Amp-hr = 11.31

3. Calculate the estimated plating current (EPA)
   EPA = CA x ACD
   EPA = 6 x 5
   EPA = 30 A

4. Calculate the plating time required (EPT).
   EPT = [Amp-hr x 60] / EPA
   EPT = [11.31 x 60] / 30/
   EPT = 22.6 minutes

5. Calculate the rotation speed (RPM).
   RPM = [FPM x 3.82] / diameter
   RPM = [50 x 3.82] / 6
   RPM = 31.8 revolutions per minute

6. Calculate volume of plating solution required (V).
   V = Amp-hr / MRU
   V = 11.31 / 44.5
   V = 0.255 liters

Finally, the operator prepares a process chart that includes this information.

Table I Solutions Group I Preparatory Solutions
Electrocleaning
Etching
Desmutting
Activating

Group II Plating Solutions for Ferrous and Non-Ferrous Metals	
Cadmium (acid)	Nickel (dense)
Cadmium (alkaline)	Nickel (alkaline)
Cadmium (No Bake) and (LHE)	Nickel (acid strike)
Chromium (dense trivalent)	Nickel (neutral for heavy build-up)
Cobalt (for heavy build-up)	Nickel (ductile, for corrosion protection)
Copper (acid)	Nickel (sulfamate, soft, low stress)
Copper (alkaline)	Nickel (sulfamate, moderate hardness)
Copper (neutral)	Nickel (sulfamate, hard, low stress)
Copper (high-speed acid)	Tin (alkaline)
Copper (high-speed alkaline for heavy build-up)	Zinc (alkaline)
Iron	Zinc (neutral)
	Zinc (bright)

Group II Brush Plating Solutions For Precious Metals	
Gold (alkaline)	Palladium
Gold (neutral)	Platinum
Gold (acid)	Rhenium
Gold (non cyanide)	Rhodium
Gold (gel)	Silver (soft)
Indium	Silver (hard)
	Silver (non-cyanide)

Group II Plating Solutions For Alloys *Metal Matrix Deposit	
Brass	Nickel-Tungsten
Babbitt Navy Grade 2	Tin-Antimony
Bronze	Tin-Zinc
*Cobalt Chromium Carbide	Tin-Indium
Cobalt-Tungsten	Tin-Lead-Nickel
Nickel-Cobalt	Zinc-Nickel (LHE)
Nickel Phosphorous	

Group III Special Purpose Solutions and Gels*	
Anodizing (chromic*)	Trivalent Chromium Conversion
Anodizing (sulfuric)	Electropolishing
Anodizing (hard coat)	Cadmium Alternatives
Anodizing (phosphoric*)	Black Optical
Anodizing (boric-sulfuric*)	

The chart contains all of the information (solutions and sequence of use, voltages, polarities, estimated plating amperage, ampere-hours, times, etc.) necessary to perform the process operations properly and without hesitation.

CONCLUSION

While the process known as selective, brush plating was emphasized in this article, other portable processes such as selective anodizing and selective electropolishing are widely used in industry as well. Selective plating is a viable alternative to tank plating and to other processes such as thermal sprays when deposit thicknesses of less than 0.035″ are required. It is a process that lets you apply a wide range of localized deposits and coatings either in the shop or out in the field with very accurate thickness control. Selective plating is a flexible and reliable process for OEM and repair applications.

MECHANICAL PLATING AND GALVANIZING

BY ARNOLD SATOW
ATOTECH USA INC., ROCK HILL, S.C.; www.atotech.com

The manufacturers of metal products recognize the need to keep fasteners from corroding. Mechanical plating is a method for coating ferrous metals, copper alloys, lead, stainless steel, and certain types of castings. The process applies a malleable, metallic, corrosion-resistant coating of zinc, cadmium, tin, lead, copper, silver, and combinations of metals such as zinc-aluminum, zinc-tin, zinc-nickel, tin-cadmium, and others. These combination coatings are often referred to as codeposits, layered deposits, or alloy mechanical plating. The mechanical plating process has been used internationally for over 50 years and is referred to by a variety of names including peen plating, impact plating, and mechanical galvanizing. Mechanical plating and galvanizing can often solve engineering, economic, and pollution-related plating issues. It offers a straightforward alternative method for achieving desired mechanical and galvanic properties with an extremely low risk of hydrogen embrittlement. In some cases, it offers a potential cost advantage over other types of metal-finishing processes.

Mechanical coatings can be characterized to some extent by the relative thickness of deposit.[1] "Commercial" or standard plating is usually considered to be in a thickness range between 5 and 12.5 μm; however, coatings up to 25 μm are often utilized. The heavier deposits are often referred to as mechanical galvanizing and sometimes utilize the coating weight designation (g/m^2) found in the hot-dip galvanizing industry. Typical coating thicknesses range from 25 to 65 μm (179 to 458 g/m^2) but can go as high as 110 μm (775 g/m^2).

The mechanical plating process is accomplished at room temperature, without an electrical charge passing through the plating solution that is necessary with electroplating. The metallic coating is produced by tumbling the parts in a mixture of water, glass beads, metallic dust or powder, and proprietary plating chemistry. The glass beads provide impacting energy, which serves to hammer or "cold-weld" the metallic particles against the surface of the parts. They perform a number of functions including assisting cleaning through a mildly abrasive scrubbing action; facilitating mixing and dispersion of the chemicals and metal powders; impacting and consolidating the metallic coating; protecting and separating parts from one another; preventing edge damage and tangling; and helping impact the plating metal into corners, recesses, and blind areas.

The glass beads or "impact media" are chemically inert and nontoxic, with high wear resistance. They are constantly recycled through the system and reused to ensure their cost effectiveness. The glass impact beads are considered the "driving force" in the mechanical plating and galvanizing process. The diameters of the most commonly used glass beads are 5 mm (0.187 in.), 1.5 mm (0.056 in.), 0.7 mm (0.028 in.), and 0.25 mm (0.010 in.). The ratio of glass bead mixture to parts in a particular load is about 1.5:1 by weight. The plating result is a tight, adherent metallic deposit formed by the building of fine, powdered metal particles to the surfaces of parts.

Special advantages of the mechanical plating process are that it greatly reduces the part susceptibility to hydrogen embrittlement; consumes comparatively low

amounts of energy; can be used to deposit a wide variety of metals in a broad range of coating thicknesses; does not use toxic chemicals; simplifies waste treatment; does not require baking of parts after plating in most cases; and provides greater uniformity and control of coatings when used for galvanizing.

HYDROGEN EMBRITTLEMENT AND MECHANICAL PLATING

A significant concern in electroplating and other metal-finishing processes is the embrittling effects of hydrogen absorbed by the part. The critical need to prevent hydrogen embrittlement was one of the major reasons for the creation and successful use of mechanical plating. The electric current used in electroplating, for example, acts to increase the potential of this condition because the process generates hydrogen at the cathode and because the negative charge acts to pull hydrogen into the part. Hydrogen embrittlement can cause unexpected development of cracks or weak regions in highly stressed areas, with subsequent total failure of the part or assembly. The risk increases for items that have elevated hardness from heat treating or cold working, especially parts made of high-carbon steels.

In electroplating and other metal-finishing operations, a major source of hydrogen gas is the reaction between acids and metals present in the plating solution. The hydrogen transfers through the metal part substrate and concentrates at high stress points and grain boundaries. The trapped hydrogen generates internal pressures that can reduce the tolerance to stresses applied in actual use. Hazardous failures in critical applications can result.

The mechanical process plates metals while eliminating or at least greatly reducing the embrittlement risk caused by the plating process itself. There is a hydrogen-producing reaction that occurs in mechanical plating, but this reaction happens mostly on the surface of the powdered zinc (or other plating metal) particles, which are approximately 5 to 10 μm in diameter. The reaction proceeds at a very slow rate and within a microscopically more porous, less oriented grain structure deposit than produced by electroplating. It is for this reason that the hydrogen gas is not likely to be trapped within or under the metal particles in the coating. The escape of the hydrogen through the deposit and away from the part substrate is more likely than absorption into the base metal.

PROCESS DESCRIPTION

The mechanical plating process requires a sequence of chemical additions added to the rotating tumbling/plating barrel. The

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amount of each depends completely on the total surface area of the parts to be plated and, therefore, it is important to calculate this number prior to each cycle. The variable-speed plating barrels rotate at a surface speed of 43 to 75 m/min (140-250 ft/min), depending on part type and at a tilt angle of about 30° from horizontal. Except for precleaning heavy oils or scale, all of the steps are performed in the same tumbling barrel, normally without rinsing or stopping the rotation. A typical process cycle includes a series of surface preparation chemical additions, designed to mildly acid clean and activate the substrate and then to apply a copper strike. The preparation chemicals normally contain sulfuric acid, surfactants, inhibitors, dispersing agents, and copper in solution. This step results in a clean, galvanically receptive part surface. The next step is the addition of a "promoter" or "accelerator" chemical, which acts as a catalyst as well as an agent that controls the rate of deposition and subsequent uniform bonding of the plating metals. A defoamer is used to control foaming caused by the surfactant additives, so loss of plating solution is avoided and operator visual monitoring is maintained.



Fig. 1. Specially lined variable-speed tumbling/plating barrel.

A series of plating metal (usually zinc) additions added as a powder or water slurry is introduced in a number of equal additions totaling an amount proportional to the plating thickness desired. Table I represents a typical sequence.

The process is conducted at room temperature between 15 and 32°C (60 and 90°F) and at a pH range of 1 to 2 to ensure proper adhesion and high metal efficiency. The low pH acts to maintain and oxide-free condition at all times on the surface of the parts as well as the plating metal particles. The process has an efficiency of about 93%, meaning that approximately 93% of the plating metal added is actually plated on the parts. The mechanical plating cycle usually takes between 30 and 45 minutes.

At the end of the cycle, the slurry of glass beads, plated parts, and plating water discharges onto a vibrating "surge hopper" and is then directed to the rinsing and glass bead separation section. This section is a water-sprayed vibrating screen area or magnetic belt, which removes the glass beads for recycling and rinses the parts. Separated parts are then dried by a heated centrifuge or a continuous dryer oven with belt or vibratory transport.

Table I. Typical Process Sequence for Mechanical Plating

Process Stop	*Time, min*
Alkaline or acid preclean (if necessary)	5
Rinse	
Surface preparation	5
Copper strike or "flash"	5
Accelerator/promoter	3
Plating metal additions (series of small equal adds)	15-20
Water polish	5

(POUNDS OF TYPICAL PARTS)

The capacity of a plating barrel varies greatly with the shape and size of the parts to be plated. The table below shows approximate barrel capacities for a number of different part types.

BARREL MODEL	CAP SCREWS (BOLTS)				
	1/4"∅ x 1"L	1/2"∅ x 2"L	3/4"∅ x 3"L	1"∅ x 6"L	1-1/4"∅ x 8"L
6 ft³	750	660	600	300	200
10 ft³	1250	1100	1000	500	400
20 ft³	2500	2200	2000	1200	1000
30 ft³	3750	3300	3000	1800	1500
40 ft³	5000	4400	4000	2400	2000
	NUTS				
	3/8"	1/2"	3/4"	1"	1-1/4"
6	750	750	650	650	300
10	1250	1250	1125	1125	700
20	2500	2500	2250	2250	1700
30	3750	3750	3375	3375	2600
40	5000	5000	4500	4500	3400
	FLAT WASHERS				
	3/8"	1/2"	3/4"	1"	1-1/4"
6	675	675	600	600	500
10	1125	1125	1000	1000	900
20	2250	2250	2000	2000	1800
30	3375	3375	3000	3000	2700
40	4500	4500	4000	4000	3600
	NAILS				
	1-1/4" roof. 0.120"∅ x 1-1/4"L	6d □omm.. 0.120"∅ x 2"L	10d □omm.. 0.148"∅ x 3"L	16d □omm.. 0.162"∅ x 3-1/2"L	
6	400	375	300	275	
10	750	625	500	475	
20	1500	1250	1000	950	
30	2250	1875	1500	1425	
40	3000	2500	2000	1900	

On average, a single plating machine system should process 6 to 7 loads in an 8 hour shift. A dual plating machine system should process 12 to 13 loads in an 8 hour shift.

Fig. 2. Barrel loading capacity chart in lb for typical parts.

APPLICABLE PARTS

Various part types for which coating opportunities were limited to electroplating, hot-dip galvanizing, painting, or organic finishing are now successfully being mechanically plated or galvanized. Parts now universally accepted for consideration include regular and self-tapping screws, bolts (including A 325), nuts, washers, and stampings; nails; chain and wire forms of all types; pole line and tower hardware for telecommunications; electrical connectors; and automotive, aircraft, and marine fasteners.

The suitability of parts considered for mechanical plating or galvanizing is determined by its size, shape, and base metal. Part types that would not withstand the tumbling action of the process are usually not suitable. Parts heavier than 1 to 2 kg (2.2-4.4 lb) or longer than about 300 mm (12 in.) are not normally coated in this manner. Parts that have deep recesses or blind holes may make the part unsuitable, because to obtain a satisfactory deposit, solution and glass beads must flow freely and have sufficient impact energy in all areas of the part surface. This must happen without glass beads permanently lodging in

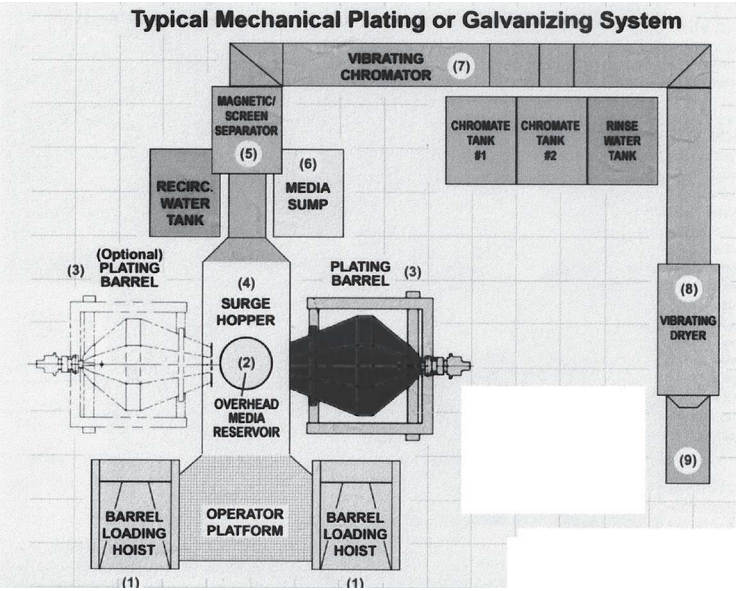


Fig. 3. Typical mechanical plating layout.

holes or recesses.

A variety of substrates are suitable for mechanical plating and galvanizing and include low carbon steel, high carbon heat-treated spring steel, leaded steel, case-hardened and carbonitrided steel, malleable iron, and stainless steel. Powder metallurgy parts can be plated by this process without prior sealing of the surface. Because mechanical plating solutions are usually chemically consumed, little excess is available to get trapped in the pores of the substrate. In addition, the initial copper strike will seal such pores and the metal powder that follows will fill and bridge them. The process can also plate onto brass, copper, lead, and certain other substrates.

EQUIPMENT

Mechanical plating equipment is a specially designed plating and material handling system. The plating takes place in stainless steel variable-speed tumbling barrels (Fig. 1). Because the entire process operates at an acidic pH of 1 to 2, the barrels must be lined with an inert, abrasion-resistant protective coating, such as urethane, neoprene, or polypropylene, to a thickness of 19 to 25 mm (0.75-1 in.).

Typical plating barrels have capacities of 0.04 to 1.13 m3 (1.5-40 ft^3), where capacity is defined as the total available working volume, typically 30 to 35% of the total volume. For example, a 0.57 m^3 (20 ft^3) plating barrel will hold approximately 910 kg (2,000 lb) of 25-mm- (1-in.)-long threaded fasteners and 1,000 kg (2,200 lb) of glass bead mix. See barrel loading capacity chart (Fig. 2).

In Fig. 3, parts to be mechanically plated are brought to the barrel loading hoist (1). Glass media are transferred from an overhead media reservoir tank (2) into the plating barrel (3). The operator's platform and control panels serve as the stag-

Table II. Budgetary Costs for Mechanical Plating Systems

Working Volume	*Cost*
Integrated Single-Barrel System with Centrifugal Dryer	
0.17 m^3 (6 ft^3)	$117,000
0.28 m^3 (10 ft^3)	$133,000
Dual-Plating Machine System with Automatic Chromating/Passivation and Dryer	
0.17 m^3 (6 ft^3)	$231,000
0.28 m^3 (10 ft^3)	$266,000
0.56 m^3 (20 ft^3)	$317,000
0.85 m^3 (30 ft^3)	$367,000
1.13 m^3 (40 ft^3)	$436,000

ing area for operator activities. After plating, the load is discharged onto a vibrating surge hopper (4). At the screen or magnetic separator (5) section, water sprays wash the impact media from the parts and into a lower media sump (6). Media is later recycled to the overhead media reservoir (2) for reuse. The separated parts continue on to an optional automatic vibratory chromating/passivation section (7) and on to a belt, vibratory, or centrifugal dryer (8).

Budgetary costs for typical complete mechanical plating and galvanizing systems are given in Table II.

The range of floor space required for an equipment installation ranges from about 46 m2 (500 ft^2) for the smaller systems to about 112 m^2 (1,200 ft^2). Ceiling minimum height requirement is about 5.5 m (18 ft). A floor pit for the lower media sump is usually required and ranges in depth from about 1 to 1.7 m (3.2-5.5 ft) and a width of about equal size.

AUTOMATION SCREEN

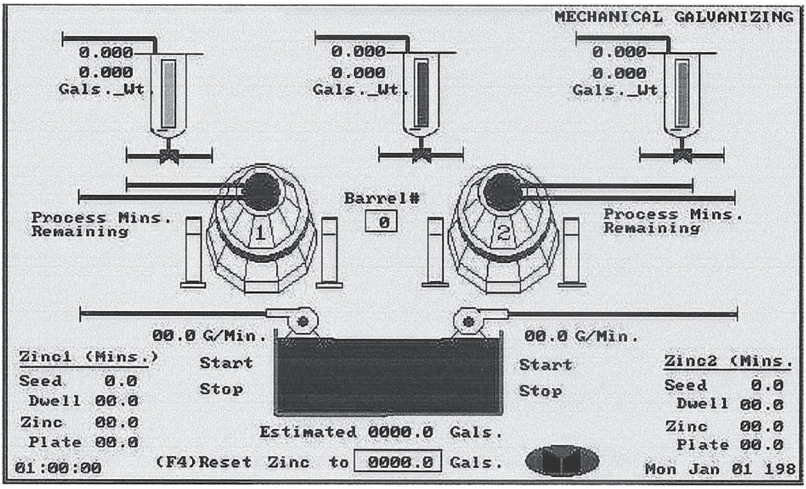


Fig. 4. One of the computer automation display screens showing cycle progress.

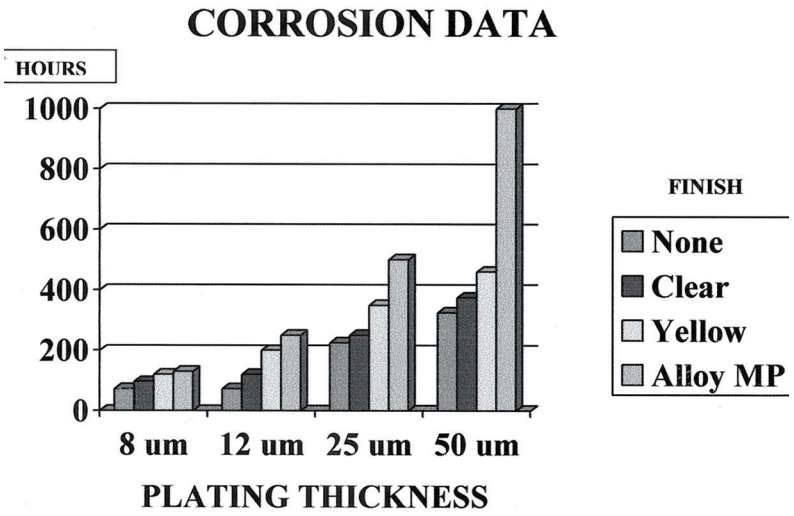


Fig. 5. Corrosion performance for various finishes.

AUTOMATION FOR MECHANICAL PLATING

Push-button or computer-controlled mechanical plating systems are now in use and available in a variety of configurations and options. They are, basically, carefully engineered chemical feed systems designed to calculate, monitor, and control much of the plating operation. It does not do away with the need for an operator at the installation, but it does cut down on the required attention time by about 50% and, therefore, provides increases in productivity.

The operator must input certain data required to establish the process parameters. This information would include the part number or code (from the computer's personalized database), the weight of the parts load, and the coating thickness desired. The system can use bar-coded work order cards, which inputs the information automatically. The computer then calculates the total surface area in the load and then the entire process cycle. A screen display shows the cyle progress (Fig. 4). When started the system signals the pumps, valves, solenoids, load cells, and meters to operate in the exact required sequence. A manual override panel is part of the system, which allows adjustments to be made if needed or to take over in the rare case of computer malfunction. Use of this advanced automated process provides welcomed enhancements to an established manual technology. It provides improved quality and reliability of coatings; increased process speed, productivity, and ease of use; operator safety—reduced liability from chemical handling and exposure; environmental compatibility and minimization of waste products; historical tracking, record keeping, and documentation; and overall cost effectiveness.

In an automated system, all chemicals are in liquid form including the plating metal. The powdered plating metal is transformed into a liquid slurry in a two-part metal slurry mixing system consisting of a mixing module and a delivery module. The mixing module combines a measured amount of water and metal dust under constant agitation and then delivers it to the delivery module for the plat-

ing process. Metering pumps in this module transfer continuously mixed slurry directly to the plating barrels via permanently fixed flexible tubing. Automation system costs vary widely according to the requirements and degree of automatic control. A range approximately between $18,000 and $100,000 will estimate costs associated with most systems from the most simple to highly sophisticated.

POSTTREATMENTS

Posttreatments for mechanical plating are similar to those used in electroplating. The coating is more receptive to postfinishing immediately after plating, before drying. A mild acid dip (1% nitric acid) will reactivate parts that have already been dried. Conversion coatings or passivates, such as clear or blue, yellow, olive drab, or black, can be applied. Special trivalent passivates are now available to meet new industry requirements regarding hexavalent chromium. Mechanically plated parts can also accept proprietary topcoats, paint, and other special postfinishes.

The color, luster, and iridescence of postfinishes on mechanical plating are somewhat different than those obtained on electroplated surfaces but are well within the normal range of acceptable appearance and performance. Corrosion resistance is demonstrated for a variety of finishes and postfinishes (Fig. 5).

With excellent corrosion protection, no hydrogen embrittlement, low energy cost, automation, and consistent coating thickness and uniformity across the wide range of deposits, mechanical plating and galvanizing remains a viable option for today's metal finisher.

REFERENCE

1. Standard Specification for Coatings of Zinc Mechanically Deposited on Iron and Steel, ASTM B 695

ELECTROLESS (AUTOCATALYTIC) PLATING

BY JAMES R. HENRY
WEAR-COTE INTERNATIONAL, ROCK ISLAND, ILL.; www.wear-cote.com

Electroless plating refers to the autocatalytic or chemical reduction of aqueous metal ions plated to a base substrate. The process differs from immersion plating in that deposition of the metal is autocatalytic or continuous.

THE ELECTROLESS BATH

Components of the electroless bath include an aqueous solution of metal ions, reducing agent(s), complexing agent(s), and bath stabilizer(s) operating in a specific metal ion concentration, temperature, and pH range.

Unlike conventional electroplating, no electrical current is required for deposition. The electroless bath provides a deposit that follows all contours of the substrate exactly, without building up at the edges and corners. A sharp edge receives the same thickness of deposit as does a blind hole.

The base substrate being plated must be catalytic in nature. A properly prepared workpiece provides a catalyzed surface and, once introduced into the electroless solution, a uniform deposition begins. Minute amounts of the electroless metal (i.e., nickel, copper, etc.) itself will catalyze the reaction, so the deposition is autocatalytic after the original surfaces are coated. Electroless deposition then continues, provided that the metal ion and reducing agent are replenished. If air or evolved gas, however, are trapped in a blind hole or downward facing cavity, this will prevent electroless deposition in these areas.

In electroless plating, metal ions are reduced to metal by the action of chemical reducing agents, which are simply electron donors. The metal ions are electron acceptors, which react with electron donors. The catalyst is the workpiece or metallic surface, which accelerates the electroless chemical reaction allowing oxidation of the reducing agent. During electroless nickel deposition, byproducts of the reduction, orthophosphite or borate and hydrogen ions, as well as dissolved metals from the substrate, accumulate in the solution. These can affect the performance of the plating bath. As nickel is reduced, orthophosphite ions (HPO_3^{2-}) accumulate in the solution and at some point interfere with the reaction. As the concentration of orthophosphite increases, there is usually a small decrease in the deposition rate and a small increase in the phosphorus content of the deposit. Ultimately, the accumulation of orthophosphite in the plating solution results in the precipitation of nickel phosphite, causing rough deposits and/or spontaneous decomposition.

The metal ion and reducer concentration must be monitored and controlled closely in order to maintain proper ratios, as well as the overall chemical balance of the plating bath. The electroless plating deposition rate is controlled by temperature, pH, and metal ion/reducer concentration. Each of the particular plating reactions has optimum ranges at which the bath should be operated (Table I). A complexing agent(s), also known as a chelator, acts as a buffer to help con-

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Table I. Typical Plating Bath Components and Operating Parameters

Electroless Bath	*Temperature*	*pH*	*Deposition Rate/hr*	*Metal Salt(s)*	*Reducing Agent(s)*	*Complexing Agent(s) or Chelators*	*Stabilizer(s)*	*pH Adjustment*
Acid nickel	77-93°C (170-200°F)	4.4-5.2 (medium P) (high P) 6.0-6.5 (low P)	12.7-25.4 μm (0.5-1 mil)	Nickel sulfate Nickel chloride	Sodium hypophosphite Sodium borohydride Dimethylamine borane (DMAB)	Citric acid Sodium citrate Succinic acid Proprionic acid Glycolic acid Sodium acetate	Fluoride compounds Heavy metal salts Thiourea Thioorganic compounds (i.e., 2-mercaptobenzothiazole, MBT) Oxy anions (i.e., iodates)	Ammonium hydroxide Sulfuric acid
Alkaline nickel	26-95°C (79-205°F)	8.5-14.0	10-12.7 μm (0.4-0.5 mil)	Nickel sulfate Nickel chloride	Sodium borohydride Sodium hypophosphite DMAB Hydrazine	Citric acid Sodium citrate Lactic acid Glycolic acid Sodium acetate Sodium pyrophosphate	Thiourea Heavy metal salts Thioorganic compounds Triethanolamine Thallium salts Selenium salts	Ammonium hydroxide Sulfuric acid Sodium hydroxide
Copper	26-70°C (79-158°F)	9.0-13.0	1.7-5 μm (0.04-0.3 mil)	Copper sulfate Copper acetate Copper carbonate Copper formate Copper nitrate	Formate Formaldehyde DMAB Sodium hypophosphite	Rochelle salt EDTA Ammonium hydroxide Pyridium-3-sulfonic acid Potassium tartrate Quadrol	Thiodiglycolic MBT Thiourea Sodium cyanide Vanadium pentoxide Potassium ferrocyanide	Hydrochloric acid Sulfuric acid Sodium hydroxide Potassium hydroxide
Gold	65-88°C (149-190°F)	10.0-13.0	2-5 μ (0.08-0.2 mil)	Gold cyanide Gold chloride Potassium aurate	DMAB Sodium hypophosphite Potassium borohydride Potassium cyanoborohydride	Sodium phosphate Potassium citrate Sodium borate Potassium tartrate EDTA	Alkali metal cyanide Alkali hydrogen fluoride Acetylacetone	Potassium hydroxide Phosphoric acid Sulfuric acid
Palladium	45-73°C (113-165°F)	8.0-12.0	2-5 μm (0.08-0.2 mil)	Palladium chloride Palladium bromide	Sodium hypophosphite DMAB Triethylamine borane	Ammonia Methylamine EDTA	Thioorganic compounds Organic cyanides Thiourea Thiocyanates	Ammonium hydroxide Hydrochloric acid
Cobalt	85-95°C (185-203°F)	9.0-11.0	2.5-10 μm (0.1-0.4 mil)	Cobalt chloride Cobalt sulfate	DMAB Sodium hypophosphite	Sodium citrate Citric acid Ammonium chloride Succinic acid	Urea Thioorganic compounds	Ammonium hydroxide Sodium hydroxide

Table II. Alkaline Electroless Nickel-

Phosphorus Bath	
Nickel sulfate	30 g/L
Sodium hypophosphite	30 g/L
Sodium pyrophosphate	60 g/L
Triethanolamine	100 ml/L
pH	10.0
Temperature	30-35°C (86-95°F)

trol pH and maintain control over the "free" metal salt ions available to the solution, thus allowing solution stability. The stabilizer(s) acts as a catalytic inhibitor, retarding potential spontaneous decomposition of the electroless bath. Few stabilizers are used in excess of 10 ppm, because an electroless bath has a maximum tolerance to a given stabilizer. The complexing agent(s) and stabilizer(s) determine the composition and brightness of the deposit. Excessive use of stabilization material(s) can result in a depletion of plating rate and bath life including poor metallurgical deposit properties.

Trace impurities and organic contamination (i.e., degreasing solvents, oil residues, mold releases) in the plating bath will affect deposit properties and appearance. Foreign inorganic ions (i.e., heavy metals) can have an equal effect. Improper balance and control will cause deposit roughness, porosity, changes in final color, foreign inclusions, and poor adhesion.

ELECTROLESS NICKEL

The most widely used engineering form of electroless plating is, by far, electroless nickel. Electroless nickel offers unique deposit properties including uniformity of deposit in deep recesses, bores, and blind holes. Most commercial deposition is done with an acid phosphorus bath owing to its unique physical characteristics, including excellent corrosion, wear and abrasion resistance, ductility, lubricity, solderability, electrical properties, and high hardness.

Electroless nickel baths may consist of four types:

1. Alkaline, nickel-phosphorus.
2. Acid, nickel-phosphorus.
   a) 1-4% P (low phosphorus)
   b) 5-9% P (medium phosphorus)
   c) 10-13% P (high phosphorus)
3. Alkaline, nickel-boron.
4. Acid, nickel-boron.

The chemical reducing agent most commonly used is sodium hypophosphite (NaH_2PO_2); others include sodium borohydride ($NaBH_4$), or an aminoborane such as n-dimethylamine borane (DMAB) [$(CH_3)_2NHBH_3$]. Typical reactions for a hypophosphite reduced bath are as follows:

$$H2PO^{2-} + H_2O \quad H^+ + HPO_3^{2-} + 2H \tag{1}$$

$$Ni^{2+} + 2H \quad Ni + 2H^+ \tag{2}$$

$$H_2PO^{2-} + H \quad H_2O + OH^- + P \tag{3}$$

Table III. High-Temperature, Alkaline Electroless Nickel-Phosphorus Bath

Nickel sulfate	33 g/L
Sodium citrate	84 g/L
Ammonium chloride	50 g/L
Sodium hypophosphite	17 g/L
pH	9.5
Temperature	85°C (185°F)

$$H_2PO^{2-} + H2O \quad H^+ + HPO_3^{2-} + H_2 \qquad (4)$$

Alkaline nickel-phosphorus deposits are generally reduced by sodium hypophosphite. These alkaline baths can be formulated at low temperatures for plating on plastics. Deposits provide good solderability for the electronics industry, and operating energy costs are reduced due to some solutions' low operating temperatures; however, less corrosion protection, lower adhesion to steel, and difficulty in processing aluminum due to high pH values are drawbacks. One such bath consists of the components shown in Table II.

An example of a high-temperature, alkaline, electroless nickel-phosphorus bath is given in Table III.

Acid nickel-phosphorus deposits normally consist of 87-94% nickel and 6-13% phosphorus, operating at 77-93°C (171-200°F), with a pH of 4.4-5.2. Low phosphorus electroless nickel baths contain 1-4% phosphorus and normally operate at 80-82°C (176-180°F), with a pH of 6.0-6.5. The reducing agent is commonly sodium hypophosphite.

The resultant deposit melting point is 890°C (1,635°F) for 8-9% phosphorus baths and will vary dependent on the amount of phosphorus alloyed in the deposit. The pH of the solution is the controlling factor affecting the phosphorus content of the deposit. The higher the pH, the lower the phosphorus content, resulting in deposit property changes. Lower phosphorus-containing deposits (i.e., 1-3%) typically have less corrosion resistance than 10% alloys. Low phosphorus deposits do have good corrosion protection against alkaline solutions such as sodium hydroxide. Also, deposits containing phosphorus in excess of 8.0% are typically nonmagnetic. When the pH drops below 4.0, subsequent nickel deposition virtually stops.

As-deposited nickel-phosphorus hardness is 500-600 Vickers hardness number (VHN), and maximum values of 1,000 VHN may be realized by post-heat-treatment of the coating at a temperature of 399°C (750°F) for 1 hour. The temperature is a dominant factor in determining the final deposit hardness. Careful consideration should be given to the choice of temperature in order not to affect

Table IV. Acid Hypophosphite-Reduced Electroless Nickel Bath

Nickel sulfate	28 g/L
Sodium acetate	17 g/L
Sodium hypophosphite	24 g/L
Lead acetate	0.0015 g/L
pH	4.4-4.6
Temperature	82-88°C (180-190°F)

Table V. Sodium Borohydride-Reduced Electroless Nickel Bath

Nickel chloride	31 g/L
Sodium hydroxide	42 g/L
Ethylenediamine, 98%	52 g/L
Sodium borohydride	1.2 g/L
Thallium nitrate	0.022 g/L
pH	>13
Temperature	93-95°C (200-205°F)

structural changes of the base substrate. Additionally, low temperatures are used (116°C/240°F) to relieve any hydrogen embrittlement that may be produced from pretreatment cycles or subsequent electroless nickel deposition.

Postbaking of the deposit produces marked structural changes in hardness and in wear and abrasion resistance. Depending upon the temperature, bath composition, and phosphorus content, this postbake cycle will totally change the initial amorphous structure, resulting in nickel phosphide precipitation creating a very hard matrix. Complete precipitation of nickel phosphides does not occur at temperatures significantly below 399°C (750°F). In general, deposits with 9.0% phosphorus and above tend to produce lower as-deposited hardness values, but give slightly higher hardness when post-heat-treated. The coating will discolor above 250°C (482°F) in an air atmosphere. Prevention of coating discoloration can be accomplished in a vacuum, inert, or reducing atmosphere oven. Physical properties affected by the post-heat-treatment include increasing hardness, magnetism, adhesion, tensile strength, and electrical conductivity while decreasing ductility, electrical resistivity, and corrosion resistance.

Thickness of the nickel-phosphorus deposit generally ranges from 2.5 to 250 μm (0.1-10.0 mil). Deposits less than 2.5 μm and greater than 625 μm are currently and successfully being performed. The latter being typical of repair or salvage applications. Thickness measurements can be carried out with electromagnetic devices (eddy current), micrometers, coulometrics, beta backscatter, and X-ray fluorescence.

Table IV gives an example of an acid hypophosphite-reduced bath.

Alkaline nickel-boron solutions utilize the powerful reducing agent, sodium borohydride, to produce a deposit containing 5-6% boron and 94-95% nickel by weight. These highly alkaline solutions operate at a pH of 12.0-14.0 and temperatures of 90-95°C (195-205°F). These baths tend to be less stable because of their high alkalinity, and bath decomposition may occur if the pH falls below 12.0. Complexing agents such as ethylenediamine are used to prevent precipitation of nickel hydroxide. As-deposited hardness values of 650 to 750 VHN are typical.

Table VI. Dimethylamine Borane-Reduced

Electroless Nickel Bath	
Nickel sulfate	25 g/L
Sodium acetate	15 g/L
n-Dimethylamine borane (DMAB)	4 g/L
Lead acetate	0.002 g/L
pH	5.9
Temperature	26°C (78°F)

Table VII. Formaldehyde-Reduced Electroless Copper Bath

Copper salt as Cu2+	1.8 g/L
Rochelle salt	25 g/L
Formaldehyde as HCHO	10 g/L
Sodium hydroxide	5 g/L
2-Mercaptobenzothiazole (MBT)	< 2 g/L
pH	12.0
Temperature	25°C (77°F)

After post-heat-treatment at 399°C (750°F) for 1 hour, values of 1,200 VHN can be produced. The melting point of borohydride-reduced deposits is 1,080°C (1,975°F).

Table V gives an example of a sodium borohydride-reduced electroless nickel bath.

Acid nickel-boron varies from 0.1 to 4% boron by weight depending on the bath formulation. The boron content of electroless nickel is reduced by DMAB. Bath parameters include a pH of 4.8-7.5, with an operating temperature range of 65-77°C (149-171°F). DMAB-reduced deposits have a very high melting temperature of 1,350°C (2,460°F). Baths containing less than 1% boron have excellent solderability, brazing, and good ultrasonic (wire) bonding characteristics. A typical DMAB-reduced bath is given in Table VI.

ELECTROLESS COPPER

Electroless copper deposits are generally applied before electroplating on plastics and other nonconductors, providing a conductive base for subsequent plating. These include acrylonitrile butadiene styrene (ABS), polystyrene, modified polyphenylene oxide, polyvinyl chloride (PVC), Noryl, polyethylene, polysulfone, structural foam, epoxy, and ceramics. In such applications, usually a thin deposit (0.127 μm; 0.05 mil) is applied, followed by an additional decorative or protective thickness of copper, nickel, or gold deposited electrolytically or electrolessly. The electroless copper in such applications provides good life in corrosive atmospheric and/or environmental exposures.

Automotive, appliance, printed wiring boards, molded interconnect devices, plastic composite connectors, multichip modules, and EMI/RFI shielding of other electronic devices represent major markets for electroless copper. In through-hole plating of printed wiring boards, the use of electroless copper has eliminated the need for an electrodeposited flash and provides excellent electrical conductivity in these hard-to-reach areas.

In the pretreatment of circuit boards, the most common method involves an acidic aqueous solution of stannous chloride ($SnCl_2$) and palladium chloride

Table VIII. Electroless Gold Bath

Gold hydrochloride trihydrate	0.01 M
Sodium potassium tartrate	0.014 M
Dimethylamine borane	0.013 M
Sodium cyanide	400.0 mg/L
pH (adjusted with NaOH)	13.0
Temperature	60°C (140°F)

Table IX. Electroless Palladium Bath

Palladium chloride	10 g/L
Rochelle salt	19 g/L
Ethylenediamine	25.6 g/L
Cool solution to 20°C (68°F) and then add:	
Sodium hypophosphite	4.1 g/L
pH (adjusted with HCl)	8.5 g/L
Temperature	68-73°C(155-165°F)

($PdCl_2$) immersion for subsequent deposition of the electroless copper. Many proprietary activators are available in which these solutions can be used separately or together at room temperature. Palladium drag into the electroless copper bath can cause solution decomposition instantly.

The pH of an electroless copper bath will influence the brightness of the copper deposit. Usually a value above 12.0 is preferred. A dark deposit may indicate low bath alkalinity and contain cuprous oxide. The plating rate is equally influenced by pH. In formaldehyde-reduced baths a value of 12.0-13.0 is generally best. Stability of the bath and pH are critical. A high pH value (14.0) results in poor solution stability and reduces the bath life. Below 9.5, solution stability is good; however, deposition slows or ceases. The principal components of the electroless copper bath (copper, formaldehyde, and caustic) must be kept within specification through replenishment. Other bath chemical components will remain within recommended ranges. Complexing agents and stabilizer levels occasionally need independent control. Other key operating parameters include temperature, air agitation, filtration, and circulation.

Various common reducing agents have been suggested, however, the best known reducing agent for electroless copper baths is formaldehyde. The complexing agent (i.e., Rochelle salt) serves to complex the copper ion to prevent solution precipitation and has an effect on deposition rates as well as the quality of the deposit. These conventional baths are stable, have plating rates of 1-5 μm or 0.04-0.2 mil/hr, and operate in an alkaline solution (pH 10.0-13.0).

An example of a formaldehyde-reduced electroless copper bath is provided in Table VII.

Recent formulations allow for alkanol amines such as quadrol-reduced baths. These high build [>10 μm/hr >0.4 mil/hr)] or heavy deposition baths operate at a lower pH without the use of formaldehyde. High build baths generally are more expensive and exhibit less stability but do not have harmful formaldehyde vapors given off during subsequent solution make up, heating, and deposition. These baths can deposit enough low stress copper to eliminate the need for an electrolytic flash. Quadrol is totally miscible with water and thus is resistant to

Table X. Electroless Cobalt Bath

Cobalt chloride	30 g/L
Sodium hypophosphite	20 g/L
Sodium citrate	35 g/L
Ammonium chloride	50 g/L
pH	9.5
Temperature	95°C (203°F)

many conventional waste treatment procedures.

ELECTROLESS GOLD

There is a growing need in the electronics industry for selective plating to conserve plating costs and to allow the electronics engineer freedom for circuit design improvement.

Many electronic components today are difficult to gold plate by electrolytic means. Thus, electroless gold is currently being used in the fabrication of semiconductor devices, connector tabs, chips, and other metallized ceramics. Most commercially available electroless gold deposits are produced first by plating a thin deposit of immersion gold, followed by electroless gold plating. There are a few true autocatalytic gold processes available with 99.99% purity.

Table VIII gives an example of an electroless gold bath.

Electroless gold can successfully be applied to Kovar, nickel, nickel alloys, electroless nickel, copper, copper alloys, electroless copper, and metallized ceramics. Electroless gold can be deposited onto already present thin electrodeposited gold to give added strength.

ELECTROLESS PALLADIUM

Electroless palladium deposits are ductile and ideal for contacts undergoing flexing (i.e., printed circuit board end connectors and electronic switch contacts). The deposit has also been used as a less expensive replacement for gold, providing tarnish resistance and solderability. Electroless palladium has been used to replace rhodium for wear applications.

Using specific bath components, the deposit can be hard and bond to electroless nickel with a bond strength greater than the tensile strength of the palladium plate itself. Metals such as stainless steel and nickel can be plated directly. Copper, brass, and other copper alloys require an electroless nickel preplate. The electroless nickel preplate can be either from a hypophosphite- or boron-reduced bath.

Table IX gives an example of an electroless palladium (hypophosphite-reduced) bath.

ELECTROLESS COBALT

Thin electroless cobalt deposits have use in the electronics industry on magnetic memory discs and storage devices primarily for their magnetic properties.

Table X gives an example of an electroless cobalt bath.

COMPOSITES AND POLYALLOYS

The uniform dispersion of micron or submicron particles in an electroless composite deposit will enhance the lubricity and the wear and/or abrasion resistance over base substrates

and conventional electroless deposits. Composites containing fluorinated carbon (CF_x), fluoropolymers (PTFE), natural and synthetic (polycrystalline) diamonds, ceramics, chromium carbide, silicon carbide, and aluminum oxide have been codeposited. Most commercial deposition occurs with an acid electroless nickel bath owing to the unique physical characteristics available to the final codeposit. The reducing agent used may be either a hypophosphite or boron complex. For Lamellar solids, starting materials are naturally occurring elemental forms like coke or graphite. Fluorinated carbon (CF_x) is produced by reacting coke with

elemental fluorine. The thermal stability of the CF_x class of solid lubricants is higher than PTFE, allowing the CFx composite to be postbaked for maximum hardness (1,100 VHN). The CF_x composite exhibits high wear resistance coupled with a low coefficient of friction.

The inclusion of these finely divided particles within an electroless matrix (15-25% by volume) involves the need to maintain uniform dispersion of the occluded material during metal deposition. Specialized equipment is required and part size, configuration, and deposit thickness are limited. Deposition rates will vary, depending upon the type of electroless bath utilized. The surface morphology of the particle used (i.e., type, size, and distribution in the matrix) will greatly influence the final codeposit properties and composition. The coefficient of friction and wear resistance of the composite are related to particle size and concentration in the electroless bath.

Applications include food processing equipment, military components, molds for rubber and plastic components, fasteners, precision instrument parts, mating components, drills, gauge blocks, tape recording heads, guides for computers, and textile machine components.

Due to the resultant matrix surface topography (when using diamonds or silicon carbide, for example), the final surface roughness must be considered. Special postplate surface finish operations must be employed to regain the required rms (microinch) finish. In severe abrasion applications involving high pressure foundry molding, it has been noted that the softer electroless nickel matrix wears first, exposing harder silicon carbide particles, which create poor drawability of the resin/binder from the mold.

Polyalloys have been developed to produce deposits having three or four elements with specific coating properties. These include applications where unique chemical and high temperature resistance or electrical, magnetic, or nonmagnetic properties are requirements. The use of nickel-cobalt-iron-phosphorus polyalloys produce magnetic (for memory) properties. Other polyalloys include nickel-iron-phosphorus, nickel-cobalt-phosphorus, nickel-phosphorus-boron, nickel-iron-boron, nickel-tungsten-phosphorus, nickel-molybdenum-boron, nickel-tungsten-tin-phosphorus, and nickel-copper-phosphorus. The final selection is dependent upon the final application and the economics of achieving the results required.

Electroless composites and polyalloys have made unique contributions to various engineering applications. Extensive field testing is ongoing to gain experience for proper applications, inclusions and sizes, plus proper electroless bath operating parameters for these new forms of electroless plating.

WASTE TREATMENT

The electroless bath has limited life due to the formation of reaction byproducts. For example, in acid electroless nickel (hypophosphite-reduced) baths, the added accumulation or concentration of orthophosphite (HPO_3^{2-}) in the solution will eventually decrease the plating rate and deposit quality, requiring bath disposal. Also, the chelators and stabilizers make it difficult to reduce the electroless metal content by alkaline precipitation. Regulations regarding effluent discharge vary globally and with respect to local POTW limits. In the United States, electroless metal legal discharge limits of 1 ppm or below are common for nickel and copper effluents.

Conventional precipitation to form metal hydroxide or sulfide sludge through continuous or batch treatment involves a series of pH adjustment steps to con-

vert dissolved metals into solids for dewatering and hazardous disposal. Emphasis must be placed on waste minimization as the first step in reducing waste treatment. Examples include ion exchange, reverse osmosis, and electrowinning or electrolytic recovery, which electroplates the spent bath into nickel or copper metal onto special cathodes helping to reduce the amount of sulfide or hydroxide hazardous sludge eventually created. The resultant plated metal produced can be reclaimed as scrap metal. Other waste minimization methods include using steel wool to plate out the electroless bath prior to further waste treatment.

ANODIZING OF ALUMINUM

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An aluminum part, when made the anode in an electrolytic cell, forms an anodic oxide on the surface of the aluminum part. By utilizing this process, known as anodizing, the aluminum metal can be used in many applications for which it might not otherwise be suitable. The anodizing process forms an oxide film, which grows from the base metal as an integral part of the metal and when properly applied imparts to the aluminum a hard, corrosion- and abrasion-resistant coating with excellent wear properties. This porous coating may also be colored using a number of methods.

Many acidic solutions can be used for anodizing, but sulfuric acid solutions are by far the most common. Chromic, oxalic, and phosphoric acids are also used in certain applications.

The morphology of the oxide formed is controlled by the electrolyte and anodizing conditions used. If the oxide is not soluble in the electrolyte, it will grow only as long as the resistance of the oxide allows current to flow. The resultant oxide is very thin, nonporous, and nonconductive. This particular property of the anodic oxide is useful in the production of electrolytic capacitors using boric and/or tartaric acids.

If the anodic oxide is slightly soluble in the electrolyte, then porous oxides are formed. As the oxide grows under the influence of the applied DC current, it also dissolves, and pores develop. It is this property that allows us to color the oxide using organic dyes, pigment impregnation, or electrolytic deposition of various metals into the pores of the coating.

By balancing the conditions used in the anodizing process, one can produce oxides with almost any desired properties, from the thin oxides used in decorative applications to the extremely hard, wear-resistant oxides used in engineering applications (hardcoating).

Colored anodized aluminum is used in a wide variety of applications ranging from giftware and novelties through automotive trim and bumper systems. Such demanding situations as exterior architectural applications or wear-resistant, abrasive conditions, such as landing gears on airplanes, are not beyond the scope of anodized aluminum. Semiprecious and precious metals can be duplicated using anodized aluminum. Gold, silver, copper, and brass imitations are regularly fabricated. New and interesting finishes are constantly being developed, which gain wide appeal across the spectrum of purchasers.

The utilization of electropolishing or chemical bright dipping in conjunction with a thin anodic oxide produces a finish whose appeal cannot be duplicated by other means. Matte finishes produced by etching the aluminum surface, affords the “pewter” look, which is oftentimes desired. Matte finishes are also the finish of choice of most architects.

EQUIPMENT

Tanks

A wide variety of materials can and have been used to build anodizing tanks. Lead-

lined steel, stainless steel, lead lined wood, fiberglass-lined concrete, and plastic tanks have all been used in the past. A metallic tank can be used as the cathode, but adequate distance between the work and the tank must be maintained to prevent shorting. Some problems are experienced using metal tanks. For instance, the anode-to-cathode ratio is generally out of balance; also, since the entire tank is an electrical conductor, uneven current flow is possible leading to uneven oxide thickness formation. This uneven oxide formation causes wide color variations in organically dyed materials and is not generally recommended.

Generally, the use of inert materials in the construction (or lining) of the anodize tank is recommended. PVC, polypropylene, or fiberglass are good inert materials for this application.

Cathodes

Cathodes can be aluminum, lead, carbon, or stainless steel. Almost all new installations are using aluminum cathodes because of their ability to reduce the energy requirements of the process. Because of the better conductivity of aluminum, the anode-to-cathode ratio becomes extremely important. It has been found that an anode-to-cathode ratio of approximately 3:1 is best for most applications. Cathode placement is also of vital importance. It is recommended that the cathodes be no longer (deeper) than the work being anodized. Placement of the cathodes along the tank sides should be such that they extend no further than the normal work length. For example most 30-ft long tanks can only handle 28-ft lengths; therefore, the cathodes should be positioned at least 1 ft from either end of the tank to keep the work material from "seeing" too much cathode and anodizing to a thicker oxide on the ends. The depth of the cathodes in the tank should not exceed the normal depth of the work being processed. If the cathodes extend deeper into the tank than the parts being anodized, there will be excessive oxide growth on the parts in the lower portion of the anodizing tank. This will result in color differences in the oxide and subsequently colored parts.

The correct alloy and temper for aluminum cathodes is vital, 6063 or 6101 alloys in the T-6 or T-5 condition are best. The overaged T-52 temper *should never be used!* Cathode material should be welded to an aluminum header bar using 5356 alloy welding wire. Bolted joints are not recommended due to the possibility of "hot joints."

Employment of aluminum cathodes has done much to improve the overall quality of anodized finishes in all areas of application.

Temperature Control

This is one of the most important factors influencing the properties of the anodic oxide and must be closely controlled to produce consistent quality. The temperature should be held to plus or minus 2^{O}F. Most installations have some means of temperature control, since large amounts of heat are generated in the anodizing process.

Lead cooling coils have been used in the past, but newer plants use external heat exchangers. The external heat exchanger has been found to be more efficient in cooling the solution while offering additional agitation. Again, as mentioned above, the presence of other metals in the tank, in conjunction with the aluminum cathodes, can cause undo electrical problems.

One of the added benefits of using a heat exchanger is agitation. Proper placement of the intake and outlet piping can insure good agitation as well as min-

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imization of temperature variations within the tank. This type of acid movement assures one of better anodizing.

Recently, the use of acid "spargers" in the bottom of the anodize tank has become popular. These spargers replace the more common air spargers now being used and give much better acid circulation and temperature control.

Agitation

To prevent localized high temperatures, some form of agitation is required in the bath. Low-pressure air, provided it is clean and oil-free, is often used. Mechanical agitation and pumping of the electrolyte through external heat exchangers are also used. Generally, compressed air is not recommended due to the presence of oils in the lines. Multiple filters in the air lines when using compressed air have not proven to be completely effective in keeping oil out of the anodize tank.

Racks

The two most common rack materials are aluminum and titanium. If aluminum is used, it should be of the same alloy as the work, or at least not be an alloy that contains copper (2xxx series). Alloys 6063 and 6061 are excellent rack materials. It must be remembered that aluminum racks will anodize along with the work and must be stripped before being used again. Titanium racks are more expensive, initially, but do not require stripping and are generally not attacked by the baths used in the anodizing process. Only commercially pure titanium can be used as rack material.

Titanium racks are not suitable for low temperature anodizing (hardcoating) where high voltages are required. The lower conductivity of the metal causes heating of the racks and eventual burning of the aluminum parts being anodized.

Power Equipment

For normal (Type II) sulfuric acid anodizing (68-72°F), a DC-power source capable of producing up to 35 V and 10 to 24 A/ft^2 should be suitable.

Some processes such as phosphoric acid, oxalic acid, hard coating, or integral color may require voltages as high as 150 V.

Power supplies come with a variety of options. Such things as constant current control, constant voltage control, adjustable ramping, end-of-cycle timers/signals/shut-offs, and a variety of other options make the anodizing process easier and more controllable.

Power supplies for hardcoat anodizing require more stringent capabilities. Those used for Type III low temperature anodizing (28-32°F) will require voltages approaching 90 V and amperages equivalent to 48 A/ft^2. Power supplies used for "room temperature" hardcoating (50-65°F) will require only 36 V and sufficient current to reach 36 to 46 A/ft^2.

SURFACE PREPARATION

The type of surface preparation prior to anodizing gives the metal finisher a choice of effects. By combining mechanical techniques, such as scratch brushing or sandblasting with buffing and bright dipping, interesting effects can be achieved. Sandblasting and shot peening have also been used to give interesting surface treatments.

The beauty of dyed anodized aluminum can be further enhanced by color buffing the work after it is sealed and dried, using a lime-type composition, preferably containing some wax. In addition to actually polishing the coating, this step

removes any traces of the sealing smut.

Irregular shaped parts, castings, etc. are best finished by brushing with a Tampico brush or by tumbling with sawdust or other suitable media.

PRETREATMENT

Cleaning

Proper and thorough cleaning of the aluminum surface prior to anodizing is one of the most important steps in the finishing process. Improperly cleaned material accounts for more reruns and rejected parts than any other single factor.

It is essential that all machining oils, greases, body oils, and other surface contaminants be removed prior to the continuation of the anodizing sequence. Both alkaline- and acid-based proprietary cleaners are available that will do an adequate job. If the oils or greases are specific in nature, some cleaners may need to be "customized" for adequate results.

What is clean? Generally, we speak of a part being clean if it exhibits a "water-break-free" surface. This means that if the water rinses off of the metal surface in a continuous sheet,

the work is considered to be clean. If, on the other hand, the water "beads" up or forms water breaks, the part still has foreign matter on the surface and continued cleaning is necessary. Once the part has been determined to be clean, subsequent finishing steps can proceed.

Etching

Etching is the removal of some of the aluminum surface from a part using



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chemical solutions. There are a number of reasons for etching aluminum:

1. To impart a matte finish to the material (lower the specularity or gloss).
2. To remove surface contaminants.
3. To hide surface imperfections (scratches, die lines, etc.)
4. To produce an overall uniform finish.

Chemical etching is accomplished using both alkaline and acid solutions. The most frequently used etch media is sodium hydroxide. Time, temperature, concentration, and contaminant level will affect the type of finish possible in an etch bath. Many proprietary solutions are available from the chemical suppliers. Close attention to the technical information included with the chemicals is important.

Rinsing

Probably one of the most abused steps in the finishing of aluminum is rinsing. Most anodizers practice some form of "water management," usually to the detriment of the other process tanks. Improper rinsing causes poor surface finish due to cross reactions of chemicals left on the surface from previous processing tanks reacting with the chemicals in further processing tanks. Cross contamination of expensive solutions is another fallacy of "water management." Cascading rinses, spray rings, or just cleaner rinse tanks with adequate overflow will go a long way in reducing poor finish and cross contamination.

Deoxidizing/Desmutting

After etching, a "smut" of residual metallic alloying materials is left on the aluminum surface. This must be removed before further processing. The use of deoxidizer/desmutters will accomplish this, leaving the treated surface clean for subsequent finishing steps.

Many alloys, during their heat treatment steps, will form heat treat oxides. If these oxides are not removed prior to etching or bright dipping, a differential etch pattern can develop, which will cause rejection of the parts. In this instance a deoxidizer must be used. The deoxidizer is designed to remove oxides, but is also extremely good at removing smut. A desmutter, on the other hand, will not remove oxides. It is apparent that a deoxidizer would be the preferred solution to have in an aluminum finishing line. *Remember, a deoxidizer will desmut but a desmutter will not deoxidize.*

Bright Dipping and Electrobrightening

A chemical or electrobrightening treatment is required where an extremely high luster is to be obtained on the aluminum surface. The electrobrightening or electropolishing treatment is particularly applicable to the super-purity aluminum now used extensively in the jewelry and optical field. Proprietary chemicals for these treatments are available from a number of suppliers. Chemical brightening is most commonly used for most applications because of it's ease of operation. A number of companies offer proprietary solutions, which will give you the bright finish you desire. Specifics on the makeup and use of these solutions is available from the chemical suppliers.

ANODIZING

Properties of the Oxide Film

The anodizing process conditions have a great influence on the properties of the

oxide formed. The use of low temperatures and acid concentration will yield less porous, harder films (hardcoating). Higher temperatures, acid contents, and longer times will produce softer, more porous, and even powdery coatings. It must be remembered that changing one parameter will change the others, since they are all interrelated.

It should also be pointed out that the alloy being processed may significantly alter the relationship between the voltage and current density, often leading to poor quality coatings. This is particularly true when finishing assembled components, which may contain more than one alloy.

Factors Influencing Shade

In order to obtain reproducible results from batch to batch, a large number of variables must be kept under close control. First to be considered are those that affect the nature of the oxide.

Alloy

The particular aluminum alloy being used has a pronounced effect on shade, especially with certain dyes. The brightest and clearest anodic oxides are produced on the purest form of aluminum, the oxides becoming duller as the amount of alloying constituents are increased. Super-purity aluminum (99.99% Al) and its alloys with small amounts of magnesium produce an extremely bright oxide, which does not become cloudy upon being anodized for extended periods.

Alloys containing copper, such as 2011, 2017, 2024, and 2219, although forming a thinner and less durable oxide than the purer forms, produce a heavier and duller shade. Magnesium in excess of 2% has a similar effect although not as pronounced. The presence of silicon imparts a gray color to the coating; alloys containing more than 5% silicon are not recommended for use with bright colors. Iron in the alloy can lead to very cloudy or "foggy" oxides.

The majority of casting alloys contain appreciable amounts of silicon, ranging as high as 13%, and present difficulty in anodizing. Use of a mixed acid dip (normally containing hydrofluoric and nitric acids) prior to anodizing is of value when high-silicon alloys are encountered.

Since the various alloys produce different shades when anodized identically, the designer of an assembled part must use the same alloy throughout if the shades of the individual components are to match.

Anodizing Conditions

Other variables affecting the nature of the oxide i.e., its thickness, hardness, and porosity) are the acid concentration and temperature of the anodizing bath, the current density (or the applied voltage, which actually controls the current density), and the time of anodizing. These factors must be rigidly controlled in order to achieve consistent results.

The "standard" sulfuric acid anodizing bath (Type II) produces the best oxides for coloring. The standard anodizing solution consists of:

Sulfuric acid, 180-200 g/L

Aluminum, 4-12 g/L

Temperature, 68-72°F

As the anodizing temperature is increased, the oxide becomes more porous and improves in its ability to absorb color; however, it also loses its hardness and its luster, due to the dissolution action of the acid on the oxide surface. As the pore size increases, sealing becomes more difficult and a greater amount of color is bled (leached) out into the sealing bath. The ideal anodizing temperature,

except where a special effect is desired, is 70°F.

Oxides produced by anodizing in chromic acid solutions may also be dyed. The opaque nature of the oxide film produced in this manner has a dulling effect upon the appearance of the dyed work. Consequently, some dyes, notably the reds, which produce pleasing shades on sulfuric acid anodized metal, are unsuitable for use with a chromic acid coating. Fade resistance of this type of dyed oxide is extremely poor, possibly because the oxide is not thick enough to contain the amount of dye needed for good lightfastness. The best chromic acid coatings for dyeing are produced with a 6 to 10% by weight solution operated at 120°F. A potential of 40 to 60 V is used, depending upon alloy, copper- and silicon-bearing materials requiring the lower voltage. The usual time is from 40 to 60 minutes.

DECORATIVE ANODIZING

Decorative anodic oxides are used in a great many applications, from lighting reflectors to automotive trim. The thickness of the oxide might range from 0.1 to 0.5 mil (2.5 to 12 microns). As mentioned above the most common electrolyte is sulfuric acid and typical conditions are listed below. Parts that are to be given bright specular finishes are usually produced from special alloys formulated for their bright finishing capabilities.

Typical decorative anodizing conditions are:

Sulfuric acid, 165-180 g/L
Temperature, 60-80°F
Current density, 10-15 A/ft^2
Voltage, depends on current density, temperature, and electrolyte
Time, 12-30 minutes depending on film thickness desired. Longer times produce thicker coatings.

ARCHITECTURAL ANODIZING

The conditions used in architectural anodizing are not much different than those used for decorative applications, except the anodizing time is usually longer and the current density may be slightly higher. In general the thickness of the oxide will be greater than for decorative coatings, and this relates to the treatment time.

Interior

For interior applications the coating will be probably 0.4 mil thick (10 microns). This means an anodizing time of about 20 minutes at 15 A/ft^2.

Exterior

For exterior uses the coating will be a minimum of 0.7 mil thick (18 microns) and this means an anodizing time of about 39 minutes at 15 A/ft^2.

INTEGRAL COLOR ANODIZING

This process, used mainly for architectural applications, requires the use of specially formulated electrolytes, usually containing organic sulfo acids with low contents of sulfuric acid and aluminum content, to produce a series of bronze to black shades. The color produced is dependent upon the time of treatment and the final voltage used. Specially formulated alloys are also required. Large amounts of heat are generated in the process due to the high current densities employed (up to 45

A/ft^2), so efficient heat exchange equipment is needed to keep the bath cool.

HARDCOATING

Hardcoating (Type III) is a name used to describe a special form of anodizing. The process, which usually employs higher acid concentrations, lower temperatures, and higher voltages and current densities is sometimes referred to as an "engineering hardcoat." This is due to the fact that hardcoating imparts a very hard, dense, abrasion-resistant oxide on the surface of the aluminum. A dense oxide is formed due to the cooling effect of the cold electrolyte (usually 30-40°F). At these temperatures, the sulfuric acid does not attack the oxide as fast as at elevated temperatures. Because of the lower temperature, the voltages needed to maintain the higher current densities also help form smaller, more dense pores, thus accounting for the hardness and excellent abrasion resistance.

Normal low temperature hardcoating is carried out under the following conditions:

Acid concentration, 180-225 g/L
Aluminum content, 4-15 g/L
Temperature, 28-32°F

There have been a number of organic additives developed in the past few years that allow the anodizer to hardcoat at elevated temperatures (50-70°F). These additives, by virtue of their chemical reaction in the oxide pores, help cool the material being anodized and retard acid dissolution of the coating.

COLORING OF ANODIC COATINGS

The coloring of anodic oxides is accomplished by using organic and inorganic dyes, electrolytic coloring, precipitation pigmentation, or combinations of organic dyeing and electrolytic coloring. After the anodizing step, the parts are simply immersed in the subject bath for coloring.

The thickness of the anodic oxide can range from 0.1 mil for pastel shades up to 1.0 mil for very dark shades and blacks. Application of electrolytic coloring will be discussed below. Suffice it to say, the combination of organic dyeing and electrolytic coloring gives a more complete palette of colors from which to choose.

Organic Dyes

The actual process of dyeing the aluminum oxide is very simple. A water solution of 0.025 to 1.0% of dyestuff at a temperature of 140°F composes the dyebath. The aluminum, previously anodized, is simply immersed in this bath for a short period of time, usually 10 to 30 minutes, The work is then sealed and is resistant to further dyeing or staining.

The equipment required, in addition to that needed for the actual anodizing operation, consists of rinse tanks with clean, flowing water; a dye tank for each color desired; and a sealing bath preferably equipped with continuous filtration.

The dye tanks must be of stainless steel, plastic, fiberglass, or some other inert substance; never of copper or steel. They must be supplied with means of maintaining a constant 140°F temperature and should be equipped with some form of agitation. Usual plant practice is to use air agitation; however, with proper filtration, the filter itself can be used as the source of agitation. With air agitation the use of water and oil traps, plus a filter on the air supply, is

necessary to prevent contamination of the dye solution. A few drops of oil spread on the surface of the dyebath is very often the cause of streaked and spotted work.

Typically, the use of blower air agitation is preferred over compressed air.

Rinsing after anodizing, followed by immediate dyeing, is of prime importance. Since some dyes will not dye aluminum in the presence of sulfate ion, poor rinsing can cause streaks and discolorations. Even in the case of dyes not affected by sulfates, any carry-over of acid causes a lowering of the pH of the dyebath, which means shade variations in succeeding batches of work.

In the design of parts to be color anodized, care must be taken to avoid the use of closed heads or seams, which are impossible to rinse. In the case of parts containing recesses, which are difficult to rinse, a neutralizing bath of sodium bicarbonate is of value. In working with coated racks, care must be taken that the rack coating does not separate, thereby forming pockets that can entrap sulfuric acid, later allowing it to seep out into the dyebath. Work must not be allowed to stand in the rinse tanks between anodizing and dyeing, but should be dyed immediately, following a thorough rinsing. For most effective rinsing, three tanks should be used. In this way the final tank, usually deionized water, will remain relatively free of acid.

The variables in the dyebath are time, temperature, concentration, and pH. Time and temperature are readily controlled in plant practice; however, regulation of concentration presents some difficulties. Fortunately, in the case of most single component dyes, concentration control is not very critical, a variation of 100% causing little change in depth of shade.

The usual dyebath concentration for full shades is 2 g/L except for black, which requires from 6 to 10 g/L. In the case of pastel shades concentrations of considerably less than 2 g/L may be required in order that the shade does not become too deep. This reduction in concentration will have a negative effect on the dye lightfastness.

Control of pH is important and a daily check (more often in smaller tanks or where high volume is a factor) should be made. The pH range between 6.0 and 7.0 gives the best results with the majority of dyes; however, a few are more effective at values close to 5.0. Initial adjustments should always be made since it is not practical for the manufacturer to standardize the dyes with respect to the pH of their solutions. These adjustments are made by addition of small amounts of acetic acid to lower the pH value and dilute sodium hydroxide or acetate to raise it. Solutions may be buffered against possible carry-in of sulfuric acid by adding 1 g/L of sodium acetate and adding sufficient acetic acid to reduce the pH to the desired value.

COLORFASTNESS OF THE DYED COATING

Of the many dyes that color anodized aluminum, possibly several hundred, it should be understood that only a few possess sufficient inherent resistance to fading to be considered for applications where exposure to direct sunlight is intended. Where items of long life expectancy are involved, for example, architectural components, even greater selectivity must be imposed, since all organic colorants now known will exhibit some fading when subjected to sunlight of sufficient intensity and duration. Also, the parameters of application as well as the colorant are involved in the resistance to premature loss or change of color. The following additional factors are considered by most authorities as affecting the lightfastness of the dyed coating.

Coating Thickness and Penetration of the Dyestuff

Accelerated and long-term exposure tests and practical experience both here

and abroad verify that an anodic oxide thickness in the order of 0.8 mil (20 microns) and its complete penetration by the colorant is required for optimum resistance to fading and weathering. This means that, in some applications, the dye time may be extended to 30 minutes for complete dye saturation.

Intensity of Shade

Usually, the greater the amount of dye absorbed, the better its resistance to fading. Also, whatever fading may occur will be less apparent to the observer. Pastel shades may, therefore, be expected to exhibit inferior light and weather fastness as compared to full strength dyeing.

Type and Degree of Sealing

Those dyes that are reactive with the nickel or cobalt salts present in the sealing bath usually require this treatment for optimum performance. It is reported that certain selected dyestuffs benefit from after-treatment with other heavy metals; for example, lead, copper, zinc, or chromium. Generally, such treatments are not utilized because of the requirement of an individual sealing tank for each dye.

In the case of extremely porous anodic oxides, for example, those formed on alloys of high copper content, effective sealing is particularly important with certain dyes to prevent color loss from sublimation of the dye or by chemical reaction in oxidizing or reducing environments.

ELECTROLYTIC COLORING (2-STEP)

This electrolytic coloring process consists of conventional sulfuric acid anodizing followed by an AC treatment in a bath containing tin, nickel, cobalt, or other metal salts to produce a series of bronze to black colors as well as blues, greens, burgundies, and golds. The most common bath is one containing tin. The colors produced are not alloy or thickness dependent and are easier to control. The process is not as energy intensive as the integral color process. It is for this reason that this process has almost entirely replaced the integral color process in recent years. Unlike sulfuric acid anodizing, the coloring process is controlled by voltage and time, rather than by current density. Depending upon the bath used, the coloring time can range from 20 sec for champagne to 10 min for black. The use of specially built AC power supplies, using electronic timing and voltage control, helps produce a finish that is reproducible time after time. Proprietary baths containing bath stabilizers, color enhancers, and other additives are being marketed and used throughout the finishing industry.

PIGMENTATION BY PRECIPITATION OF INSOLUBLE COMPOUNDS

Before the development of special organic dyes for coloring anodized aluminum, the precipitation of various insoluble metal compounds within the anodic oxide was used commercially. The treatment consisted of alternatively immersing the anodized surface in concentrated solutions of suitable metal salts until a sufficient amount of the pigment was precipitated to produce the desired color. Although seldom used in today's state of the art, a number of these reactions are listed below:

Lead nitrate (or acetate) with potassium dichromate—yellow
Lead nitrate (or acetate) with potassium permanganate—red
Copper sulfate with ammonium sulfide—green

Ferric sulfate with potassium ferrocyanide—blue
Cobalt acetate with ammonium sulfide—black

Ferric oxalates (ferric ammonium oxalate or ferric sodium oxalate) applied to conventional anodic oxides in the same manner as organic dyes are, under proper conditions, hydrolyzed to deposit ferric hydroxide within the coating pores, imparting a gold to orange color of outstanding resistance to fading. Special proprietary chemicals are available for this treatment.

The deposit of ferric oxide produced in the above manner may, in addition, be converted to ferric sulfide, the resultant shade of which is black. Alternatively, a bronze shade may be formed by reduction of the ferric oxide with pyrogallic acid.

Cobalt acetate reduction, although commercially used in Europe, is not well known in the U.S. It consists of saturating a conventional anodic oxide with the cobalt solution and then reacting this with potassium permanganate to produce a cobalt-manganese dioxide complex. The resultant bronze shade has excellent lightfastness and offers some potential for architectural applications.

MULTICOLOR ANODIZING

The application of two or more colors for the production of nameplates, instrument panels, automotive and appliance trim, etc. has now achieved sufficient commercial importance that a number of large firms deal exclusively with such items.

The following methods of multicolor anodizing are possible:

The *multiple anodizing process,* which entails a complete cycle of anodizing, dyeing, and sealing; application of a resist to selected areas; stripping of the entire anodic oxide from the remaining unprotected surfaces; and repetition of this entire procedure for each color.

The *single anodizing method*, wherein an anodic oxide of sufficient thickness and porosity to absorb the dye required for the darkest shade is first applied. This oxide is then dyed and left unsealed, a resist applied, and the dye alone discharged or bleached out with a solution that leaves the anodic oxide intact. The operation is then repeated for each successive shade. Finally, the resist is removed with a suitable solvent, and the entire surface sealed. In certain cases, where a dark shade is to be applied after a pastel shade, a modification of this technique omits the bleaching step with the supplementary dye being applied directly over the preceding color.

The use of a *specialized combination ink-and-resist* enables information or designs to be printed directly on the previously formed anodic oxide in several colors. The background color may then be applied by conventional dyeing methods, while the ink serves as a stop-off for the printed areas.

Preanodized, photo-sensitized aluminum alloy material is available, wherein the image, in black, may be produced by photographic methods, and the background colored by the conventional dye immersion method.

SEALING OF ANODIC COATINGS

Hydrothermal Sealing (200-212°F)

To achieve the maximum protective qualities and corrosion resistance required for finished articles, the anodic oxide must be sealed after it is formed and/or colored. The sealing process consists of immersing the anodized parts in a solution of boiling water or other solution such as nickel acetate, wherein the aluminum oxide is hydrated. The hydrated form of the oxide has greater volume than the

unhydrated form and thus the pores of the coating are filled or plugged and the coating becomes resistant to further staining and corrosion. The use of nickel containing seals will, in most cases, prevent leaching of dyes during the sealing operation.

When sealing with the nickel acetate bath, a smutty deposit may form on the work. This can be minimized by the addition of 0.5% boric acid to the bath or by the use of acetic acid to lower the pH of the solution to 5.3 to 5.5. Too low a pH, however, causes leaching out of the dye. Use of 0.1% wetting agent in this bath also aids in preventing formation of the smut. Proprietary sealing materials designed to completely eliminate this smut are now available from chemical suppliers.

The sealing tank should be of stainless steel or other inert material and must be maintained at 200°F. Use of a filter enables a number of colors to be sealed in the same bath without danger of contamination.

Mid-Temperature Sealing (160-190°F)

Due to the higher energy costs inherent in hydrothermal sealing, chemical manufacturers have developed "mid-temperature" seals (160-190°F). These seals, which contain metal salts such as nickel, magnesium, lithium, and others, have become very popular due to the lower energy costs and their ease of operation.

One disadvantage of the lower temperature is the tendency of organically dyed parts to leach during sealing. This can be compensated for by a slight increase in the bath concentration and by operating the solution at the upper temperature limits (190°F).

"Nickel-free" seals (or more "environmentally friendly" seals, as they are called) are fast becoming the seal of choice where clear or electrolytically colored parts are concerned. Because there is nothing to leach, these mid-temperature seals accomplish hydration of the oxide without the use of the heavy metal ions. When the seals become contaminated or are no longer effective, they can be discharged to the sewer without subsequent treatment (except possible pH adjustment). This offers the finisher a safer alternative to the effluent treating necessary with heavy metal containing seals.

Room Temperature (Cold) Seals (70-90°F)

A significant modification in the sealing of anodized aluminum was the development of "room temperature sealing" (70-90°F). Unlike the high temperature and mid-temperature seals, which depend on hydration for sealing, the cold seals rely on a chemical reaction between the aluminum oxide and the nickel fluoride contained in the seal solution. Unfortunately, this reaction is slow at ambient temperatures and the sealing process can proceed up to 24 hours; however, it has been found that a warm water rinse (160°F) after the cold seal immersion will accelerate the sealing process, allowing for handling and packing of the sealed parts. The sealing of organically dyed parts in cold seals has been found to be advantageous. Light stability testing (fade resistance) has shown that parts sealed in cold seals gain additional lightfastness.

OTHER ELECTROLYTES

A number of other electrolytes are used for specialized applications.

Chromic acid is used in marine environments, on aircraft as a prepaint treatment, and in some cases when finishing assemblies where acid may be entrapped. Although the film produced is extremely thin, it has excellent corrosion resistance and can be colored if desired.

A typical bath might contain from 50 to 100 g/L of chromic acid, and be run at about 95 to 105°F. There are two main processes, one using 40 V and a newer process using 20 V. The equipment needed is similar to that used in sulfuric acid processes.

Oxalic acid is sometimes used as an anodizing electrolyte using similar equipment. This bath will produce films as thick as 2 mils without the use of very low temperatures and usually gives a gold or golden bronze color on most alloys. The typical concentration is from 3 to 10% oxalic acid at about 80 to 90°F, using a DC voltage of about 50 V.

Phosphoric acid baths are used in the aircraft industry as a pretreatment for adhesive bonding. They are also very good treatments before plating onto aluminum. A typical bath might contain from 3 to 20% of phosphoric acid at about 90°F, with voltages as high as 60 V.

SUMMARY

Aluminum is a most versatile metal. It can be finished in a variety of ways. It can be made to resemble other metals, or can be finished to have a colorful as well as a hard, durable finish unique unto itself. Only the imagination limits the finish and colors possible with anodized aluminum.

CHROMATE CONVERSION COATINGS

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Chromate conversion coatings are produced on various metals by chemical or electrochemical treatment with mixtures of hexavalent chromium and certain other compounds. These treatments convert the metal surface to a superficial layer containing a complex mixture of chromium compounds. The coatings are usually applied by immersion, although spraying, brushing, swabbing, or electrolytic methods are also used. A number of metals and their alloys can be treated; notably, aluminum, cadmium, copper, magnesium, silver, and zinc.

The appearance of the chromate film can vary, depending on the formulation of the bath, the basis metal used, and the process parameters. The films can be modified from thin, clear-bright and blue-bright, to the thicker, yellow iridescent, to the heaviest brown, olive drab, and black films. A discussion of specific formulations is not included in this article because of the wide variety of solutions used to produce the numerous types of finishes. It is intended to present sufficient general information to permit proper selection and operation of chromating baths. Proprietary products, which are designed for specific applications, are available from suppliers.

PROPERTIES AND USES

Physical Characteristics

Most chromate films are soft and gelatinous when freshly formed. Once dried, they slowly harden or "set" with age and become hydrophobic, less soluble, and more abrasion resistant. Although heating below 150°F (66°C) is of benefit in hastening this aging process, prolonged heating above 150°F may produce excessive dehydration of the film, with consequent reduction of its protective value. Coating thickness rarely exceeds 0.00005 in., and often is on the order of several microinches. The amount of metal removed in forming the chromate film will vary with different processes.

Variegated colors normally are obtained on chromating, and are due mainly to interference colors of the thinner films and to the presence of chromium compounds in the film. Because the widest range of treatments available is for zinc, coatings for this metal afford an excellent example of how color varies with film thickness. In the case of electroplated zinc, clear-bright and blue-bright coatings are the thinnest. The blue-brights may show interference hues ranging from red, purple, blue, and green, to a trace of yellow, especially when viewed against a white background. Next, in order of increasing thickness, come the iridescent yellows, browns, bronzes, olive drabs, and blacks.

Physical variations in the metal surface, such as those produced by polishing, machining, etching, etc., also affect the apparent color of the coated surface. The color of the thinner coatings on zinc can also be affected indirectly by chemical polishing, making the finish appear whiter.

Corrosion Prevention

Chromate conversion coatings can provide exceptionally good corrosion resis-

tance, depending upon the basis metal, the treatment used, and the film thickness. Protection is due both to the corrosion-inhibiting effect of hexavalent chromium contained in the film and to the physical barrier presented by the film itself. Even scratched or abraded films retain a greatdeal of their protective value because the hexavalent chromium content is slowly leachable in contact with moisture, providing a self-healing effect.

The degree of protection normally is proportional to film thickness; therefore, thin, clear coatings provide the least corrosion protection, the light iridescent coatings form an intermediate group, and the heavy olive drab to brown coatings result in maximum corrosion protection. The coatings are particularly useful in protecting metal against oxidation that is due to highly humid storage conditions, exposure to marine atmospheres, handling or fingerprint marking, and other conditions that normally cause corrosion of metal.

Bonding of Organic Finishes

The bonding of paint, lacquer, and organic finishes to chromate conversion coatings is excellent. In addition to promoting good initial adhesion, their protective nature prevents subsequent loss of adhesion that is due to underfilm corrosion. This protection continues even thought he finish has been scratched through to the bare metal. It is necessary that the organic finishes used have good adhesive properties, because bonding must take place on a smooth, chemically clean surface; this is not necessary with phosphate-type conversion coatings, which supply mechanical adhesion that is due to the crystal structure of the coating.

Chemical Polishing

Certain chromate treatments are designed to remove enough basis metal during the film-forming process to produce a chemical polishing, or brightening, action. Generally used for decorative work, most of these treatments produce very thin, almost colorless films. Being thin, the coatings have little optical covering power to hide irregularities. In fact, they may accentuate large surface imperfections. In some instances, a leaching or "bleaching" step subsequent to chromating is used to remove traces of color from the film.

If chemical-polishing chromates are to be used on electroplated articles, consideration must be given to the thickness of the metal deposit. Sufficient thickness is necessary to allow for metal removal during the polishing operation.

Absorbency and Dyeing

When initially formed, many films are capable of absorbing dyes, thus providing a convenient and economical method of color coding. These colors supplement those that can be produced during the chromating operation, and a great variety of dyes is available for this purpose. Dyeing operations must be conducted on freshly formed coatings. Once the coating is dried, it becomes nonabsorbent and hydrophobic and cannot be dyed. The color obtained with dyes is related to the character and type of chromate film. Pastels are produced with the thinner coatings, and the darker colors are produced with the heavier chromates. Some decorative use of dyed finishes has been possible when finished with a clear lacquer topcoat, though caution is required because the dyes may not be lightfast.

In a few cases, film colors can be modified by incorporation of other ions or dyes added to the treatment solution.

Hardness

Although most coatings are soft and easily damaged while wet, they become reasonably hard and will withstand considerable handling, stamping, and cold form-

ing. They will not, however, withstand continued scratching or harsh abrasion. A few systems have been developed that possess some degree of "wet-hardness," and these will withstand moderate handling before drying.

Heat Resistance

Prolonged heating of chromate films at temperatures substantially above 150°F (66°C) can decrease their protective value dramatically. There are two effects of heating that are believed to be responsible for this phenomenon. One is the insolubilization of the hexavalent chromium, which renders it ineffective as a corrosion inhibitor. The second involves shrinking and cracking of the film, which destroys its physical integrity and its value as a protective barrier.

Many factors, such as the type of basis metal, the coating thickness, heating time, temperature, and relative humidity of the heated atmosphere, influence the degree of coating damage. Thus, predictions are difficult to make, and thorough performance testing is recommended if heating of the coating is unavoidable.

The heat resistance of many chromates can be improved by certain posttreatments or "sealers." Baking at paint-curing temperatures after an organic finish has been applied is a normal practice and does not appear to affect the properties of the treatment film.

Electrical Resistance

The contact resistance of articles that have been protected with a chromate conversion coating is generally much lower than that of an unprotected article that has developed corroded or oxidized surfaces. As would be expected, the thinner the coating, the lower the contact resistance, i.e., clear coatings have the least resistance, iri-

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Table I. Common Uses of Chromate Conversion Coatings

	General Usage				
Metal	*Corrosion Resistance*	*Paint Base*	*Chemical Polish*	*Metal Coloring*	*Remarks*
Aluminum	X	X		X	Economical replacement for anodizing if abrasion resistance is not required. Used to "touch-up" damaged areas on anodized surfaces.
Cadmium	X	X	X	X	
Copper	X	X	X	X	Thin coatings prevent "spotting out"of brass and copper electrodeposits. No fumes generated during chemical polishing.
Magnesium	X	X			
Silver	X				
Zinc	X	X	X	X	

descent yellow coatings have slightly more, and the heavy, olive drab coatings have the greatest. If exposure of an article to corrosive conditions is anticipated, the choice of a coating thickness normally involves a compromise between a very thin film—which, although having very low initial contact resistance, is likely to allow early development of high electrical resistance corrosion products—and a heavier film, with somewhat higher initial contact resistance, but which is likely to remain relatively constant for a longer period under corrosive conditions.

Fabrication

Resistance Welding. Thin chromate films do not interfere appreciably with spot, seam, or other resistance-welding operations. Aluminum coated with a thin, nearly colorless film, for example, can be spot welded successfully with no increase in welding machine settings over those required for bare metal. Metal coated with thicker, colored films also can be resistance welded. The increased contact resistance of thicker coatings, however, necessitates using slightly higher machine settings.

Fusion Welding. These operations, likewise, are not hampered by the presence of chromate films. It has been reported, in fact, that chromate treatments on aluminum actually facilitate inert gas welding of this metal and its alloys, producing contamination-free welds.

Soldering. Cadmium and silver surfaces coated with thin chromate films can be soldered without difficulty using a mild organic flux. Conflicting reports exist regarding the solderabilty of chromated zinc surfaces.

Mechanical Fastening. The assembly of chromated parts using bolts, rivets, and other mechanical fastening devices usually results in local damage to the chromate film. Corrosion protection in these areas will depend upon the effectiveness of the self-healing properties of the surrounding coating.

Summary of Common Uses

Table I summarizes the most common applications of chromate conversion coatings.

MATERIALS OF CONSTRUCTION

Generally, suppliers of proprietaries recommend materials for use with their products, which are resistant to oxidants, fluorides, chlorides, and acids. Materials that have been found

to be satisfactory for most chromating applications are stainless steels and plastics. Stainless steels such as 304, 316, 317, and 347 are suitable for tanks and

heaters where chlorides are absent. Containers and tank linings can be made from plastics such as polyvinyl chloride (PVC), polyvinylidine chloride (PVDC), polyethylene, and polypropylene. Acid-resistant brick or chemical stoneware is satisfactory for some applications, but is subject to attacks by fluorides.

Parts-handling equipment is made of stainless steel, plastisol-coated mild steel, or plastic.

Mild steel can be used for leaching tanks because the solutions are generally alkaline, whereas tanks for dyeing solutions, which are slightly acid, should be of acid-resistant material.

Usually, ventilation is not necessary because most chromate solutions are operated at room temperature and are nonfuming. Where chromating processes are heated, they should be ventilated.

FILM FORMATION

Mechanism

The films in most common use are formed by the chemical reaction of hexavalent chromium with a metal surface in the presence of other components, or "activators," in an acid solution. The hexavalent chromium is partially reduced to trivalent chromium during the reaction, with a concurrent rise in pH, forming a complex mixture consisting largely of hydrated basic chromium chromate and hydrous oxides of both chromium and the basis metal. The composition of the film is rather indefinite, because it contains varying quantities of the reactants, reaction products, and water of hydration, as well as the associated ions of the particular systems.

There are a number of factors that affect both the quality and the rate of formation of chromate coatings. Of the following items, some are peculiar to chromating; many derive simply from good shop practice. A working understanding of these factors will be helpful in obtaining high-quality, consistent results. Different formulations are required to produce satisfactory chromate films on various metals and alloys. Similarly, the characteristics of the chromate film produced by any given solution can vary with minor changes in the metal or alloy surface. Commonly encountered examples of this follow.

Effect of Basis Metals

Aluminum Alloys. The ease with which coatings on aluminum can be produced, and the degree of protection afforded by them, can vary significantly with the alloying constituents and/or the heat treatment of the part being processed. In general, low alloying constituent metals that are not heat treated are easiest to chromate and provide the maximum resistance to corrosion. Conversely, wrought aluminum, which is high in alloying elements (especially silicon, copper, or zinc) or which has undergone severe heat treatment, is more difficult to coat uniformly and is more susceptible to corrosive attack. High silicon casting alloys present similar problems. The effect of these metal differences, however, can be minimized by proper attention to the cleaning and pretreatment steps. Most proprietary treatment instructions contain detailed information regarding cleaning, desmutting, etc., of the various alloys.

Magnesium Alloys. As in the case of aluminum, the alloying element content and the type of heat treatment affect the chromating of magnesium. With the exception of the dichromate treatments listed as Type III in Military Specification MIL-M-3171, all of the treatments available can be used on all the magnesium alloys.

Zinc Alloys. Chromate conversion coatings on zinc electroplate are affected by impurities codeposited with the zinc. For example, dissolved cadmium, copper, and lead in zinc plating solutions can ultimately cause dark chromated films. Similarly, dis-

solved iron in noncyanide zinc plating solutions can create chromating problems. Furthermore, the activity of zinc deposits from cyanide and noncyanide solutions can differ sufficiently to produce variations in the chromate film character.

Variations in the composition of zinc die casting alloys and hot-dipped galvanized surfaces can also affect chromate film formation; however, in the latter case, the result is usually difficult to predict, due to the wide variations encountered in spelter composition, cooling rates, etc. Large differences in the chromate coating from spangle to spangle on a galvanized surface are not uncommon. This is especially evident in the heavier films.

Copper Alloys. Since chromate treatments for copper and its alloys can be used to polish chemically as well as to form protective films, the grain structure of the part becomes important, in addition to its alloying content. Whereas fine-grained, homogeneous material responds well to chromate polishing, alloys such as phosphor bronze and heavily leaded brass usually will acquire a pleasing but matte finish. In addition, treatment of copper alloys, which contain lead in appreciable amounts, may result in the formation of a surface layer of powdery, yellow lead chromae.

Effects of pH

One of the more important factors in controlling the formation of the chromate film is the pH of the treatment solution. For any given metal/chromate solution system, there will exist a pH at which the rate of coating formation is at a maximum. As the pH is lowered from this point, the reaction products increasingly become more soluble, tending to remain in solution rather than deposit as a coating on the metal surface. Even though the rate of metal dissolution increases, the coating thickness will remain low. Chemical-polishing chromates for zinc, cadmium, and copper are purposely operated in this low pH range to take advantage of the increased rate of metal removal. The chromate films produced in these cases can be so thin that they are nearly invisible. Beyond this point, further lowering of the pH is sufficient to convert most chromate treatments into simple acid etchants.

Increasing the pH beyond the maximum noted above will gradually lower the rate of metal dissolution and coating formation to the point at which the reaction, for all practical purposes, ceases.

Hexavalent Chromium Concentration

Although the presence of hexavalent chromium is essential, its concentration in many treatment solutions can vary widely with limited effect, compared with that of pH. For example, the chromium concentration in a typical aluminum treatment solution can vary as much as 100% without substantially affecting the film-formation rate, as long as the pH is held constant. In chromating solutions for zinc or cadmium, the hexavalent chromium can vary fairly widely from its optimum concentration if the activator component is in the proper ratio and the pH is constant.

Activators

Chromate films normally will not form without the presence of certain anions in regulated amounts. They are commonly referred to as "activators' and include acetate, formate, sulfate, chloride, fluoride, nitrate, phosphate, and sulfamate ions. The character, rate of formation, and properties of the chromate film vary with the particular activator and its concentration. Consequently, many proprietary formulations have been developed for specific applications and they are the subject of numerous patents. Usually, these proprietary processes contain the optimum concentrations of the activator and other components; therefore, the user need not be

concerned with the selection, separate addition, or control of the activator.

OPERATING CONDITIONS

In addition to the chemical make-up of the chromating solution, the following factors also govern film formation. Once established for a given operation, these parameters should be held constant.

Treatment Time. Immersion time, or contact time of the metal surface and the solution, can vary from as little as 1 second to as much as 1 hour, depending on the solution being used and metal being treated. If prolonged treatment times are required to obtain desired results, a fault in the system is indicated and should be corrected.

Solution Temperature. Chromating temperatures vary from ambient to boiling, depending on the particular solution and metal being processed. For a given system, an increase in the solution temperature will accelerate both the film-forming rate and the rate of attack on the metal surface. This can result in a change in the character of the chromate film. Thus, temperatures should be adequately maintained to ensure consistent results.

Solution Agitation. Agitation of the working solution, or movement of the work in the solution, generally speeds the reaction and provides more uniform film formation. Air agitation and spraying have been used for this purpose. There are, however, a few exceptions where excessive agitation will produce unsatisfactory films.

Solution Contamination

Although the presence of an activator in most treatment solutions is vital, an excessive concentration of this component, or the presence of the wrong activator, can be very detrimental. Most metal-finishing operations include sources of potential activator contamination in the form of cleaners, pickles, deoxidizers, and desmutters. Unless proper precautions are taken, the chromate solution can easily become contaminated through drag-in of inadequately rinsed parts, drippage from racks carried over the solution, etc.

A common source of contamination is that resulting from improperly cleaned work. If allowed to go unchecked, soils can build on the surface of the solution to the point at which even clean work becomes resoiled on entering the treatment tank, resulting in blotchy, uneven coatings.

Other contaminants to be considered are those produced by the reactions occurring in the treatment solution itself. With very few exceptions, part of the trivalent chromium formed and

part of the basis metal dissolved during the coating reaction remain in the solution. Small amounts of these contaminants can be beneficial, and "broken-in" solutions often produce more consistent results. As the concentration of these metal contaminants increases, effective film formation will be inhibited. For a certain period, this effect can be counteracted by adjustments, such as lowered pH and increased hexavalent chromium concentration. Eventually, even these techniques become ineffective, at which point the solution must be discarded or a portion withdrawn and replaced with fresh solution.

Rinsing and Drying

Once a chromate film has been formed satisfactorily, the surface should be rinsed as soon as possible. Transfer times from the chromating stage to the rinsing stage should be short in order to minimize the continuing reaction that takes place on the part.

Although rinsing should be thorough, this step can also affect the final character

Table II. Typical Salt Spray Data for Electroplated Zinc

Treatment	*Hours to White Corrosion*
Untreated	<8
Clear chromate	24-100
Iridescent yellow	100-200
Olive drab	100-500

of the chromate film and should be controlled with respect to time and temperature, for consistent results.

Prolonged rinsing or the use of very hot rinsewater can dissolve, or leach, the more soluble hexavalent chromium compounds from a freshly formed coating, resulting in a decrease in protective value. If a hot rinse is used to aid drying, avoid temperatures over about 150°F (66°C) for more than a few seconds. This leaching effect sometimes is used to advantage. In instances in which a highly colored or iridescent coating may be objectionable, a prolonged rinse in hot water can be used as a "bleaching" step to bring the color to an acceptable level. Instead of hot water leaching, some systems incorporate dilute acids and alkalis to accelerate this step.

Solution Control

Because most chromate processes are proprietary, it is suggested that the suppliers' instructions be followed for solution make-up and control. Even though specific formulations will not be discussed, certain general principles can be outlined, which apply generally to chromate solutions. The combination of hexavalent chromium concentration, activator type and concentration, and pH, i.e., the "chemistry" of the solution, largely determines the type of coating that will be obtained, or whether a coating can be obtained at all, at given temperatures and immersion times. It is important that these factors making up the "chemistry" of the solution be properly controlled. As the solution is depleted through use, it is replenished by maintenance additions, as indicated by control tests or the appearance of the work.

Fortunately, analysis for each separate ingredient in a chromate bath is not necessary for proper control. A very effective control method uses pH and hexavalent

Table III. Typical Salt Spray Data for Copper and Brass

Treatment	*Hours to Green Corrosion*
Copper, untreated	<24
Copper, bright chromate	24
Copper, heavy chromate	50
Brass, untreated	24
Brass, bright chromate	100
Brass, heavy chromate	150

Table IV. Typical Salt Spray Data for Aluminum

Hours to White Corrosion			
Alloy	*No Treatment*	*Clear*	*Yellow-Brown*
3003	24	60-120	250-800
2024[a]	<24	40-80	150-600
413.0	<24	12-24	50-250

[a]Heat treatment will affect the final results.

chromium analysis. The pH is determined with a pH meter and the chromium is determined by a simple titration. Indicators and pH papers are not recommended because of discoloration by the chromate solution. Additions are made to the solution to keep these two factors within operating limits. The amount of control actually required for a given treatment depends on how wide its operating limits are, and on the degree of uniformity of results desired. Control by pH alone is adequate in some cases.

COATING EVALUATION

Chromate conversion coatings are covered by many internal company standards and/or U.S. government and American Society for Testing and Materials (ASTM) specifications. These standards usually contain sections on the following methods of evaluation.

Visual Inspection

The easiest way to evaluate chromate conversion coatings is to observe the color, uniformity of appearance, smoothness, and adhesion. Type of color and iridescence is a guide to film thickness, which is considered proportional to protective value; however, visual inspection by itself is not sufficient to indicate the protective value of the coating, especially if the film has been overheated during drying.

Accelerated Corrosion Test

The salt spray test, ASTM B 117, is the most common accelerated test developed in specification form. Although some disagreement exists as to the correlation of salt spray tests to actual performance, it remains in many specifications. Variations in results are often obtained when tested in different salt spray cabinets, and even in different locations within the same cabinet. Coatings should be aged for at least 24 hours before testing, for consistent results. Generally, specifications require a minimum exposure time before visible corrosion forms. Typical salt spray test data are provided in Tables II to IV.

Humidity Tests

There appears to be no standard specification covering humidity tests for unpainted chromate conversion coatings. Evaluations are conducted under various conditions and cycles. Humidity tests may be more useful than salt spray tests, as they correspond to the normal environment better than the salt spray, except in marine atmospheres.

Water Tests

Immersion tests in distilled or deionized water have proven valuable in simulating such conditions as water accumulation in chromated zinc die castings, e.g., carburetors and fuel pumps.

Coatings applied on hot-dipped galvanized surfaces in strip mills are often tested by stacking wet sheets and weighing the top sheet. Periodic checks are made to determine when corrosion products first develop. The tests should be conducted at relatively constant temperatures to ensure consistent results.

Chemical and Spot Tests

The amount of hexavalent chromium in the film can be an indication of the corrosion protection afforded by the coating. Analytical procedures for small amounts of chromium on treated surfaces are comparatively rapid, quantitative, and reproducible. Consequently, chemical analysis for the chromium content of the film appears to be a valuable tool. It would not be suitable, however, for predicting the

performance of bleached, overheated, excessively dehydrated coatings.

Total coating weight is sometimes used as an indication of corrosion resistance. It is derived by weighing a part having a known surface area before and after chemically stripping only the chromate film.

Spot tests are used to test corrosion resistance by dissolving the chromate coating and reacting with the basis metal. The time required to produce a characteristic spot determines empirically the film thickness or degree of corrosion protection. It is advisable to use these tests as comparative tests only, always spotting an untreated and treated surface at the same time. Frequently, the spot tests are sufficient only to indicate differences between treated and untreated surfaces. Reproducibility is not good because aging affects the results.

Performance Tests for Organic Finishes

Paint, lacquer, and other organic finishes on chromate conversion coatings are tested in numerous ways to evaluate bonding and corrosion protection. These include pencil-hardness, cross-hatch, bending, impact, and tape tests with or without prior exposure to water or salt spray.

SPECIFICATIONS

A list of the more commonly used specifications covering chromate conversion coatings on different basis metals follows. Only the basic specification or standard number is listed, and reference should be made only to the appropriate revision of any particular document.

Aluminum

AMS 2473—Chemical Treatment for Aluminum Base Alloys—General Purpose Coating
AMS 2474—Chemical Treatment for Aluminum Base Alloys—Low Electrical Resistance Coating
ASTM D 1730—Preparation of Aluminum and Aluminum Alloy Surfaces for Painting
MIL-C-5541—Chemical Films and Chemical Film Material for Aluminum and Aluminum Alloys
MIL-C-81706—Chemical Conversion Materials for Coating Aluminum and Aluminum Alloys
MIL-W-6858—Welding, Resistance: Aluminum, Magnesium, etc.; Spot and Seam

Cadmium

AMS 2400—Cadmium Plating
AMS 2416—Nickel-Cadmium Plating, Diffused
AMS 2426—Cadmium Plating, Vacuum Deposition
ASTM B 201—Testing Chromate Coatings on Zinc and Cadmium Surfaces
MIL-C-8837—Cadmium Coating (Vacuum Deposited)
QQ-P-416—Plating, Cadmium (Electrodeposited)

Magnesium

AMS 2475—Protective Treatments, Magnesium Base Alloys
MIL-M-3171—Magnesium Alloy, Process for Pretreatment and Prevention of Corrosion on
MIL-W-6858—Welding, Resistance: Aluminum, Magnesium, etc.; Spot and Seam

Silver

QQ-S-365—Silver Plating, Electrodeposited, General Requirements for

Zinc

AMS 2402—Zinc Plating
ASTM B 201—Testing Chromate Coatings on Zinc and Cadmium Surfaces
ASTM D 2092—Preparation of Zinc-Coated Steel Surfaces for Painting
MIL-A-81801—Anodic Coatings for Zinc and Zinc Alloys
MIL-C-17711—Coatings, Chromate, for Zinc Alloy Castings and Hot-Dip Galvanized Surface
MIL-T-12879—Treatments, Chemical, Prepaint and Corrosion Inhibitive, for Zinc Surfaces
MIL-Z-17871—Zinc, Hot-Dip Galvanizing
QQ-Z-325—Zinc Coating, Electrodeposited, Requirements for

SPECIAL TREATMENTS

Solutions containing chromium compounds are used in some processes where disagreement exists as to whether these form "true" chromate conversion coatings or combination coatings, or act as passivating processes.

Electrolytic Processes

Although early chromate conversion coatings for zinc were electrolytically applied, this method has been largely replaced by immersion processes. More recently, the use of electric current has reappeared with solutions containing mixtures of chromates, phosphates, fluorides, etc., to produce "anodic coatings." The coatings, however, are not similar to anodic coatings such as those produced on aluminum. The coatings on zinc surfaces are complex combinations of chromates, phosphates, oxides, etc. They are formed with 100-200 V AC or DC, and the fritted coating will withstand more than 1,000 hr of salt spray. The process is used where outstanding corrosion resistance is needed. The coating also exhibits superior hardness, heat resistance, thickness, and dielectric strength when compared with normal chromate conversion coatings. Colors range from dark green to charcoal for different processes.

Electrolytic treatments using chromium compounds are also applied to steel strip, where chromium along with oxides, etc., are deposited in a very thin, discontinuous film. These processes, which promote lacquer and paint adhesion, may be more chromium plate than chromate coating.

Coatings on Beryllium

It has been reported that chromate conversion coatings can be applied to beryllium to retard high-temperature oxidation in humid air.

Chromate-Phosphate Treatments

Chromate-phosphate treatments are based on chromate-phosphate mixtures and form a combination conversion coating on aluminum. The coating can appear practically colorless to a light-green hue. These treatments have been used to impact color for decorative purposes or to provide an imposed base for subsequent lacquer or paint operations.

TRIVALENT CHROME CONVERSION COATING FOR ZINC AND ZINC ALLOYS

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In the late 1990s the End-of-Life-Vehicle (ELV) directives were introduced in Europe, mandating the recycling of 85% of vehicles by weight by the year 2006. Recycled components should be free of compounds or elements known to be hazardous to man or the environment. Among the restricted items are carcinogenic hexavalent chromium compounds. Consequently, the directive imposed a limit of 2 g of Cr(6) per vehicle to be met by July 2003. Leachable hexavalent chrome can be found in the conversion coating layer used to passivate zinc and zinc alloy plated surfaces. The amount of Cr(6) varies from 5 to 400 mg/M^2 depending on the type of passivation used, and is typically low for light blue coatings and heavier for the thicker yellow and olive green types.

To insure compliance with the new regulation and eliminate the need for constant monitoring, the European car industry opted for the total removal of hexavalent chrome from their plated finishes. The U.S. car industry soon adopted the same restrictions and standardized finishes across their worldwide operations.

The search for a viable Cr(6)-free conversion coating with similar functional properties led researchers ultimately to the selection of trivalent chrome passivation as the most adequate alternative to date. Availability of raw materials, safety, economical considerations, and ease of adaptability to existing finishing plants were important factors in the selection of this technology as a viable replacement process.

TRIVALENT CHROME PASSIVATION TECHNOLOGY

Trivalent chromium compounds are readily available, noncarcinogenic, and safe to handle. Some compounds are used extensively in many applications such as dyeing and waterproofing of fabrics, printing, wood preservation, chrome plating, and other industrial processes. Trivalent chrome conversion coating technology was introduced commercially in the late 1980s as an earlier attempt at replacing carcinogenic hexavalent chrome from as many processes in metal finishing as possible. Although there were no regulations or specifications requiring this change at the time, platers realized the environmental and safety advantages from such a substitution, along with improved and more reliable performance. The first generation of Cr(3) conversion coatings was limited to producing blue-bright passivation designed for light service conditions, meeting 12 to 24 hr of neutral salt spray (NSS) to white zinc corrosion. Further development was needed to meet the full range of automotive and other industry requirements for extended corrosion resistance.

The mechanism of Cr^{6+} conversion coating and its corrosion resistance was used in developing a comparable substitute process.

Upon immersion of zinc plated parts in hexavalent chromating solutions, zinc is oxidized at the interface by the Cr^{6+}, which is reduced to Cr^{3+}, dissolves at a controlled rate in the acidic solution, and reacts with Cr^{3+} to form zinc chromium oxide compounds. An increase in the pH at the interface causes the trivalent chrome compounds to precipitate on the surface, forming a gelatinous film

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Table I. Average Film Composition of Hexavalent Yellow Chromate Conversion Coating

Composition	*% by wt*
Cr^{6+}	8.7
Cr^{3+}	28.2
S (as sulfate)	3.27
Zn^{2+}	2.12
Na^{+}	0.32
Water	19.3
Oxygen	Bal.

consisting of hydrated chromic-chromate, chromium hydroxide, and zinc and other metal oxides. The film traps some soluble hexavalent chrome as well from the solution. The reaction is fast and takes place at ambient temperatures.

Trivalent chrome passivating solutions work on the same basic principle except for the omission of Cr^{6+} oxidation step. They rely on the direct reaction of Cr^{3+} with the dissolved zinc and produce insoluble barrier layers of zinc chromium oxide precipitated on the surface in a similar fashion as with Cr(6) passivation, although under different reaction kinetics.

Table I shows an average composition of a hexavalent chrome yellow conversion coating film over zinc plate. The film consists of 8 to 10% of leachable Cr(6). This is the portion of the film responsible for the self-healing effect associated with this type of passivation. If the film is scratched or mechanically damaged, moisture dissolves the leachable Cr(6) restoring the conversion film and resealing the damaged area. This mechanism works as long as the Cr(6) content is not dehydrated by exposure to temperatures above 50 to 60°C for an extended period of time. The balance of the film composition consists of insoluble trivalent chrome compounds of zinc, oxides, sulfates, and water. This portion of the film, defined as a barrier coating, provides the bulk of the corrosion protection and accounts for about 90% by weight of the film. It is worthwhile noting that trivalent compounds amount to a third of the composition as Cr(3). The thickness of a typical yellow hexavalent chrome passivation film on zinc plate was measured at 350 nm.

It was postulated that excluding the hexavalent chrome portion from this film while maintaining its thickness would still provide essentially similar corrosion resistance properties. Some differences are to be expected such as a change in the yellow appearance typically associated with Cr(6) compounds.

Table II. Operating Conditions and Coating Films

Parameters	*Cr(6) Yellow Passivation*	*Cr(3) Thin Layer Passivation*	*Cr(3) Thick Layer Passivation*
Make up, % volume	0.5-1.5%	2-8%	10-13%
pH	1-2	1.8-2.4	1.6-2.2
Temperature, °C	20-25	20-25	55-56
Time, Sec	30-45	30-60	30-60
Agitation	Mechanical or air	Mechanical or air	Mechanical or air
Activation	Dilute acid	Dilute nitric or sulfuric	Dilute nitric or sulfuric
Film color	Yellow iridescent	Blue bright iridescent	Light green hue
Film thickness, nm	300-350	60-80	300-350

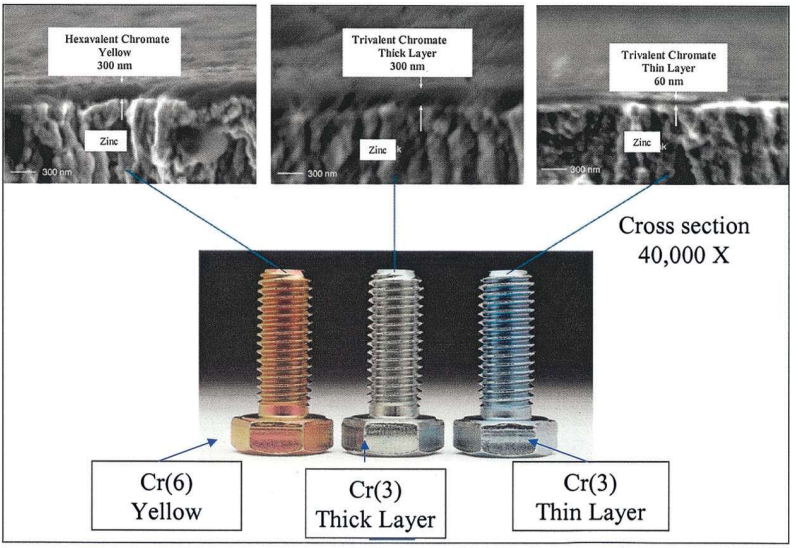


Fig. 1. Passivation film thickness.

First-generation trivalent chrome conversion processes were based on fairly stable Cr(3) complexes, which slowed their reactivity rates even at high temperatures. They produced film thicknesses of 20 to 30 nm with limited corrosion resistance. To produce thicker passivation layers, a second-generation trivalent passivation process was developed. It incorporates accelerators, modified complexors, and is operated at higher concentration and temperature to drive the reaction kinetics at a faster rate. When applied as recommended, film thicknesses of 300 to 380 nm, equivalent to those produced from yellow Cr(6) passivating solutions, were obtained. The film in this case consists of an insoluble barrier layer free of hexavalent chrome.

Table II and Fig. 1 compare operating conditions and resulting conversion coating films produced by various passivating solutions.

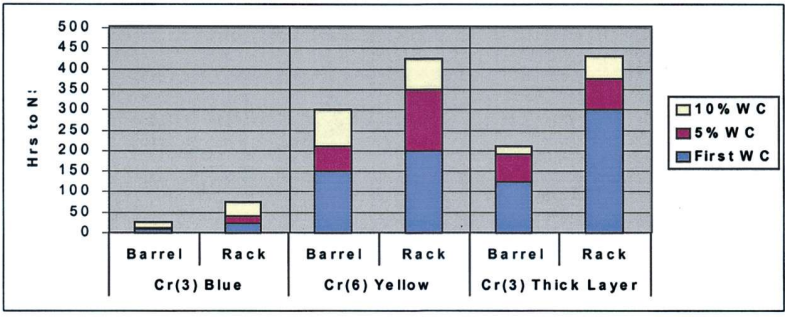


Fig. 2. Comparison of neutral salt spray results for Cr(6) versus Cr(3) passivation on zinc (WC [minus] white corrosion).

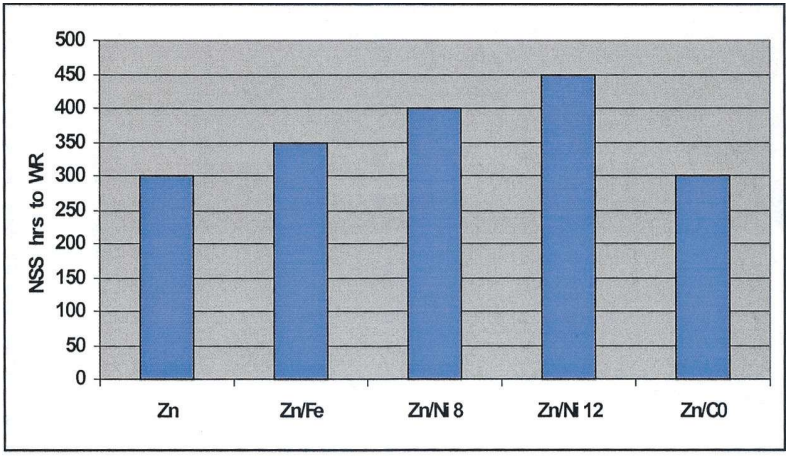


Fig. 3. Neutral salt spray results for Cr(3) thick layer passivation of zinc and zinc alloys.

TRIVALENT CHROMATE PASSIVATION PROPERTIES

Trivalent chrome passivation films are similar to hexavalent types as far as the barrier portion of the coating is concerned in many respects; however, the absence of soluble Cr(6) compounds contributes to a range of new properties.

Corrosion Resistance

NSS corrosion testing data per ASTM B 117 of zinc and zinc alloy plated surfaces with Cr(6) and Cr(3) passivation are illustrated in Figs. 2 and 3. Results support the concept of thick layer trivalent chrome passivation being a viable alternative to conventional hexavalent chromate. In all cases, except for barrel plated work, its performance matches or exceeds that of hexavalent types. This is due to mechanical damage to the passivation film during bulk processing and the absence of self-healing properties. This shortcoming is overcome by the use of sealers or topcoats to protect the film. Postpassivation treatment increases corrosion resistance further, and provides the flexibility to add a range of properties such as lubricity, torque-tension modification for fasteners, and developing various colored finishes.

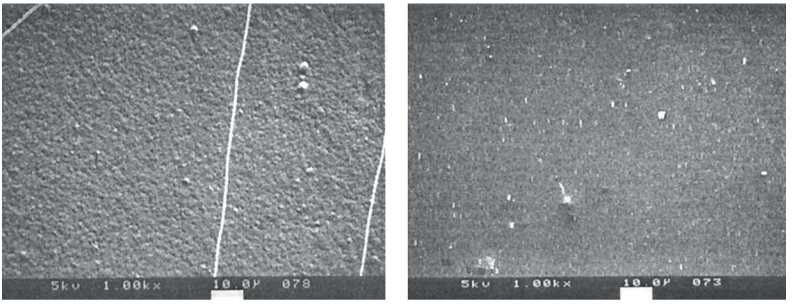


Fig. 4. Scanning electron micrograph of Cr(6) at left and Cr(3) at right. Passivation films dried at room temperature prior to heat treatment at 1,000[times].

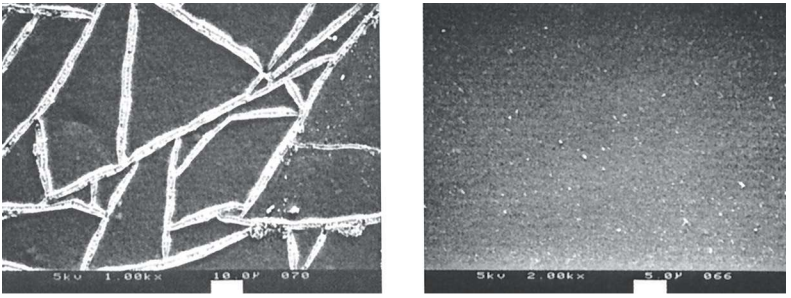


Fig. 5. Scanning electron micrographs of Cr(6) at left and Cr(3) at right. Passivation films after heat treatment at 200°C for 1 hr at 1,000[times].

Heat Resistance

An advantage of trivalent chrome passivation is its superior resistance to high temperatures. Unlike hexavalent chrome passivation films, they can be heated to 200°C or more for extended periods of time and still maintain up to 70% of their original resistance. Hexavalent chromate films dehydrate and fail entirely when heated above 55°C for more than a few minutes. Figs. 4 and 5 show the surface analysis of both types of conversion coatings before and after heat treatment. After the coatings have formed and dried, hexavalent chromate films show a pattern of cracks or fissures as a result of partial dehydration of the adsorbed Cr(6) content. Upon heat treating, total dehydration takes place and Cr^{6+} is reduced to Cr^{3+}, widening and deepening the cracks, exposing zinc, and resulting in premature corrosion failure. By contrast, the trivalent chrome passivation film, consisting of the more stable oxidation state Cr(3) compounds, is more homogeneous and crack free. It remains unchanged after heat treatment. This property is used to great advantage when zinc plated parts must be heat treated for hydrogen embrittlement relief. This is done typically without passivation, which would otherwise be destroyed. The need to replate with a thin layer of zinc after baking to apply an adherent conversion coating is eliminated. Parts passivated with trivalent chrome can be heat treated with no change in appearance and minimum loss of corrosion protection. The choice of sealers and topcoats must be carefully considered if parts are to be heat treated as some types of sealers could reduce this advantage either by corrosive chemical attack or by dehydrating and inducing cracking in the underlying passivation film.

Appearance

Trivalent chrome passivation produces a range of colored films. Thin layers are typically iridescent blue, while thicker coatings are pale green to yellow blue depending on whether the zinc is alloyed and the specific alloying element. Since hexavalent chrome is the source of yellow color in conventional conversion coatings, this color is not usually available in Cr(6)-free coatings unless induced by dyes or other metals and their oxides. The use of transparent sealers and topcoats can modify the appearance of the coating producing silver-white or pale-colored films free of iridescence. Black coatings may be obtained with specially modified trivalent chrome passivating solutions containing metals, such as cobalt or iron, but are difficult to control. Deep uniform black finishes are best produced on zinc-iron alloys. Other alternatives for black finishes over trivalent

chrome coatings include organic topcoats applied by the dip-spin process, suitable for bulk-processed parts such as fasteners and other barrel-plated work. After passivation and rinsing in such a process, parts are transferred into baskets, immersed in the blackening solution, spin-dried in a centrifuge under controlled rotational speed to remove excess liquid, then dried at a specified curing temperature.

POSTPASSIVATION TREATMENT

The use of postpassivation may be necessary in order to accomplish one or more of the following functions:

1. Modify the color of the conversion coating film
2. Provide specific lubrication or coefficient of friction for threaded components
3. Extend the corrosion resistance particularly for barrel and bulk processed parts.

There are several commercially available types of postpassivation treatments. Thorough testing of the selected system under simulated end use conditions is recommended in order to qualify the process for the intended application. This may include heat treatment prior to accelerated corrosion or torque-tension testing on components for near engine exposure.

Sealers

These are types of products that will react with the conversion coating film and result in more durable resistant finishes. Examples of sealers are silicate-based products applied at either room or elevated temperatures. The latter will leach out a small portion of the passivation film and leave a heavier protective layer of silicate reaction products on the surface. This type of sealers may not be adequate for high-temperature exposure depending on the type and degree of alkalinity of the residual silicate film and their resistance to cracking. Aged residual film alkalinity may represent hazardous handling problems and should be adequately investigated. Other types of sealers may contain phosphates, silanes, and transition metals.

Topcoats

These may be organic lacquers, polymers, lubricants, waxes, oils, and oil emulsions with suspended particles and coloring dyes. They may be applied by immersion, spray, or dip-spinning. A topcoat used commercially for zinc plate consists of coatings containing zinc or aluminum flakes to provide protection against galvanic corrosion between the fasteners and magnesium or aluminum surfaces. The dip-spin process has also been used to apply black finishes with torque modification properties for fasteners and washers. Generally, drying prior to the application of topcoats produces more uniform, heavier films with better corrosion protection.

TYPICAL PROCESS SEQUENCE

1. Zinc or zinc alloy plate
2. Rinse
3. Activate (dilute acid)
4. Trivalent chrome passivate
5. Drag out rinse (optional)
6. Rinse (counter-current flow)

Table III. Automotive Standards 8-9 μm of Zinc Plate with Hexavalent Chrome-Free Passivation and Sealer (NSS Test Requirements per ASTM B 117)

Auto Maker	*Hrs—White Corrosion*	*Hrs—Red Corrosion*	*Heat Treatment Required*	*Conditions*
GM			May be specified	
3044				
Clear/Blue/Black	120	240		150°C/1 hr
Yellow-Iridescent	120	360		150°C/1 hr
Ford				
WSS-M12P17B1/B3				
Clear/Silver white	96	384	No	
Clear/Silver white	72	360	Yes	120°C/4 hrs
Daimler Chrysler			May be specified	
PS 1207 - R				
Iridescent—Rack	200			
Iridescent—Barrel	160			
Irridescent—Rack	120			
No sealer				
Iridescent—Barrel	100			
No sealer				

As of Aug. 2001 (Subject to change).

7. Dry (optional or as recommended)
8. Seal and/or topcoat
9. Dry

PROCESS CONTROL

Trivalent chromate conversion coatings are applied over acid or alkaline electroplated zinc and zinc alloys in conventional plating lines replacing existing hexavalent chrome tanks, with little or no modification to the line. Provisions for heating may be required along with proper ventilation. Postpassivation may be used in-line if it is compatible with the operation and space for extra stations is available. Organic topcoats, especially for barrel plating processes, are best applied off-line.

The critical operating parameters are the chrome content, pH, and temperature.

Analytical methods for trivalent chrome using spectrophotometric or simple titration techniques are commonly used and readily available. Chrome content affects the ultimate film thickness. Temperature and pH control the reaction kinetics, film strength, and adhesion.

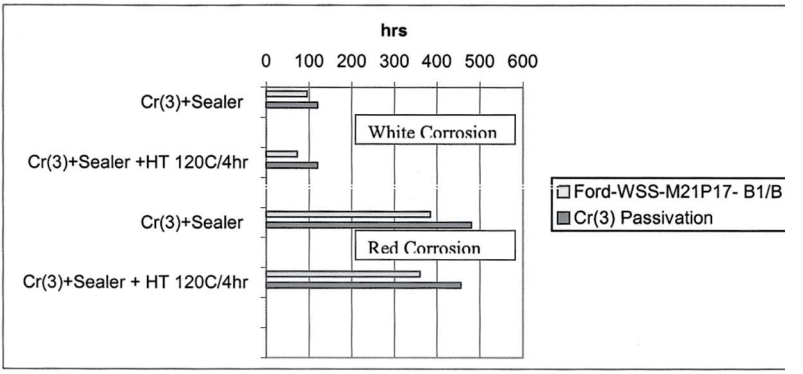


Fig. 6. Cr(3) passivation surpasses requirements for Ford.

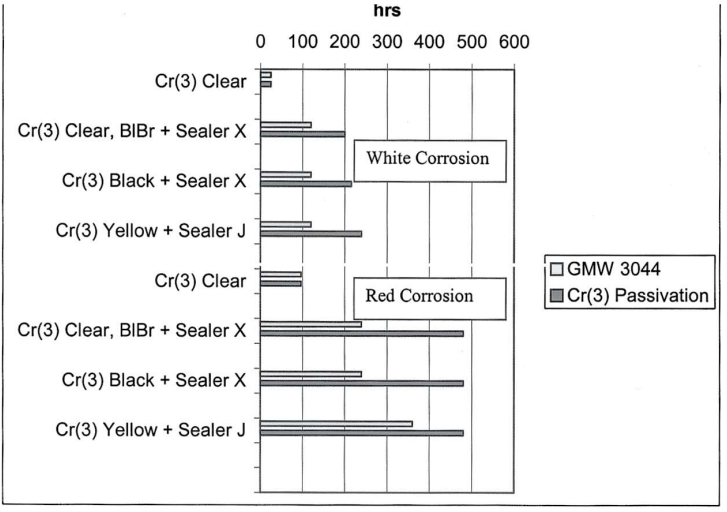


Fig. 7. Cr(3) passivation meets or surpasses requirements for GM.

EFFECT OF CONTAMINANTS

The most common contaminants are zinc and iron resulting from processed parts. Excessive amounts of these metals result in the formation of uneven thin coatings and yellowing of the deposit with possible reduction in corrosion resistance. Removal methods of these metals by precipitation and selective ion exchange are available.

Drag-in of alkalinity affects the bath pH and can be corrected with mineral acids as recommended for the specific process.

BATH LIFE

Trivalent chrome passivating solutions have much longer bath life than their hexavalent counterparts. There is no composition imbalance resulting from gradual depletion of Cr(6) and buildup of reduced Cr(3). The corrosive effect is lower, and dissolution and buildup of zinc and iron are reduced. As a result, the solution composition is more stable over time. Unless there is gross contamination, these baths will perform satisfactorily for long periods of time. Under proper steady state conditions, the solution can last indefinitely.

The use of a drag-out tank and multiple counter-current flow rinsing after the passivation step is recommended. Solution from the drag-out can be returned to the process tank, reducing chemical consumption drastically. Evaporators can be used with the drag-out tank to improve the reuse rate of the chrome solution. When passivation is operated at an elevated temperature, the returned solution volume is balanced by the evaporation in the process tank. Evaporators can also be installed on the chromating tank with no adverse effect on its components.

WASTE TREATMENT

Since the process is hexavalent chrome-free, the classical sulfite reduction step is eliminated. In principle, simple neutralization will precipitate chromium and oth-

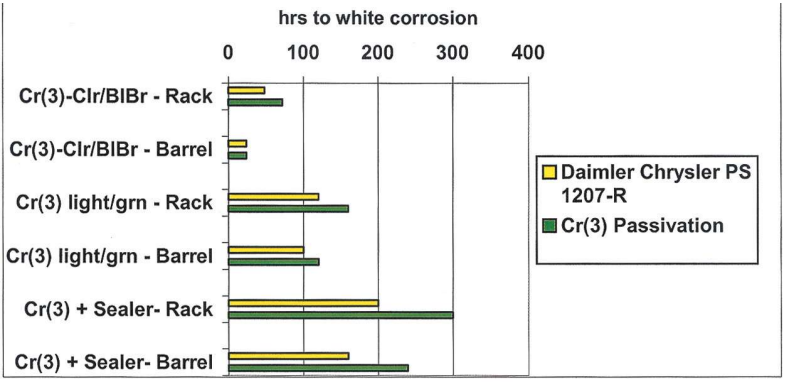


Fig. 8. Cr(3) passivations meets or surpasses requirements for DaimlerChrysler.

er metal hydroxides. An efficient method to improve total separation of chrome from its complexed form consists of lowering the solution pH with sulfuric acid, followed by lime neutralization and settling. Accurate methods of treatment, however, must be developed for the specific passivating process used to meet local and federal waste disposal requirements. The combination of reduced solution replacement and lower use of treatment chemicals improves the economics of the process.

SPECIFICATIONS

Several U.S. and European automotive specifications are now available calling for hexavalent chrome-free conversion coatings for zinc and zinc alloy plating. These specifications take into account the need for sealers and topcoats in order to achieve desired performance criteria. Additionally, some specifications require heat-treating components prior to NSS as part of the qualifying testing criteria. Table III lists some of the U.S. automotive specifications published as of this writing. Figs. 6, 7, and 8 illustrate sample performance data of commercially available trivalent chromate passivation in relation to these specifications. The performance shown reflects results obtained from actual production lines and can be exceeded through process modification and optimization.

ACCURATE THICKNESS TESTING VIA PHASE-SENSITIVE EDDY CURRENT

BY MIKE JUSTICE, PRESIDENT, UPA TECHNOLOGY, WEST CHESTER, OHIO

With the advancements in science and electronics in recent years, metal finishers currently have many choices for the measurement of plating and coating thickness. This article focuses on using the phase sensitive eddy current method.

Phase-sensitive eddy current (PSEC) is an instantaneous, non-destructive and contact method used worldwide for the thickness measurement of many different coatings and platings applications.

PSEC measures coating thickness based on the conductivity difference between the coating and the base material. (A conductivity difference of 20% or more is required in order to measure using this technique.) Eddy current is designated by ASTM B659-90, which states "that the magnitude of eddy currents is a function of the relative electrical conductivities of the coating and substrate materials and the coating thickness."

Specially designed eddy current probes can be chosen according to the application thickness range of the coating, and the size of the parts being measured. Measurements are made by holding the probe perpendicular to the part with the probe tip in contact to the surface.

There are actually two types of eddy current techniques that are used for measuring coating thickness. The most common type is "amplitude" eddy current, which is capable only of measuring non-conductive coatings over conductive (non-ferrous) substrates. The most common applications for amplitude eddy current are for measuring anodizing and organic finishes on aluminum substrates.

While the phase-sensitive eddy current technique also measures anodizing, the real advantage comes in the possibility of measuring many different applications, even with the same probe. Since PSEC measurements are based on having at least a 20% difference in conductivity between the coating and substrate, the variation of applications is almost unlimited.

We could not list all of the various applications that PSEC is capable of measuring, but some of the many possibilities include: Ni/Fe, Cu/Fe, Ag/SS, Cu/EPG, RFI & EMI coatings on plastic, Silicide/SS, Sn/Fe and Cu/Fe, Anodizing/Al, Al/Glass, Al/SS or Cr/Al. The most common use of PSEC is for measuring zinc, copper or cadmium thickness on steel fasteners.

INSTRUMENT CALIBRATION AND THICKNESS STANDARDS

Typical applications for measuring plating thickness such as zinc/steel require calibration of the instrument using plated thickness standards. The specific thickness of the calibration standards depends on the frequency of the probe.

ASTM specifies using calibration standards identical to the parts being measured. In the case of PSEC, this means making calibration standards having the same characteristics in both the coating and substrate as the parts being plated.

Most eddy current instruments incorporate a base correction feature that adjusts for different properties of substrates. Differences in plating deposit conductivity can also be corrected by incorporating an algebraic factor. Though these system adjustments are helpful, using a "factor" to change the original cal-

ibration causes a loss of NIST traceability. Thus, to obtain maximum accuracy, thickness standards should be made from the same plating bath and substrate materials as the parts that will be measured. Otherwise, to confirm the accuracy a different measurement method should be used for comparison purposes. Most eddy current instruments also include the magnetic induction capability for this purpose.



Eddy current instruments are rugged enough to use at the end of a plating line. Photo courtesy of *Micro Metal Finishing*.

EDDY CURRENT ADVANTAGES

Eddy current instruments are rugged, with the electronics virtually sealed, and can be used directly at the end of a plating line or other hostile work environments.

Another benefit: eddy current is much less affected by subtle changes of the magnetic properties of steel or iron substrates. Most low-carbon steel substrates can be measured using a single calibration and only one set of standards would be needed for measuring thousands of different parts such as screws, washers, bolts or brackets.

Curved and irregularly shaped parts can be measured with little additional error and typically without the necessity of parts fixturing. This is due to the small measurement areas (field effect) of microprobes. Plating thickness can also be measured on rough, uneven surfaces without affecting he overall accuracy. Thickness distribution can also be scanned by sliding the probe along critical surfaces of the parts.

With PSEC, there is a high degree of measurement precision (repeatability) even on thin metallic coatings. Since most plating specifications are typically less than 0.5 mils, this is an important feature. For example, vacuum deposits for EMI/RFI applications, such as aluminum or copper on plastic substrates are commonly below 0.1 mils, but can be accurately measured even below 1 micron by eddy current using the appropriate probe and thickness standards.

Platings such as zinc can be measured even under a coat of paint with no loss of accuracy. The "lift off" of the probe from the surface will not affect accuracy of the zinc measurement.

EDDY CURRENT PROBES

A wide variety of specially designed probes are available from the manufacturers for use in measuring virtually any application or part. Probes with different tip diameters are sized to accommodate the size and shape of the parts being mea-

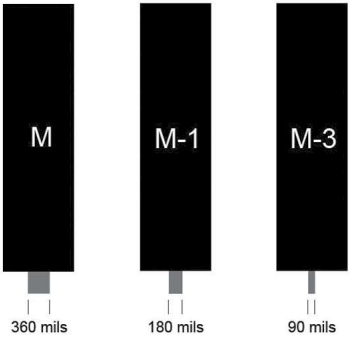
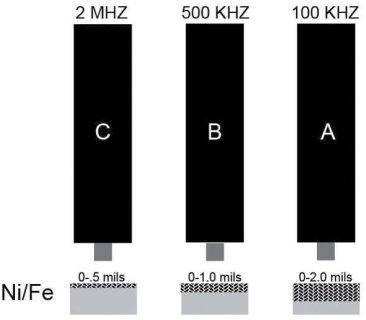


Illustration of three probes with the measuring areas detailed.



Probe frequency determines measurement range.

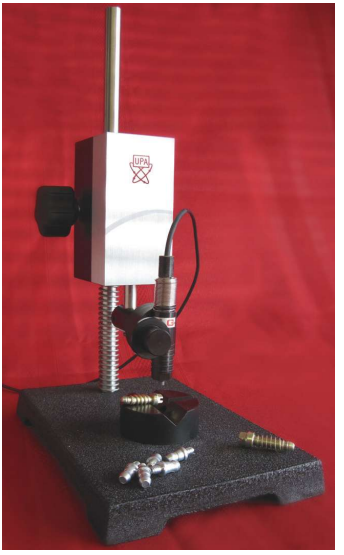
sured. Probes with smaller tips can measure on very small areas of parts less than 90 mils. Smaller probe tips are subject to increased wear and are more easily worn or damaged, so probes are also produced with larger diameter tips for measuring on larger parts such as plated brackets or castings.

Depth of measurement penetration is a function of the conductivity of the coating and substrate as well as the frequency of the probe being used. The specific frequency for the probe is chosen depending on the application plus the coating thickness specification. Lower frequency probes penetrate deeper into the parts than higher frequencies. The higher the probe frequency, the better the accuracy will be for measuring thinner coatings.

Right angle probes are also available that can be used to determine thickness inside bores as small as .250″ diameter. Placing and holding the probe steady at the proper angle inside a bored hole is very difficult, increasing likelihood of measurement error due to improper probe positioning.

To obtain the maximum accuracy achievable, a probe stand should be used for measuring inside internal bores or on small part surfaces.

With PSEC the same probe can often be used for measuring different applications. For example, conductive coatings on steel and non-conductive coatings on conductive substrates can be measured using the same probe.



Picture of probe stand being used to measure small parts.
Picture courtesy of UPA technology

SUMMARY

Phase-sensitive eddy current technology provides an excellent option to metal finishers for measurement of many application combinations. With phase-sensitive

eddy current systems available for about $6,000, the eddy current method provides a relatively inexpensive alternative for accurately determining coating thickness.

Eddy current systems are easy to operate with menu-driven, prompting software, so even non-technical operators can make instantaneous, accurate and repeatable thickness measurements directly on the process line for improved throughput, quality control and fewer rejections. Many of the largest volume platers use eddy current systems at the end of the plating line for direct process control and incorporate X-Ray in the quality lab for final inspection. Using this combination of technologies ensures the most efficient method to achieve conformance to thickness specifications

BIO

Mike Justice, president of West Chester, Ohio–based UPA Technology, has 25 years experience in instrumentation and standards for the measurement of coatings. He earned his B.S. degree in Industrial Technology from Ohio State University. He can be reached at info@upa.com



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VOLUMETRIC COMPLEXOMETRIC METHOD TO DETERMINE SULFATE CONTENT IN CHROMIUM PLATING SOLUTION

BY DR. V. PERSITS, ISRAEL AEROSPACE INDUSTRIES, PETAH, TIKVA

Abstract. *The complexometric method involves the use of glycerin, in the presence of HCI (1:1), to reduce chromium (VI) to chromium (III). Sulfate is precipitated by barium in the presence of Cr (III) and the sediment separated by centrifuging, when the solution is separated from precipitated barium sulfate by means of vacuum suction. The precipitate is dissolved with excess EDTA in ammonium environment, using heating block, and unreacted EDTA is back titrated with standardized magnesium chloride.*

Concentration of sulfate in chromium plating solutions can be determined by various methods: by centrifugation, gravimetrically, with some volumetric methods and etc. [1,2,3]

The centrifugation is used in plating shops for the rapid determination of sulfate in chromium plating bath, (sulfate–as barium sulfate). H`owever the determination of sulfate by centrifugation is rapid but relatively inaccurate compared to classic analytical methods (gravimetric and volumetric).

In the gravimetric method the determination of sulfate –barium sulfate is precipitated, washed, dried and weighed. The gravimetric methods are generally accurate and are often used for the check work when a substance is determined more than one method. (*Israel Aerospace Industries LTD.)

However, gravimetric method for determination of sulfate is very time consuming and may be less accurate in case of chromium plating bathes, because coprecipitation chromium (III) and other ions with barium sulfate (the color of precipitate $BaSO_4$, precipitated from chromium plating solutions, is yellow-green or white-green, but not white; the ratio $CrO_3 : SO_4$ in the solution is ~100:1. The concentration of iron and other metals could be up to 15g/l.)

The sulfuric acid in the plating solution serves as the "catalyst" that is essential if any plating is to take place. It must be present within very narrow limits (2.5–3 g/l) to control the quantity and character of the deposit. Therefore, it is desirable to have more than one method (in addition to the gravimetric method) for the determination of sulfate in chromium plating solutions. This provides an accurate method to determine the sulfate (2.5 –3 g/l) in the presence of 100-fold excess of chromic acid and other metals, presented in chromium baths (Fe, Cu, Ni, Mg).

Volumetric-complexometric method for the determination of sulfates in electrolytes has few advantages, namely speed, accuracy, and selectivity. [2]

W.W. White and M.C. Henry [4] were described the method, "The determination of sulfate in chromium plating baths by EDTA titration."[4] They used hydroxylamine hydrochloride to reduce chromium (VI) to chromium (III). Barium sulfate was precipitated in the presence of chromium (III) and separated from the mother solution via centrifuge, followed by decantation. The pre-

Sample	Volumetric EDTA methd, g/l								Gravimetric method, g/l
	Aliquiot, ml	Aliquiot + 0.1N H_2SO_4	n	R=Xmax - Xmin, g/l	$\overline{X} \pm \varepsilon$ g/l	S_r	Added, mg	Determined, mg	
Synthetic chromium solution*	4 ml		8	0.09	2.72 ± 0.026	0.032			
		4 ml + 1 ml					4.8	4.85	
Bath 17	4 ml		8	0.13	2.65 ± 0.038	0.046			2.81
Bath 18	4 ml		8	0.05	2.86 ± 0.015	0.018			2.92
		4 ml + 1 ml					4.8	4.73	
		4 ml + 2 ml					9.6	9.85	

Synthetic solution : HEEF - 25R +1N H_2SO_4(248 g/l CrO_3 + 2.7 g/l SO_4)

Table 1. Comparison and reproducible results of the determination of sulfates in chromium plating solution.

cipitate was dissolved with excess EDTA, and the unreacted EDTA was back titrated with standardized magnesium chloride. This back titration method is regarded as an accurate procedure for the determining sulfate. [3]

However, one performing the procedure [4] could have serious errors: incomplete forming and precipitating of barium sulfate, (after adding 10% $BaCl_2$, solution with precipitate $BaSO_4$ was maintained only for 5min, at 75°C) and there could be possible loss of the precipitate during separation of precipitated barium sulfate by means of decanting.

In order to overcome these problems and to improve the accuracy of the method, this work suggested the following changes in the procedure:

1. Precipitate $BaSO_4$ is maintained for 2 hours at 75°C, while during the first hour the suspension is stirred.

2. In order to separate the solution in the centrifuge tube without losing any of the precipitated $BaSO_4$, a vacuum device was used. (Fig.1,2)

3. According [3] the reduction of Cr (VI) to Cr (III) during the determination of the sulfate in the presence of a high concentration of hexavalent chromium, should be performed, using glycerin. We replaced the reducing agent hydroxyl-amine hydrochloride on the reducing agent glycerin with HCI to reduce Cr (VI) to Cr (III). Glycerin with hydrochloric acid rapidly and effectively reduce the chromium (VI), thus preventing the coprecipitation with barium sulfate. Hydrochloric acid provides the environment for complete precipitation of $BaSO_4$.

4. In order to guarantee the complete dissolution of precipitate $BaSO_4$ into EDTA + NH_4OH mixture, centrifuge tubes were heated in an aluminum heating block with stirring, until all precipitate was dissolved. The dissolution takes few minutes. These improvements enabled the determination of sulfate in the chromium plating bath with a good accuracy. The EDTA method is faster than the gravimetric method for the determination of sulfate and is quite accurate.

EXPERIMENTAL

Reagents and apparatus. All the materials were reagent grade and were used without further purification. Distilled and deionized water were used in the preparation of all solutions. Solutions were stored in glass and polyethylene bottles. Used deionized water (m-1-2 microSiemens).

Indicator Eriochrom Black T: powder 2g EBT+198g NaCl.
Standard solution EDTA 0,1M (37,224g $C_{10}H_{14}N_2Na_2O_8 \times {}_2H_2O$ +5g NaOH) transfer into volumetric flask of 1liter and dilute to mark with deionized water(μ-1-2).
EDTA 0.02M. 200ml 0.1M EDTA transfer to volumetric flask 1liter and dilute with deionized water to mark.

Solution of magnesium chloride.
Solution 1: Fixanal 8,362g $MgCl_2 \times 6H_2O$ (1g of magnesium) was transfer to vol-

umetric flask 1liter and dilute with deionized water to mark.
Solution 2: 0,5g of Mg – (4.181g $MgCl_2$ x6H_2O), 500 ml of solution 1 dilute to 1liter with deionized water. The solution 2: magnesium chloride was standardized against 0,02M EDTA solution, as follows: transfer 20ml of 0.02 M EDTA solution into the beaker. Add 100 ml of distilled water and 5ml of solution NH_4OH (1:1). Add indicator Eriochrom Black T to blue color. Titrate with St.solution magnesium chloride to change color from blue to reddish. The end point is reached when the solution turns reddish such that one additional drop of titrant produced no visible change in color.

Hydrochloric acid (1:1). Mix 1volume of concentrated HCl (d- 1.19g/cm3) with 1volume of distilled water.
Glycerin (chemical pure).
Barium chloride 10%. Dilute 10g of $BaCl_2$ into 100 ml of deionized water.
Ammonium hydroxide (1:1). Mix 1 volume of concentrated NH_4OH (25%, anal.) with 1volume distilled water.

Safeguard Centrifuge (Clay-Adams Inc) was used for centrifuging of the solutions. Glass centrifuge tubes (h-135mm, d-25mm); Paster pipet (borosilicate glass l-140mm). Device for separating the solution in the centrifuge tube from the precipitate barium sulfate and aluminum alloys heating block [Al-200mm x 85mm x 125mm (h)] with openings for centrifuge tubes were used in this work.

Procedure. Pipette 4.0ml of plating solution into 50 ml glass centrifuge tube. Place the centrifuge tube with solution into beaker with distilled water (water bath). Add 10ml HCl (1:1) and 10ml glycerin and mix the solution by stirrer – Cr (VI) reduced to Cr (III). Place water bath (with centrifuge tubes) on the hot plate and heat to about 75°C. Add 15ml of barium chloride, 10%. Maintain the temperature of the suspension around 75°C for 2 hours, while stirring the suspension during the first hour. Cool the suspension to room temperature. Centrifuge the suspension for at least 10 min.

Separate the solution from the precipitate, being careful not to lose any of precipitate of $BaSO_4$. Wash the precipitate with 40 ml of deionized water. Separate solution from the precipitate by the same way. Chromium (III), excess $BaCI_2$, and other ions are separated efficiently from the barium sulfate precipitate after centrifuging and washing 5 times. Add 5 ml NH_4OH (conc.) and 20ml of 0,02 M EDTA into centrifuge tube with precipitate. Place centrifuge tube into an aluminum heating block with openings for centrifuge tubes. Heat the block with four centrifuge tubes on the hot plate and stir constantly with stirrer until all precipitate has dissolved. Cool the solution to room temperature. Transfer the solution into the beaker and wash centrifuge tube with deionized water. Add 5ml of NH_4OH (1:1) and indicator Eriochrom Black T, to make the solution light blue. Titrate the solution with standardized magnesium chloride solution. The endpoint is reached when the solution turns reddish such that one additional drop of titrant produces no visible change in color.

$$SO_4{}^{g}/_{l} = \frac{[A\text{-}KxB]x1.9212}{C}$$

A - ml 0.02M EDTA (20ml);
B - ml $MgCl_2$, used for titration the excess of EDTA 0.02M;
C - ml of sample, used;

$$K = \frac{X}{Y}$$, where

X - 20ml 0.02M EDTA;
Y - ml $MgCl_2$, corresponding 20 ml 0.02 M EDTA
One ml 0.02M EDTA corresponds 1.9212mg of sulfate.

RESULTS AND DISCUSSION

The obtained results summarized in Table 1, which represents a comparison of results the determination of sulfate in two working chromium plating baths and synthetically prepared chromium–sulfate solution, using gravimetric method and EDTA titration method. A number of samples were analyzed using the method of standard additions. Table 1 shows that the proposed volumetric EDTA method can be applied successfully for the simple and accurate determination of sulfate in chromium plating baths without a significant systematic error even in presence of 100 - fold excess of chromium (VI) and other of metals (iron, chromium (III), cupper, nickel), which usually are observed in chromium plating baths.

The method involves the use of glycerin in presence of HCl (1:1) to rapidly and effectively reduce the valence state of chromium (VI) to chromium (III). Hydrochloric acid provides the environment for complete precipitation of $BaSO_4$ in the presence of chromium (III) and other ions. Barium sulfate is separated from the mother solution by centrifuging. Next, the solution is separated from precipitated $BaSO_4$, after washing the precipitate with deionized water via a vacuum device. Aluminum alloys heating block is used for full and rapid dissolving precipitate $BaSO_4$ into EDTA + NH_4OH mixture, providing accurate EDTA volumetric method determination of sulfate in chromium plating bath.

The volumetric EDTA method are most simple, rapid, sensitive and have satisfactory precision and accuracy in range 2.5–3 g/l sulfate and 232–262g/l of chromic acid.

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BIO

Dr. Vera Persits was granted her M.Sc. in chemistry from Rostov State University in 1971. She earned her Ph.D. in analytical chemistry from Leningrad (currently Saint Petersburg) State University in 1982. The theme of the doctorate was "Investigation of process of electro-thermal atomization and their utilization for the elaboration of methods for the determination of zinc, cadmium, lead, tin, bismuth and antimony in steels and alloys." Dr. Persits authored and co-authored 20 articles and has two patents in analytical chemistry. She worked as a senior scientific worker at Scientific-Industrial firm of Machine-building technology in Moscow until 1991. Since 1992 Dr. Persits worked at IAI (Israely Air Industries) as a chemical engineer in the field of plating.

CONTROL AND CHEMICAL ANALYSIS OF PLATING SOLUTIONS

BY SUDARSHAN LAL, MECHANICSBURG, PA.

The quality of plated deposits primarily depends on factors such as current density, solution composition, temperature, effective bath pH, additives concentration, speed (rpm for barrel plating or line speed for reel to reel), and solution agitation in the tank. Apart from mechanical factors, tight control of main ingredient and additive concentrations in a plating bath is extremely important to achieve successful plating operations. Plating solutions must be maintained at the recommended limits, as suggested by the manufacturers. Sometimes, the limits may not be so rigid, and bath parameters need to be optimized by a given job shop based on the type and layout of the plating line.

The status of a given bath is dependent on the rate of its depletion due to plating operations and proper replenishment. The operator should monitor bath components frequently in order to maintain chemistries within a controlled window. The depletion of primary bath components mainly depends on the following factors:

1. Drag-out into rinse tanks causing loss of useful chemicals depending on mode of draining.
2. Evaporation rate of plating baths depending on temperature, air flow, and mechanical agitation in the tank.
3. Imbalance in anode and cathode efficiencies. Soluble anodes may increase or decrease metal content due to current efficiencies. The current efficiency issues may be ascribed to side reactions occurring at the anode and cathode. For insoluble anodes, metal replenishments are frequently required.
4. Depletion of additives due to co-deposition in electrodeposits and breakdown products.
5. Drastic pH changes in the bath, which may cause precipitation or turbidity.
6. Impurities introduced due to tech-grade chemical additions and leaching of impurities from extraneous objects that have fallen into the tanks.

Wet chemical methods have been routinely employed in monitoring major bath components. Advanced automatic instrumentation is also available for analysis of inorganic and organic species. Plating baths are usually analyzed offline after harvesting samples from various tanks. Metal ions are monitored using atomic absorption spectrophotometry (AA), inductively coupled plasma (ICP), wet titrations, colorimetry, polarography, and ion selective electrodes, depending on laboratory facilities.

The analytical methods for analysis of plating solutions should be simple, direct, and operator friendly. In order to facilitate this, a standard operating procedure should be documented, and adequate records with tank ID, date and time

Property	*Atomic Absorption (AA)*	*Inductively Coupled Plasma (ICP)*
Temperature limits	1,800–3,100 K	700 K
Ionization	Partial	Complete
Matrix effect	Yes	None
Multi-elements	Yes, limited	Many elements analyzed simultaneously
Sensitivity	ppm levels	ppb levels
Cost	Lower	Too costly
Solution viscosity	Interferes due to viscosity, solution diluted	Interferes due to viscosity, solution diluted
Application to plating solutions	Yes	Yes
Analysis of waste streams	Yes	Yes
Suspended solids in solution	Analyze after micro-filtration	Analyze after micro-filtration
Analysis versatility	Main component	Main component and trace levels

Table 1: Atomic Absorption (AA) vs. Inductively Coupled Plasma (ICP)

of analysis, and any additions made for replenishment should be maintained, preferably using commercial software programs such as True Logic or Lab Wizard Software. Small job shops are urged to maintain paper copies for each shift, as well as any notes from troubleshooting operations. Bulk ingredients in the baths are easily determined mostly using titrimetric methods, which require simple laboratory equipment. Trace impurities in solutions may be determined by a certified laboratory equipped with the desired instrumentation for micro-determinations

SAMPLING

Sampling is an extremely important step, and the sample should be representative of a given tank. Tanks should be identified and their levels recorded to check the decrease in tank volume due to evaporation, drag-out, or spillage. Ideally, sampling should be done at 10 different locations in larger tanks, and a composite sample should be prepared. The log sheet should have entries such as:

1. Tank ID
2. Date and time of analysis
3. Analytical method used
4. Results
5. Recommended high and low limits
6. Analyst signature

Bath Type	*Parameter*	*Analytical Method*
Soak cleaner*	pH	Electrode, pH paper
	Total alkalinity	Acid-base titration
	CO_3^{--} and HCO_3^-	Acid-base titration, pH titration
Electro-cleaner*	pH	Electrode, pH paper
	Total alkalinity	Acid-base titration
	CO_3^{--} and HCO_3^-	Acid-base titration, pH titration

*Emulsified oils should be removed occasionally from these tanks.

Table 2: Analysis of Soak Cleaners and Electro-cleaners

Bath Type	*Parameters*	*Analytical Method*
Watts' nickel	pH	Electrometric pH electrode
	Ni	EDTA titration, AA, ICP, XRF
	Sulfate	Titrations, turbidity (N/A)
	Chloride	$AgNO_3$ titration, potentiometry
	Boric acid	Acid-base titration/mannitol
Sulfamate nickel	pH	Electrometric pH electrode
	Ni	EDTA titration, AA, ICP, XRF
	Chloride	$AgNO_3$ titration, potentiometry
	Boric acid	Acid-base titration/mannitol
Woods' nickel	pH	Electrometric pH electrode
	Ni	EDTA titration, AA, ICP, XRF
	Chloride	$AgNO_3$ titration, potentiometry
Electroless nickel	pH	Electrometric pH electrode
	Ni	Titration
	Hypophosphite	Redox titration
	Orthophosphite	Redox titration
	Inorganic additive	Polarography, CSV, IC

Table 3: Analysis of Nickel Baths for Various Parameters

troubleshooting, testing, & analysis

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Bath Type	*Parameters*	*Analytical Method*
Alkaline gold	$KAu(CN)_2$	AA, ICP, gravimetric
	KCN	Titration, ISE, IC, colorimetry
	K_2CO_3 or KOH	Titration
	Phosphates/citrates	NA
	pH	Electrode
Acid cyanide gold	$KAu(CN)_2$	AA, ICP, gravimetric
	Citric acid	NA
	Cobalt or nickel	AA, ICP
	pH	Electrode
Neutral gold (additive free)	$KAu(CN)_2$	AA, ICP, gravimetric
	KH_2PO_4	NA
	pH	Electrode
	Grain refiners: Tl, As	AA, ICP, polarography
Non-cyanide gold	$NaAuCl_4$	AA, ICP, gravimetric
	Na_2SO_3	NA
	$Na_2S_2O_3$	NA
	Na_2HPO_4	NA
	pH	pH electrode

NA = not analyzed.
Table 4: Analysis of Gold Baths

After additions to the tank and adequate mixing, an analysis should be performed again to check desired parameters. Normally, well-established plating shops have reasonably good laboratories and are well equipped to keep track of their chemistries. Some job shops depend on analytical support from chemical bath suppliers, which are usually away from site, and they have key parameters analyzed once or twice a month. The drawback of off-site analysis is that bath components cannot be adjusted in a timely manner.

Reagent-grade standardized solutions should be procured from a reliable supply house. A well-trained chemist may prepare his own solutions and standardize versus primary standards. The initial receipt date and expiration date of these solutions should be recorded. Deionized or distilled water should used in the analysis.

Common standard solutions such as HCl, H_2SO_4, NaOH, Na_2SO_3, $AgNO_3$, I2, $K_2C_r2O_7$, $KMnO_4$, and KCSN are available in 0.1-N concentrations.

Bath Type	Parameters	Analytical Method
P-salt/sulfamate $Pd(NH_3)_2 (NO_2)_2$ salt	Pd metal	AA, ICP, spectrophotometry
	Ammonia sulfamate	NA
	Ammonia hydroxide	pH electrode
Palladosamine chloride $Pd(NH_3)_4Cl_2$	Pd metal	AA, ICP, spectrophotometry
	Ammonia chloride	NA
	Ammonia hydroxide	pH electrode
Palladium chloride $PdCl_2$	Pd metal	AA, ICP, spectrophotometry
	Ammonia chloride	NA
	Hydrochloric acid	pH titration
Pd-Ni alloy (80/20) Pd-Co alloy (80/20)	Lead metal	AA, ICP, spectrophotometry
	Nickel metal	AA, ICP
	Ammonia chloride	NA
	Ammonia hydroxide	pH electrode

Table 5: Analysis of Pd, Pd-Ni, and Pd-Co Baths

ANALYTICAL TECHNIQUES

It is important to review the flow sheet of a given plating process (rack, barrel, reel to reel) and understand the sequence of the operation. This guides the operator to prepare for a safe start by analyzing the plating baths needed in the process. Most job shops use traditional wet methods.

The commercial use of instrumental techniques is limited due to complex operations, maintenance, frequent calibrations, personnel training, and the expense of initial investment. The workload of a plating plant can justify the use of any instrumental technique, such as AA, ICP, chromatographic techniques, or any dedicated electrochemical method. The following outline may be helpful in understanding their relationship.

a) Photometric methods:

1. Spectrophotometry
2. Colorimetry (measures color intensity at a given wavelength)
3. Turbidimetry (measurement of radiation passing through suspension)
4. Nephelometry (measurement of radiations scattered from suspension)

All methods are based upon the absorption of light.

b) Spectrophotometric methods are based on emission of light. For example:

1. Flame photometry
2. Flame spectroscopy
3. Mass spectrometry (MS)

Bath Type	*Parameters*	*Analytical Method*
Tin-lead	Tin, Lead	AA, ICP, titrations
H_2SO_4, HBF_4 alkylsulfonic	Sulfuric acid	Acid-base titration
	Additives	Spectro, HPLC, IC, hull cell
Tin-sulfate/H_2SO_4	Tin	AA, ICP, titration
Tin/MSA	Acids	Titration
Tin/Cl/F, tin-pheonolsulfonic acid	Additives	Spectro, HPLC, IC, hull cell
Immersion tin	Tin	AA, ICP, titration
Alkaline tin	Tin	AA, ICP, titration
Tin-Bi,Tin-Ag,Tin-Bi-Ag	Sn, Bi, Ag	AA, ICP

Table 6: Tin-Lead, Pure Tin, and Lead-free Tin Alloys

4. X-ray fluorescence (XRF)

c) Electroanalytical methods involving electric current and potential.
1. Electrogravimetric
2. Conductimetric
3. Potentiometric
4. Coulometric
5. Polarography
6. Amperometric

d) Chromatography is a method of separation of components.
1. Gas chromatography (GC) is suitable for volatile compounds by separation on a specific column and speciation by GC-MS.
2. Column, thin layer, and paper chromatography are seldom used in plating bath analysis.
3. High-performance liquid chromatography (HPLC) involves separation of components using suitable columns and eluents. The separated species can be identified by MS.
4. Ion chromatography (IC) deals with separation of anions or cations using specific columns and detection achieved by UV-Vis, refractive index, and variations in conductivity. The separations occur due to the difference in ionic mobilities and differential distribution coefficients of various components.

Solvents conforming to spectroscopy and chromatography grades should be used to eliminate background noise.

TITRIMETRIC METHODS

The active component of a plating bath sample is stiochiometrically titrated with a standard solution of a required titrant. The end point of a titration may be visually determined with a color change of the indicator or by an electrometric

method. Indicators are auxiliary reagents added to samples and aid in end-point determination. For low concentrations, volumetric methods yield inaccurate results due to obscured end points. For accurate determinations, the method should be selective and free from interferences, with crisp end points.

The details of volumetric titrations are simple, and supply houses provide procedures for analysis. For accuracy and precision, standardized reagent-grade solutions in conjunction with A-grade pipettes and burettes should be used. Automatic titrators (Metrohm, Fisher) and digital burettes are gaining popularity for their reproducibility and accuracy. The role of chemical interferences should be considered for a given multi-component bath.

GRAVIMETRIC METHODS

Gravimetric methods involve the separation of the desired component from other constituents by chemical precipitation, isolation, washing, and weighing after drying. These methods are time consuming, but for precious metals the gravimetric method is considered a referee method. Some metals (Cu, Ag) are determined by electrodepositing on pre-weighed platinum cathodes. The gravimetric methods are employed for chloride, sulfate, carbonate, phosphate, and certain metals.

INSTRUMENTAL TECHNIQUES

In wet chemical methods, the chemical property of the component is utilized in its determination, whereas instrumental methods utilize the physical property of the component. The analyst should weigh the cost, degree of precision, and accuracy for a given instrumental method. Plating solutions can be analyzed using the following instrumental methods:

1. ***Spectroscopic methods***: A given substance is analyzed by the measurement of emitted light from the excited atoms by radiant energy, AC, or DC arc. Each element has characteristic wavelengths depending on its electronic configuration. A distinct set of wavelengths are generated and separated by a monochromator, and intensities of various wavelengths are measured by a spectrograph or photoelectric detectors (spectrophotometry). Spectroscopic methods are unique and specific and are employed for trace quantitative analysis. The accuracy of spectrographic methods is not very high, with limit of detection at about 3%. Sensitivities are much smaller for high-energy elements, such as zinc, than for elements of low energy, such as sodium.

2. ***Flame photometry (FP):*** A liquid sample is atomized at constant air pressure and aspirated into a flame (1,800–3,100 K) as fine mist. At high temperatures the solvent evaporates, forming a solid, which then vaporizes, dissociating the atoms into a ground state. The valence electrons of the ground state are excited by the flame energy to their higher energy level and fall back to the ground state. The intensities of emitted spectrum lines are determined by spectrograph or spectrophotometer. The flame photometer is calibrated with standards of a known matrix and concentrations. The intensity of a given spectral line is compared and

quantified against the standard. Solutes and solvents affect the signal intensity causing inaccuracy in results. Elements with adjacent wavelengths interfere. FP is mainly used for analysis of: Al, B, Cr, Co, Cu, In, Fe, Pb, Li, Mg, Ni, Pd, Pt, K, Rh, Ru, Ag, Na, Sr, Sn, and Zn.

3. ***Emission spectrometry (ES):*** ES involves exciting a cast metal or a solution by electric discharge by AC or DC in a graphite cavity. Graphite electrodes are favored due to the least spectral interference and a temperature of 4,000–6,000 K. At these higher temperatures, elements emit a higher number of spectral line characteristics of each element. The method is mostly qualitative, and density of a given line provides semi-quantitative results. ES is sparsely used, mainly for trace analysis.

4. ***X-ray fluorescence (XRF):*** XRF is based on the excitation of samples by an X-ray source of high energy, resulting in the emission of fluorescence radiation. The concentration of elements being determined is proportional to the intensity of its characteristic wavelength. XRF is a non-destructive technique and can be applied in measuring the constituents of plating baths, such as Cd, Cr, Co, Au, Ni, Ag, Sn, and Zn. The method is less sensitive compared with ES, and for XRF, proper calibration standards with similar matrices should be employed. Applications have been developed by Spectra-Asoma Instruments. Coating thickness and its composition can also be determined using XRF after calibrations.

5. ***Mass spectrometry (MS):*** This technique utilizes gas or vapors derived from liquids or solids that are bombarded by a beam of electrons in an ionization chamber, causing ionization and resulting in the rupture of chemical bonds. Charged moieties are formed and may contain elements, molecules, and fragments and are separated by electric and magnetic fields based on mass to charge (m/e) ratio. Based on the mass spectrum, best possible fit from the software library is suggested. MS is only applicable to substances that have sufficient vapor pressure and is good for compounds with a boiling point <450°C. This technique is used in speciation and molecular weight determination.

6. ***Inductively coupled plasma (ICP):*** A liquid sample is aspirated in a stream of argon gas and ionized by an applied radio-frequency field. The field is inductively coupled to the atomized gas by a coil surrounding a quartz torch that supports and encloses the plasma. The sample aerosol is heated in plasma, molecules become almost completely dissociated, and then, atoms emit light at their characteristics frequencies. A high temperature of 7,000 K of argon plasma produces efficient atomic emissions and provides low detection limits for many elements. ICP allows simultaneous analysis of many elements in a short time with sensitivity to parts per billion (ppb) levels. A comparison of both techniques is given in Table 1.

ICP instrumentation is not practical for small plating operations due to the initial cost and its prohibitive operating expenses.

7. ***Photometric methods:*** Photometry is based on the absorption of UV light

(200–400 nm) or visible radiant energy (400–1,000 nm) by species in solution. The absorption is proportional to the concentration of absorbing species in solution and valid up to 2% concentration. Colorimetric methods involve comparing the color produced by a standard containing a known quantity. Errors in this method may be due to turbidity, sensitivity to the eye, color blindness, dilutions, photometer filters, chemical interferences, and temperature variations.

8. ***Atomic absorption (AA):*** Metals in plating baths and wastewater effluents are readily determined by AA spectrophotometry. Optimum ranges, detection limits, and sensitivities of metals vary with different instruments. The solution is directly aspirated in the flame (air-acetylene or nitrous oxide-acetylene), which absorbs radiations from a hollow cathode lamp of a given metal. The difference between flame photometry and AA is that flame photometry measures the amount of emitted light, whereas AA measures the absorbed light. Graphite furnace-AA is utilized for ppb levels of metal ions.

ANALYTICAL METHODS FOR ADDITIVES AND SURFACTANTS

Plating baths, in addition to electrolytes and metal salts, also contain certain proprietary organic chemicals, such as wetting agents, grain refiners, and brighteners.

Additives play a significant role in controlling the material properties of deposits. Additive concentrations may be determined by cyclic stripping voltammetry (CSV), polarography, spectrophotometry, HPLC, and IC. Voltammetric techniques are employed to study solution composition (oxidizable or reducible) and valence states using the current–potential relationship in an electrochemical cell. Current–time response of a microelectrode provides useful information about a system. The common electrodes used include dropping mercury electrodes (DME), hanging mercury drop electrodes (HMDE), thin-film mercury electrode, and solid electrodes, such as gold, platinum, and glassy carbon. Additives are indirectly determined by CSV by studying their influence on deposition of metal from the plating bath using a rotating platinum disk electrode.[13]

Anionic, cationic, and non-ionic surfactants may be present in plating baths. After extraction in hexane or another suitable solvent, color is developed using a specific reagent. The intensity of absorbed light at a given wavelength provides an estimate of surfactant concentration. Anionic surfactants are measured as methylene blue active substances (MBAS), but the method is not specific and is prone to interferences. Non-ionic surfactants are measured as cobalt thiocyanate active substances (CTAS). The methods are not specific and may be used as an empirical correlation.

Brighteners may be empirically estimated by plating brass panels for 1 or 2 minutes at 2 or 5 amperes in a hull cell. Plated panels indicate the useful current density range for bright deposits, and additions to plating tanks are made based on these results.

OPERATIONS CARRIED OUT IN COMMON PLATING PROCESSES

Substrate preparation using chemical etchants: In order to achieve a robust deposit, it is extremely important to prepare the substrate to be free of soils, scales, rust, and oily residues. The parts may be mechanically polished, buffed with varying

degrees of abrasive compounds, belt polished, undergo simple tumbling, and/or impact blasting in the presence of various types of media. It is imperative to remove any residual contaminants from these operations prior to starting the plating sequence.

For removing shop soils on parts, the workpieces are soaked in organic solvents such as petroleum naptha, stirred to loosen residues, de-scaled, pickled, and de-smutted. For de-scaling, usually 20–30% aqueous solutions of HCl or H_2SO_4 in the presence of proprietary inhibitors are employed, and their strength can be monitored by titrations. The potency of these solutions should be frequently monitored depending on the surface area processed each day. Obstinate and aged scales are loosened by immersion in hot alkaline potassium permanganate solutions. The concentration and type of de-scaling chemistries should be selected for their compatibility with substrates.

Alkaline cleaners: Alkaline cleaning solutions usually contain sodium hydroxide, sodium carbonate, trisodium phosphate, sodium metasilicates, and proprietary surfactants as wetting agents. Total alkalinity is monitored for such solutions. Ultrasonic cleaning may be achieved by introducing high-frequency sound waves (20–80 kHz) causing cavitation on parts, thus removing soils. Anodic and cathodic cleaning involves the liberation of hydrogen or oxygen, which promotes scrubbing action on the parts, causing the following reactions to occur:

At anode: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

At cathode: $4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$

Periodic reverse (PR) electro-cleaning is also employed in special cases.

Table 2 presents a summary of the methods for analysis of soak cleaners and electro-cleaners for efficient cleaning and maintenance. For semi-transparent solutions, a suitable range refractometer may be employed for estimation of total detergent concentration.

Nickel plating baths: Several nickel plating baths—such as matte, semi-bright, and bright—usually containing nickel sulfate, nickel chloride, nickel sulfamate, boric acid, and proprietary additive packages (comprising carriers, wetting agents or surfactants, brighteners, auxiliary brighteners, grain refiners) have been formulated. All sulfate, all chloride, high sulfate nickel, and black nickel baths are formulated for engineering applications. The primary parameters—such as nickel, boric acid, and pH—are routinely monitored (Table 3). The estimation of additives, carriers, and wetting agents are treated separately. Electroless nickel baths for low, medium, and high phosphorus content are monitored for pH, Ni, hypophosphite, and orthophosphite.

There are a series of binary nickel alloy baths with other metals such as P, Co, Cr, Mo, Mn, Pd, S, W, Au, Cu, Ge, In, Ru, Ag, Tl, and ternaries like Co-Ni-P, Co-Ni-Fe, and Fe-Cr-Ni. Standard analytical techniques are used for bath control.

Gold plating baths: Several types of gold plating baths have been formulated based on end uses, such as decorative, soft gold, nickel- and cobalt- hardened gold

for industrial electronics, and miscellaneous applications involving repairs and electroforming. Low-speed and high-speed gold baths have been designed for use in rack, barrel, and reel-to-reel applications, namely:

1. Alkaline gold cyanide for gold and gold alloys
2. Neutral gold cyanide for high-purity gold plating
3. Acid gold cyanide for bright, hard gold and its alloys
4. Non-cyanide gold with sulfite, thiosulfate
5. Electroless gold

Non-cyanide gold and electroless gold baths are used for special applications. The analytical methods for gold baths are summarized in Table 4.

Silver plating baths: Both cyanide and non-cyanide silver baths are used in the electroplating industry. Parameters such as silver metal, free cyanide, pH, and brighteners are routinely measured by common analytical methods. Electroless silver baths are employed in special applications.

Palladium, palladium-nickel, and Pd-cobalt baths: Palladium , Pd-Ni, and Pd-Co (80/20 alloy composition) baths containing sulfate and chloride at acid and alkaline pH have been employed in engineering finishes. The analysis methods are summarized in Table 5.

Tin and tin-lead baths: Tin-lead baths—(with electrolytes fluoboric acid, sulfuric acid, alkyl sulfonic acid, and methane sulfonic acid (MSA)—have been employed in the industry in conjunction with proprietary brighteners. With the advent of new technologies and RoHS compliance requirements, several new tin chemistries have been developed. Presently, MSA-based chemistries are more popular than sulfate-based chemistries, especially the proprietary additive packages claiming whisker resistance in highly reliable electronic applications. Immersion tin baths are used in special applications where low tin thickness is required. Tin and lead metal concentrations are conveniently determined by AA, ICP, and titrimetric methods, whereas additives are estimated using hull cell, HPLC, IC, or spectrophotometric methods (Table 6).

Copper baths: Several electrolytic copper baths, namely acid copper (sulfuric acid, fluoboric acid), cyanide copper, alkaline non-cyanide, and pyrophosphate copper are available. Copper metal may be determined by AA, ICP, and titrations. Pyrophosphates and orthophosphates are determined by EDTA titrations. Additives consist of organic chemicals, such as carriers, levelers, and brighteners, which are estimated using chromatographic methods, IC, CVS, and CPVS for aged baths. Electroless copper baths containing Cu, EDTA, formaldehyde, and proprietary additives are used for dedicated applications. Copper is analyzed by AA, ICP, and titrations. Formaldehyde may be measured by titration and colorimetric procedures.

Zinc and zinc alloy baths: Zinc baths with cyanide, non-cyanide, and acid zinc are formulated for rack and barrel applications. Zn-Ni, Zn-Fe, Zn-Co, and Zn-Cu are also employed. Metals are analyzed using AA, titrations, or colorimetric methods.

Brighteners are estimated using bent cathodes, jiggle cell, and other applicable instrumental methods.

Chrome plating: Chromic acid in the presence of sulfuric acid and additives is employed in high-speed chrome applications. Trivalent and hexavalent chromium are determined by ion chromatography and titrations. A hydrometer may also be employed for chromium estimation after correcting for sulfate content.

Iron and iron alloys: Iron alloys such as Fe-C, Fe-B, Fe-P, Fe-Cr-Ni, Fe-Co, Fe-Zn, and Fe-Ni are used in special applications. Metals can be determined by AA or ICP. Iron (II) is estimated by titrations, spectrophotometry, and Fe(III) reduced to Fe(II) for titrations.

Imbalance in plating processes is manifested in solutions due to varying anode or cathode efficiencies, depending on the mechanism. For example, at high anode efficiencies (soluble anodes), a high pH is encountered, resulting in higher metal ion concentrations. On a micro-scale, high variations in pH are observed in the immediate vicinity of the electrodes. Conversely, in the case of high cathode efficiency, pH is lowered. In cases of high deposition rates, quick depletion of metal ions in the bath necessitates frequent addition of metal salts. In the case of gold and silver baths, high-free cyanide may be due to low anode efficiency and low-free cyanide may trigger high anode efficiency.

CONCLUSIONS

Metals may be determined by wet titrations, UV-Vis, colorimetry, AA, ICP, and XRF. Acids and alkalis are determined by acid–base and electrometric titrations. Additives are quantitatively analyzed by chromatographic methods (GC, HPLC, IC), CVS, and hull cells. Surface tension (Sensadyne), solution baume, and refractive index may be used, where applicable, for indirect estimation of a particular parameter. The difficulty is that no single instrument can analyze all the components. A plating facility should develop a logical approach to control solution composition and follow the schedule.

Poor control of bath constituents is a major problem and can lead to decreased reliability of parts. Substandard, poor-quality parts produced using an imbalanced process leads to customer complaints and rework, negatively impacting the reputation of the plating shop. The primary reason is due to limited analytical capabilities for the analysis of additives (which are usually a mixture of two or more chemicals). For troubleshooting, adequate resources are very important, and these analytical methods are the backbone of successful plating operations. The analysis of baths should not be discounted, and job shops should conduct frequent analyses of baths to ensure robust SPC process control.

Author's note: *This article provides an overview of popular analytical methods used in process control but does not claim its completeness. Special applications may require amended methods or simple tests, such as specific gravity, baume, refractive index, conductivity, etc., to suit a shop's needs in day-to-day operations. Additionally, the author does not endorse any commercial products mentioned in this paper. Plating shops should evaluate baths, analytical techniques, and ancillary procedures for best results in their operations.*

NOTES

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EXAMINING THE HULL CELL

BY JOE FOX, FINISHING TEST SUPPLY, INC., PAINESVILLE, OHIO

The hull cell was first outlined by R.O. Hull in a 1939 paper titled "Current density characteristics, their determination, and application" (Proceedings of the American Electroplaters' Society). The biggest advantage of the hull cell is its ability to allow a skilled operator to check the deposit properties at varying current densities, and all on one test panel.

The hull cell can examine the effects of the following:

- **Operational variables, such as pH current density, temperature, and agitation**
- **Organics and metallic contamination**
- **Base salt constituents and addition agents**
- **Brightness range of plating deposit**
- **Covering power**

Unlike quantitative analysis, the hull cell test gives the analyst a snapshot or picture of the solution. In order to interpret the snapshot, other pictures are required for comparison.

The aim of this article is to provide standards and training to educate the analyst. More complete information will be available in Part III of this series, slated for the May issue of *Metal Finishing*. (Part II will appear in the April issue.)

DESIGN

The hull cell is a miniature plating tank that is trapezoidal in its configuration. The unique shape and dimensions of the hull cell are depicted in Figure 1 for various sizes. Different sizes exist mainly for the sake of convenience. Original cells were based on 1,000 ml, but smaller cells were later developed. The 267-ml size was chosen because a 2-g addition to the hull cell equals 1 oz/gal addition to the plating bath.

The small cells are often criticized for being too small because rapid changes in composition and solution temperature can occur. For example, the 267-ml hull cell can have a 10% change in addition agent concentration in just one 5-minute panel. This is dependent on the initial concentration and the consumption rate of the addition agent system.

The angle of inclination of the cathode, shape, and spacing are critical to provide the current distribution that previous research has determined to be advantageous. The depth of the solution can be altered, but the current must also be changed to allow for area and subsequent current changes. Figure 1 shows a typical hull cell and temperature controller.

HULL CELL COMPOSITION

The hull cell should be constructed from a non-conductive material that is chemically inert from the solution being tested. Acrylic and polypropylene are

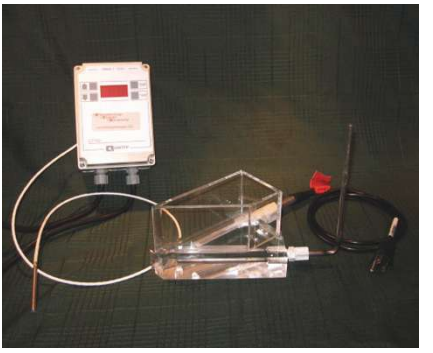


Figure 1: Hull cell and temperature controller.



Figure 2: Brass- and zinc-coated steel panels.

commonly used.

ANODE

The anodes are typically 2.25 × 2.25 inches and are fitted close to the cell wall. In addition, the anodes are normally flat. If the solution is subject to high anode polarization, then the anode should be corrugated, ridged, or made from gauze to increase the effective anode area.

The anode material should be carefully chosen. Impurities in the anode composition can affect the outcome of the tests. Therefore, the same anode material should always be used for a series of tests. It is common practice to use filter paper or a small anode bag to trap any anode fines or sludge that may interfere with the test. However, it is not sound practice to use filter paper because it could impede proper solution replenishment in the anode film. If quantitative evaluation of the solution conditions and the anode is required, then the anode area will usually need to be increased to provide the proper anode-to-cathode ratio.

CATHODE

The cathode is used to judge the condition of the plating solution. The ideal condition would entail having the test panel made from the same composition as the work being plated, however, this is easier said than done. Generally, polished brass panels and zinc-coated steel panels are used. The condition and composition of the cathode surface have a great effect on the outcome of the test. Therefore, the cathode material and preparation must be standardized.

Steel panels are zinc coated to prevent rusting during storage; usually the zinc is stripped in a 50%/volume solution of hydrochloric acid, rinsed, scratched with 400-grit wet/dry sandpaper, wiped with a clean paper towel to remove the smut, then rinsed and placed in the electrolyte for the plating test. Operators must be careful not to touch or fingerprint the area that will undergo testing. Scratching the bottom of the test panel provides the operator with an idea of the leveling ability of the plating solution.

Brass panels are generally coated with a peelable plastic. It is common practice to remove the coating; scratch the bottom edge with 400-grit sandpaper; soak or direct-current clean the panel in a suitable brass cleaner; rinse; place in 5% by volume sulfuric acid; rinse; and then place in the electrolyte for testing.

CURRENT SUPPLY

Direct current must be used for hull cell tests. The current supply should be capable of supplying a maximum of 12 V. Twelve volts is normally not required, but it is beneficial to have the capability. Amperage is normally 5 amps or less, but 10 amps is again beneficial to have if needed. Ripple should be less than 5%. The ammeter should read in 0.2-amp increments or less to allow for proper control.

CURRENT DISTRIBUTION

For the tests to be effective, the current density should have a wider range than is encountered in practice. The equation below shows a logarithmic curve as follows:

$$\text{Current density} = I(C_1 - C_2 \log L)$$

where L indicates the distance along the cathode, I indicates total cell current, and C1 and C2 are constants based on the nature of the electrolyte.

Hull determined these constants from a number of electrolytes and found that they did not differ from one another. As a result, the values were averaged, and a general-purpose formula was derived:

For the 1,000-ml cell:

$$\text{Current density at any point} = I(18.8 - 28.3 \log L)$$

For the 267-ml cell:

$$\text{Current density at any point} = I(27.7 - 48.7 \log L)$$

This applies to the limits of L = 0.25 and L = 3.25 inches, where the current density is in amps/ft^2, I is in amperes, and L is in inches.

Deviations from these are to be expected, particularly from cyanide electrolytes, as these solutions may have fluctuations in current due to cathode polarization.

PART II

TESTING METHODS FOR ELECTROPLATING BATHS

The jiggle cell is unique in that it is the best test equipment for mimicking actual plating tank conditions. The jiggle cell utilizes a bent cathode panel, and it can be used for most plating solutions provided that the materials of construction are adequate for the solution being tested. Most jiggle cells are made of either polypropylene or acrylic.

JIGGLE CELL CATHODE

The jiggle cell cathode is usually 1 inch wide × 7 inches long. The jiggle cell cathode panel is usually bent on a mandrel supplied by the equipment manufacturer. Figure 1 shows brass- and zinc-plated steel panels as purchased, after bending on a mandrel.

Figure 1 depicts the various 1-inch-square areas after bending the panel.



Figure 1: Jiggle cell panels
(Images courtesy of Finishing Test Supply).



Figure 2: Air- and mechanically agitated jiggle cell.

There is a bottom, a face, a recess, and, finally, another face area. These images closely reproduce the types of contours and areas generally found on production parts in the plating tank.

The bottom of the panel is useful for representing the lower portion of parts in the plating tank. Typical problems include pitting or air pattern haziness on the bottom of the panels.

The two faces are good for representing the vertical areas of parts in the plating tanks. The recessed area mimics a typical recess on plating tank parts. It also represents the shelf or top of parts in a plating tank.

JIGGLE CELLS

Jiggle cells are usually supplied in various configurations:

Air or mechanical agitation with heat and temperature control: This type of unit will allow the operator to check both air and mechanically agitated plating baths. The heating controls allow the operator to also check heated and unheated plating solutions. The motor on the right will move the cathode up and down, providing the mechanical agitation (Fig. 2).

Air agitation with heat and temperature control: This unit will do air-agitated solutions but not mechanically agitated solutions. The unit does not have a motor to move the cathode panel up and down. See the example in Figure 3.

JIGGLE CELL ANODES

Jiggle cell anodes are usually 1 inch wide × 7 inches or longer. The anode material will usually match the anode material used in the plating bath to be tested. The anode should be bagged to prevent anode fines or sludge from entering the solution. Figure 4 shows examples of various jiggle cell anodes.

Test Procedure

The test procedure should be standardized to allow for reproducibility between tests. All steps should be taken to ensure that the conditions in the jiggle cell closely match the conditions in the plating tank. Particular attention should be paid to the agitation, current density, and temperature.

The finishing test equipment supplier will usually provide the user with recommended tips for the various plating tests.

The cathode will need to be carefully prepared for each test with a standard-

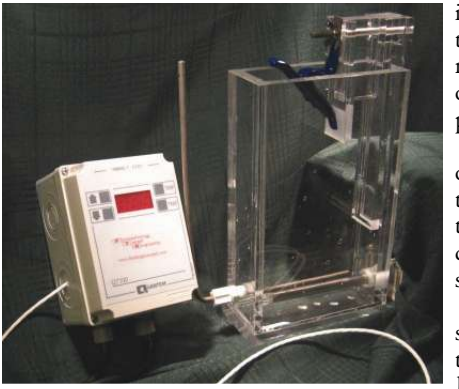


Figure 3: Air-agitated jiggle cell.



Figure 4: Jiggle cell anodes.

ized procedure. Care should be taken to ensure that the cathode panel is not contaminated from fingerprints or handling marks, poor cleaning, or poor activation.

The test cell will need to be rinsed out after each test. It is recommended to have jiggle cells devoted to each type of plating solution to prevent cross contamination from different solution types.

Unique anodes and anodes bags should also be used on different solution types. An example would be semibright sulfur-free nickel and bright nickel plating solutions.

The plating tests are normally run on the solution from the plating bath and then evaluated. The solution chemistry or operating conditions are then changed and another plating test is performed. The two panels should then be compared to determine if there is any improvement.

SPECIALIZED TESTS

It is common practice to use the jiggle cell for testing the ductility of nickel deposits. Users will use an unbent jiggle cell cathode and cut or shear off the bottom of the panel to reduce the surface area (and subsequent solution additive depletion). This is commonly used for semibright and bright nickel ductility evaluations.

CONCLUSIONS

The jiggle cell is the single piece of test equipment that represents the actual plating conditions in the plating tank. It is especially useful for under shelf and shelf area troubleshooting.

PART III

TESTING METHODS FOR ELECTROPLATING BATHS

The hull cell and jiggle cell are the two most widely used test equipment paraphernalia for electroplaters and electroplating addition agent suppliers. The interpretation of these test results is important. The operator must make a judgment based on previous tests on known acceptable plating solutions.

The tables that follow list the common causes and the corrective actions needed to improve a particular plating bath problem. The operator should look at one of the possible causes at a time to determine the correct action. The causes and necessary remedies are listed from the most to least frequent causes.

It should be noted that when running more than one test on a solution, the composition in the hull cell can change rapidly. Therefore, it is recommended that the concentrations of the solution be adjusted if fresh solution is not available for each test.

OTHER HULL CELL APPLICATIONS

Covering power. Hull cells can be used to also test the covering power of solutions. Tests are usually run at 0.2 amp for 1 minute. This gives a current density of approximately 12 to 0.4 ASF. This current density will usually provide an accurate determination of covering power. The effects of addition agents can also be investigated.

Cleaning and base metal compatibility. Hull cells can be used to evaluate the base metal's ability to accept electroplating. Hull cells can also be used to check the cleaning process prior to electroplating. When proprietary addition agents are used, it is good practice to contact the supplier for specific recommendations.

Problem	*Possible Cause*	*How to Correct*
Cloudy deposit MCD or HCD	1. Low brightener 2. Low pH 3. Organic contamination 4. Metallic contamination	1. Increase concentration of brightener 2. Adjust pH 3. Carbon treatment 4. High pH + carbon treatment
Dull deposit LCD area	1. High brightener 2. Metallic contamination 3. Low carrier 4. High agitation	1. "Dummy" solution at 4–5 ASF 2. "Dummy" solution at 4–5 ASF 3. Add carrier 4. Reduce agitation rate
Cloudy deposit LCD area	1. Low brightener 2. Low pH 3. Low index	1. Adjust brightener concentration 2. Adjust pH 3. Add index
Poor leveling	1. Low brightener 2. Low carrier	1. Add brightener 2. Add carrier
Poor ductility	1. High brightener 2. Low carrier 3. High pH 4. Metallic contamination 5. Organic contamination	1. "Dummy" solution at 4–5 ASF 2. Add carrier 3. Adjust pH 4. "Dummy" solution at 4–5 ASF 5. Carbon treatment
Burning	1. Low nickel salts/boric acid 2. High CD 3. Low temperature 4. Low agitation 5. Chromate contamination 6. Metallic contamination	1. Add nickel salts/boric acid 2. Reduce CD 3. Adjust temperature 4. Increase agitation rate 5. High CD "dummy" + high pH treatment 6. High pH + carbon treatment
Skip plating	1. High brightener 2. Metallic contamination (e.g., Zn, Cd, Pb) 3. Chromate contamination	1. "Dummy" solution at 4–5 ASF 2. "Dummy" solution at 4–5 ASF 3. High CD "dummy" + high pH treatment
Bright Nickel: Panels are usually plated at 2 amps for 5 minutes on steel panels.		

Problem	*Possible Cause*	*How to Correct*
Cloudy deposit MCD or HCD	1. Low leveler 2. Low pH 3. High control agent 4. High STEP Additive 5. Organic contamination 6. Metallic contamination (e.g., Fe, Si, Al, Cr^{+3}) 7. Low agitation	1. Increase concentration of leveler 2. Adjust pH upward 3. Reduce control agent concentration (carbon filter) 4. Temporarily discontinue additions 5. Carbon treatment 6. High pH + carbon treatment 7. Increase agitation
Cloudy deposit LCD Area	1. Low leveler 2. Low pH	1. Adjust leveler concentration 2. Adjust pH
Dull deposit LCD Area	1. Metallic contamination	1. "Dummy" solution at 4–5 ASF
Poor leveling	1. Low leveler 2. Low control agent 3. Low pH 4. High STEP additive 5. Low agitation	1. Add leveler 2. Add control agent 3. Adjust pH 4. Temporarily discontinue additions 5. Adjust agitation
Poor ductility	1. High Leveler 2. Low control agent 3. High pH 4. Metallic contamination (e.g., Zn, Pb, Cd) 5. Organic contamination	1. Reduce leveler concentration 2. Add control agent 3. Adjust pH 4. "Dummy" solution at 4–5 ASF 5. Carbon treatment
Burning	1. Low nickel salts/boric acid 2. High CD 3. Low temperature 4. Low agitation 5. Chromate contamination 6. Metallic contamination	1. Add nickel salts/boric acid 2. Reduce CD 3. Adjust temperature 4. Increase agitation rate 5. High CD "dummy" + high pH treatment* 6. High pH + carbon treatment
Skip plating	1. High leveler 2. Low control agent 3. Metallic contamination (e.g., Pb, Zn, Cd, Cr^{+6})	1. "Dummy" solution at 4–5 ASF 2. Add control agent 3. "Dummy" solution at 4–5 ASF
Semibright Nickel–Non-Coumarin: Panels are usually plated at 2 amps for 5 minutes on steel panels.		

Problem	*Possible Cause*	*How to Correct*
Poor covering power	1. Low current density 2. Poor electrical contact 3. High sulfate (low ratio) 4. High catalyst 5. High temperature	1. Increase current density 2. Ensure positive electrical contact 3. Lower sulfate (add barium carbonate) 4. Temporarily add chromic acid 5. Lower temperature
HCD burn uniform in shape, not patchy	1. Low temperature 2. Current density too high 3. Chromic acid too low 4. Low sulfate (high ratio) 5. Low catalyst	1. Adjust temperature 2. Adjust current density 3. Increase chromic acid 4. Analyze and adjust sulfate 5. Adjust catalyst to within range
Whitewash	1. Low sulfate 2. Low catalyst	1. Analyze and adjust sulfate 2. Adjust catalyst to within range

Hexavalent Chromium–Mixed Catalyst: Panels are usually plated at 5 amps for 2 minutes on nickel-plated steel panels.

Problem	*Possible Cause*	*How to Correct*
Dark smudges on work	1. High pH 2. Low wetting agent 3. Low complexer 4. Low chromium concentration	1. Adjust pH 2. Add wetting agent 3. Add complexer 4. Add chromium
White deposit at LCD cutoff	1. Zn, Pb contamination	1. "Dummy" solution at 15 ASF
White patches on work	1. Lead contamination 2. Poor cleaning prior to nickel 3. Part dries prior to chromium plating	1. "Dummy" solution at 15 ASF 2. Improve cleaning 3. Keep parts slightly wet
Poor coverage	1. Low pH 2. Low specific gravity 3. Zn, Pb contamination 4. High air agitation 5. High temperature	1. Correct pH 2. Add conductivity salts 3. "Dummy" at 15 ASF 4. Reduce air agitation 5. Reduce temperature
Dark deposits overall	1. High temperature 2. High pH 3. Metallic contamination	1. Adjust temperature 2. Adjust pH 3. "Dummy" solution at 15 ASF

Trivalent Chrome (Sulfate Chloride System): Panels are usually plated at 5 amps for 2 minutes on nickel-plated steel panels.

Problem	*Possible Cause*	*How to Correct*
Poor leveling	1. Insufficient agitation 2. Solution temperature is less than 70°F 3. Copper content of solution is too low 4. Brightener concentration is too low 5. Chloride content is out of normal range	1. Increase agitation 2. Increase solution temperature to 70°F 3. Increase copper content of solution 4. Add brightener 5. Analyze and adjust chloride
Pitting	1. Grease or oil contamination in plating bath 2. Particulate matter in bath	1. Carbon treat bath 2. Filter bath
Streaking in deposit	1. Excessive brightener additions 2. Organic contamination	1. "Dummy" solution at 15 ASF. 2. Carbon treat solution
Burnt deposit HCD	1. Insufficient agitation 2. Solution temperature is less than 70°F 3. Copper content of solution is too low 4. Brightener concentration too low 5. Chloride content is out of normal range	1. Increase agitation 2. Increase solution temperature 3. Increase copper content 4. Increase brightener 5. Analyze and adjust chloride
Acid Copper: Panels are usually plated at 2 amps for 10 minutes on brass panels.		

Problem	*Possible Cause*	*How to Correct*
LCD skip plate	1. High brightener 2. High zinc	1. Dummy plate solution 2. Reduce zinc metal
Burnt deposit HCD	1. Low zinc metal 2. Low brightener	1. Increase zinc metal concentration 2. Add brightener
Appearance After Nitric Post Dip or Clear Chromate		
Black stain in HCD, overall yellow deposit	1. Iron contamination	1. Reduce iron contamination
Black or brown stain in LCD	1. Copper contamination	1. Reduce copper contamination
Bright Acid Chloride Zinc: Panels are plated at 3 amps for 5 minutes on steel panels.		

CHEMICAL ANALYSIS OF PLATING SOLUTIONS*

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Plating solutions must be routinely analyzed in order to maintain the recommended bath formulation and to preempt the occurrence of problems related to improper levels of bath constituents. Contaminant levels in the solutions must also be monitored. Manufacturers of plating systems establish optimum specifications to ensure maximum solution efficiency and uniformity of deposits. The various factors that cause the concentrations of bath constituents to deviate from their optimum values are as follows:

1. drag-out;
2. solution evaporation;
3. chemical decomposition; and
4. unequal anode and cathode efficiencies.

A current efficiency problem is recognized by gradual but continuous changes in pH, metal content, or cyanide content (see Table I).

The techniques employed for the quantitative analysis of plating solutions are classified as volumetric (titrimetric), gravimetric, and instrumental. Volumetric and gravimetric methods are also known as "wet" methods. The analyst must select the method that is best suited and most cost effective for a particular application.

The wet methods outlined here are simple, accurate, and rapid enough for practically all plating process control. They require only the common analytical equipment found in the laboratory, and the instructions are sufficiently detailed for an average technician to follow without any difficulty. The determination of small amounts of impurities and uncommon metals should be referred to a competent laboratory, as a high degree of skill and chemical knowledge are required for the determination of these constituents.

Hull cell testing (see the section on plating cells elsewhere in this *Guidebook*) enables the operator to observe the quality of a deposit over a wide current density range.

VOLUMETRIC METHODS

When titrants composed of standard solutions are added to a sample that contains a component whose concentration is to be quantitatively determined, the method is referred to as a volumetric method. The component to be determined must react completely with the titrant in stoichiometric proportions. From the volume of titrant required, the component's concentration is calculated. The simplicity, quickness, and relatively low cost of volumetric methods make them the most widely used for the analysis of plating and related solutions.

Volumetric methods involve reactions of several types: oxidation-reduction, acid-base, complexation, and precipitation. Indicators are auxiliary reagents, which usually signify the endpoint of the analysis. The endpoint can be indicated

by a color change, formation of a turbid solution, or the solubilization of a turbid solution.

Some volumetric methods require little sample preparation, whereas others may require extensive preparation. Accuracy decreases for volumetric analyses of components found in low concentrations, as endpoints are not as easily observed as with the components found in high concentrations.

Volumetric methods are limited in that several conditions must be satisfied. Indicators should be available to signal the endpoint of the titration. The component-titrant reaction should not be affected by interferences from other substances found in the solution.

GRAVIMETRIC METHODS

In gravimetric methods, the component being determined is separated from other components of the sample by precipitation, volatilization, or electroanalytical means. Precipitation methods are the most important gravimetric methods. The precipitate is usually a very slightly soluble compound of high purity that contains the component. The weight of the precipitate is determined after it is filtered from solution, washed, and dried. Gravimetric methods are used to supplement the available volumetric methods.

Limitations of gravimetric methods include the requirement that the precipitated component has an extremely low solubility. The precipitate must also be of high purity and be easily filterable.

Species that are analyzed gravimetrically include chloride, sulfate, carbonate, phosphate, gold, and silver.

INSTRUMENTAL METHODS

Instrumental methods differ from wet methods in that they measure a physical property related to the composition of a substance, whereas wet methods rely on chemical reactions. The selection of an instrument for the analysis of plating solutions is a difficult task. Analysts must decide if the cost is justified and if the analytical instrument is capable of analyzing for the required substances with a high degree of accuracy and precision. Instruments coupled to computers can automatically sample, analyze, and record results. Mathematical errors are minimized and sample measurements are more reproducible than with wet methods. Instrumental methods are also extremely rapid when compared with wet methods.

Unlike humans, instruments cannot judge. They cannot recognize improper sample preparation or interfering substances. Erroneous results are sometimes produced by electronic and mechanical malfunctions.

Analytical instruments frequently used in the analysis of plating solutions can be categorized as spectroscopic, photometric, chromatographic, and electroanalytical. Spectroscopic methods (flame photometry, emission spectrometry, X-ray fluorescence, mass spectrometry, and inductively coupled plasma) are based on the emission of light. Photometric methods (spectrophotometry, colorimetry, and atomic absorption) are based on the absorption of light. Chromatographic methods (ion chromatography) involve the separation of substances for subsequent identification. Electroanalytical methods (potentiometry, conductometry, polarography, amperometry, and electrogravimetry) involve an electric current in the course of the analysis.

The instrumental methods, comprehensively reviewed below, are most applicable to plating environments.

SPECTROSCOPIC METHODS

Spectroscopy is the analysis of a substance by the measurement of emitted

light. When heat, electrical energy, or radiant energy is added to an atom, the atom becomes excited and emits light. Excitation can be caused by a flame, spark, X-rays, or an AC or DC arc. The electrons in the atom are activated from their ground state to unstable energy shells of higher potential energy. Upon returning to their ground state, energy is released in the form of electromagnetic radiation.

Because each element contains atoms with different arrangements of outermost electrons, a distinct set of wavelengths is obtained. These wavelengths, from atoms of several elements, are separated by a monochromator such as a prism or a diffraction grating. Detection of the wavelengths can be accomplished photographically (spectrograph) or via direct-reading photoelectric detectors (spectrophotometers). The measurement of intensity emitted at a particular wavelength is proportional to the concentration of the element being analyzed.

An advantage of spectroscopy is that the method is specific for the element being analyzed. It permits quantitative analysis of trace elements without any preliminary treatment and without prior knowledge as to the presence of the element. Most metals and some nonmetals may be analyzed. Spectroscopic analysis is also useful for repetitive analytical work.

Disadvantages of spectroscopic analysis include the temperature dependence of intensity measurements, as intensity is very sensitive to small fluctuations in temperature. The accuracy and precision of spectrographic methods is not as high as some spectrophotometric methods or wet analyses. Spectrographic methods are usually limited to maximum element concentrations of 3%. Additionally, sensitivity is much smaller for elements of high energy (e.g., zinc) than for elements of low energy (e.g., sodium).

Applications of spectroscopy include the analysis of major constituents and impurities in plating solutions, and of alloy deposits for composition.

Flame Photometry

In flame photometry (FP), a sample in solution is atomized at constant air pressure and introduced in its entirety into a flame as a fine mist. The temperature of the flame (1,800-3,100^{O}K) is kept constant. The solvent is evaporated and the solid is vaporized and then dissociated into ground state atoms. The valence electrons of the ground state atoms are excited by the energy of the flame to higher energy levels and then fall back to the ground state. The intensities of the emitted spectrum lines are determined in the spectrograph or measured directly by a spectrophotometer.

The flame photometer is calibrated with standards of known composition and concentration. The intensity of a given spectral line of an unknown can then be correlated with the amount of an element present that emits the specific radiation.

Physical interferences may occur from solute or solvent effects on the rate of transport of the sample into the flame. Spectral interferences are caused by adjacent line emissions when the element being analyzed has nearly the same wavelength as another element. Monochromators or the selection of other spectral lines minimize this interference. Ionization interferences may occur with the higher temperature flames. By adding a second ionizable element, the interferences due to the ionization of the element being determined are minimized.

An advantage of FP is that the temperature of the flame can be kept more nearly constant than with electric sources. A disadvantage of the method is that the sensitivity of the flame source is many times smaller than that of an electric arc or spark.

FP is used for the analysis of aluminum, boron, cadmium, calcium, chromium, cobalt, copper, indium, iron, lead, lithium, magnesium, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, tin, and zinc.

Emission Spectrometry

In emission spectrometry (ES), a sample composed of a solid, cast metal or solution is excited by an electric discharge such as an AC arc, a DC arc, or a spark. The sample is usually placed in the cavity of a lower graphite electrode, which is made positive. The upper counterelectrode is another graphite electrode ground to a point. Graphite is the preferred electrode material because of its ability to withstand the high electric discharge temperatures. It is also a good electrical conductor and does not generate its own spectral lines.

The arc is started by touching the two graphite electrodes and then separating them. The extremely high temperatures (4,000-6,000°K) produce emitted radiation higher in energy and in the number of spectral lines than in flame photometry. Characteristic wavelengths from atoms of several elements are separated by a monochromator and are detected by spectrographs or spectrophotometers. Qualitative identification is performed by using available charts and tables to identify the spectral lines that the emission spectrometer sorts out according to their wavelength. The elements present in a sample can also be qualitatively determined by comparing the spectrum of an unknown with that of pure samples of the elements. The density of the wavelengths is proportional to the concentration of the element being determined. Calibrations are done against standard samples.

ES is a useful method for the analysis of trace metallic contaminants in plating baths. The "oxide" method is a common quantitative technique in ES. A sample of the plating bath is evaporated to dryness and then heated in a muffle furnace. The resultant oxides are mixed with graphite and placed in a graphite electrode. Standards are similarly prepared and a DC arc is used to excite the sample and standards.

X-ray Fluorescence

X-ray fluorescence (XRF) spectroscopy is based on the excitation of samples by an X-ray source of sufficiently high energy, resulting in the emission of fluorescent radiation. The concentration of the element being determined is proportional to the intensity of its characteristic wavelength. A typical XRF spectrometer consists of an X-ray source, a detector, and a data analyzer.

Advantages of XRF include the nondestructive nature of the X-rays on the sample. XRF is useful in measuring the major constituents of plating baths such as cadmium, chromium, cobalt, gold, nickel, silver, tin, and zinc. Disadvantages of XRF include its lack of sensitivity as compared with ES.

X-ray spectroscopy is also used to measure the thickness of a plated deposit. The X-ray detector is placed on the wavelength of the element being measured. The surface of the deposit is exposed to an X-ray source and the intensity of the element wavelength is measured. A calibration curve is constructed for intensity against thickness for a particular deposit. Coating compositions can also be determined by XRF.

Mass Spectrometry

In mass spectrometry (MS), gases or vapors derived from liquids or solids are bombarded by a beam of electrons in an ionization chamber, causing ionization and a rupture of chemical bonds. Charged particles are formed, which may be composed of elements, molecules, or fragments. Electric and magnetic fields then separate the ions according to their mass to charge ratios *(m/e)*. The amount and type of fragments produced in an ionization chamber, for a particular energy of the bombarding beam, are characteristic of the molecule; therefore, every chemical compound has a distinct mass spectrum. By establishing a mass spectrum of several pure compounds, an observed pattern allows identification and analysis

of complex mixtures.

The mass spectrum of a compound contains the masses of the ion fragments and the relative abundances of these ions plus the parent ion. Dissociation fragments will always occur in the same relative abundance for a particular compound.

MS is applicable to all substances that have a sufficiently high vapor pressure. This usually includes substances whose boiling point is below 450°C. MS permits qualitative and quantitative analysis of liquids, solids, and gases.

Inductively Coupled Plasma

Inductively coupled plasma (ICP) involves the aspiration of a sample in a stream of argon gas, and then its ionization by an applied radio frequency field. The field is inductively coupled to the ionized gas by a coil surrounding a quartz torch that supports and encloses the plasma. The sample aerosol is heated in the plasma, the molecules become almost completely dissociated and then the atoms present in the sample emit light at their characteristic frequencies. The light passes through a monochromator and onto a detector.

The high temperature (7,000°K) of the argon plasma gas produces efficient atomic emission and permits low detection limits for many elements. As with atomic absorption (AA), ICP does not distinguish between oxidation states (e.g., Cr^{3+} and Cr^{6+}) of the same element—the total element present is determined. Advantages of ICP include complete ionization and no matrix interferences as in AA. ICP allows simultaneous analysis of many elements in a short time. It is sensitive to part-per-billion levels.

Disadvantages of ICP include its high cost and its intolerance to samples with greater than 3% dissolved solids. Background corrections usually compensate for interferences due to background radiation from other elements and the plasma gases. Physical interferences, due to viscosity or surface tension, can cause significant errors. These errors are reduced by diluting the sample. Although chemical interferences are insignificant in the ICP method, they can be greatly minimized by careful selection of the instrument's operating conditions, by matrix matching, or by buffering the sample.

ICP is applicable to the analysis of major components and trace contaminants in plating solutions. It is also useful for waste-treatment analysis.

PHOTOMETRIC METHODS

Photometric methods are based on the absorption of ultraviolet (200-400 nm) or visible (400-1,000 nm) radiant energy by a species in solution. The amount of energy absorbed is proportional to the concentration of the absorbing species in solution. Absorption is determined spectrophotometrically or colorimetrically.

The sensitivity and accuracy of photometric methods must be frequently checked by testing standard solutions in order to detect electrical, optical, or mechanical malfunctions in the analytical instrument.

Spectrophotometry and Colorimetry

Spectrophotometry involves analysis by the measurement of the light absorbed by a solution. The absorbance is proportional to the concentration of the analyte in solution. Spectrophotometric methods are most often used for the analysis of metals with concentrations of up to 2%.

Spectrophotometers consist of a light source (tungsten or hydrogen), a monochromator, a sample holder, and a detector. Ultraviolet or visible light of a definite wavelength is used as the light source. Detectors are photoelectric cells that measure the transmitted (unabsorbed) light. Spectrophotometers differ from photometers in that they utilize monochromators, whereas photometers use fil-

ters to isolate the desired wavelength region. Filters isolate a wider band of light.

In spectrophotometric titrations, the cell containing the analyte solution is placed in the light path of a spectrophotometer. Titrant is added to the cell with stirring, and the absorbance is measured. The endpoint is determined graphically. Applications of this titration include the analysis of a mixture of arsenic and antimony and the analysis of copper with ethylene diamine tetra acetic acid (EDTA).

The possibility of errors in spectrophotometric analyses is increased when numerous dilutions are required for an analysis.

Colorimetry involves comparing the color produced by an unknown quantity of a substance with the color produced by a standard containing a known quantity of that substance. When monochromatic light passes through the colored solution, a certain amount of the light, proportional to the concentration of the substance, will be absorbed. Substances that are colorless or only slightly colored can be rendered highly colored by a reaction with special reagents.

In the standard series colorimetric method, the analyte solution is diluted to a certain volume (usually 50 or 100 ml) in a Nessler tube and mixed. The color of the solution is compared with a series of standards similarly prepared. The concentration of the analyte equals the concentration of the standard solution whose color it matches exactly. Colors can also be compared to standards via a colorimeter (photometer), comparator, or spectrophotometer.

The possible errors in colorimetric measurements may arise from the following sources: turbidity, sensitivity of the eye or color blindness, dilutions, photometer filters, chemical interferences, and variations in temperature or pH.

Photometric methods are available for the analysis of the following analytes:

Anodizing solutions: Fe, Cu, Mn
Brass solutions: Fe
Cadmium solutions: Fe, Ti, Zn, Cu, Ni
Chromium solutions: Cr, Fe, Ni, Cu, Se
Acid copper solutions: Cl, Fe
Alkaline copper solutions: Fe, Se
Gold solutions: Au, Ni, In, Co, Cu, Fe, PO_4
Iron solutions: Mn, NH_3
Lead and tin-lead solutions: Pb
Nickel solutions: Cr, Cu, Zn, Fe, Co, NH_3
Palladium solutions: Pd, Cr, NH_3
Platinum solutions: Pt
Rhodium solutions: Rh
Silver solutions: Ni, Cu, Sb
Acid tin solutions: Fe, Cu
Alkaline tin solutions: Cu, Pb, Zn
Acid zinc solutions: Cu, Fe
Alkaline zinc solutions: Cu, Fe
Wastewater: Cr^{6+}, Ni, Cu, Fe, Zn, Pb, Al, B, NO_3, NO_2, PO_4, Cl, CN, wetting agents.

Atomic Absorption

Metals in plating and related solutions can be readily determined by AA spectrophotometry. Optimum ranges, detection limits, and sensitivities of metals vary with the various available instruments.

In direct-aspiration atomic absorption (DAAA) analysis, the flame (usually air-

acetylene or nitrous oxide-acetylene) converts the sample aerosol into atomic vapor, which absorbs radiation from a light source. A light source from a hollow cathode lamp or an electrodeless discharge lamp is used, which emits a spectrum specific to the element being determined. The high cost of these lamps is a disadvantage of the AA method. A detector measures the light intensity to give a quantitative determination.

DAAA is similar to flame photometry in that a sample is aspirated into a flame and atomized. The difference between the two methods is that flame photometry measures the amount of emitted light, whereas DAAA measures the amount of light absorbed by the atomized element in the flame. In DAAA, the number of atoms in the ground state is much greater than the number of atoms in any of the excited states of the spectroscopic methods. Consequently, DAAA is more efficient and has better detection limits than the spectroscopic methods.

Spectral interferences occur when a wavelength of an element being analyzed is close to that of an interfering element. The analysis will result in an erroneously high measurement. To compensate for this interference, an alternate wavelength or smaller slit width is used.

When the physical properties (e.g., viscosity) of a sample differ from those of the standard, matrix interferences occur. Absorption can be enhanced or suppressed. To overcome these interferences, matrix components in the sample and standard are matched or a release agent, such as EDTA or lanthanum, is added.

Chemical interferences are the most common interferences encountered in AA analysis. They result from the nonabsorption of molecularly bound atoms in the flame. These interferences are minimized by using a nitrous oxide-acetylene flame instead of an air-acetylene flame to obtain the higher flame temperature needed to dissociate the molecule or by adding a specific substance (e.g., lanthanum) to render the interferant harmless. Chemical interferences can also be overcome by extracting the element being determined or by extracting the interferant from the sample.

The sensitivity and detection limits in AA methods vary with the instrument used, the nature of the matrix, the type of element being analyzed, and the particular AA technique chosen. It is best to use concentrations of standards and samples within the optimum concentration range of the AA instrument. When DAAA provides inadequate sensitivity, other specialized AA methods, such as graphite furnace AA, cold vapor AA, or hydride AA, are used.

In *graphite furnace AA* (GFAA), the flame that is used in DAAA is replaced with an electrically heated graphite furnace. A solution of the analyte is placed in a graphite tube in the furnace, evaporated to dryness, charred, and atomized. The metal atoms being analyzed are propelled into the path of the radiation beam by increasing the temperature of the furnace and causing the sample to be volatilized. Only very small amounts of sample are required for the analysis.

GFAA is a very sensitive technique and permits very low detection limits. The increased sensitivity is due to the much greater occupancy time of the ground state atoms in the optical path as compared with DAAA. Increased sensitivity can also be obtained by using larger sample volumes or by using an argon-hydrogen purge gas mixture instead of nitrogen. Because of its extreme sensitivity, determining the optimum heating times, temperature, and matrix modifiers is necessary to overcome possible interferences.

Interferences may occur in GFAA analysis due to molecular absorption and chemical effects. Background corrections compensate for the molecular absorption interference. Specially coated graphite tubes minimize its interaction with some elements. Gradual heating helps to decrease background interference, and permits

determination of samples with complex mixtures of matrix components.

The GFAA method has been applied to the analysis of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin.

Cold vapor atomic absorption (CVAA) involves the chemical reduction of mercury or selenium by stannous chloride and its subsequent analysis. The reduced solution is vigorously stirred in the reaction vessel to obtain an equilibrium between the element in the liquid and vapor phases. The vapor is then purged into an absorption cell located in the light path of a spectrophotometer. The resultant absorbance peak is recorded on a strip chart recorder.

The extremely sensitive CVAA procedure is subject to interferences from some organics, sulfur compounds, and chlorine. Metallic ions (e.g., gold, selenium), which are reduced to the elemental state by stannous chloride, produce interferences if they combine with mercury.

Hydride atomic absorption (HAA) is based on chemical reduction with sodium borohydride to selectively separate hydride-forming elements from a sample. The gaseous hydride that is generated is collected in a reservoir attached to a generation flask, and is then purged by a stream of argon or nitrogen into an argon-hydrogen-air flame. This permits high-sensitivity determinations of antimony, arsenic, bismuth, germanium, selenium, tellurium, and tin.

The HAA technique is sensitive to interferences from easily reduced metals such as silver, copper, and mercury. Interferences also arise from transition metals in concentrations greater than 200 mg/L and from oxides of nitrogen.

Ion Chromatography

In ion chromatography (IC), analytes are separated with an eluent on a chromatographic column based on their ionic charges. Because plating solutions are water based, the soluble components must be polar or ionic; therefore, IC is applicable to the analysis of plating and related solutions.

Ion chromatographs consist of a sample delivery system, a chromatographic separation column, a detection system, and a data handling system.

IC permits the rapid sequential analysis of multiple analytes in one sample. The various detectors available, such as UV-visible, electrochemical, or conductivity, allow for specific detection in the presence of other analytes. IC is suitable for the analysis of metals, anionic and cationic inorganic bath constituents, and various organic plating bath additives. It is also used for continuous on-line operations.

Interferences arise from substances that have retention times coinciding with that of any anion being analyzed. A high concentration of a particular ion may interfere with the resolution of other ions. These interferences can be greatly minimized by gradient elution or sample dilution.

IC has been applied to the analysis of the following analytes in plating and related solutions:

Metals: Aluminum, barium, cadmium, calcium, trivalent and hexavalent chromium, cobalt, copper, gold, iron, lead, lithium, magnesium, nickel, palladium, platinum, silver, tin, zinc.

Ions: Ammonium, bromide, carbonate, chloride, cyanide, fluoborate, fluoride, hypophosphite, nitrate, nitrite, phosphate, potassium, sodium, sulfate, sulfide, sulfite.

Acid Mixtures: Hydrofluoric, nitric, and acetic acids.

Organics: Brighteners, surfactants, organic acids.

ELECTROANALYTICAL METHODS

Electroanalytical methods involve the use of one or more of three electrical quan-

tities—current, voltage, and resistance. These methods are useful when indicators for a titration are unavailable or unsuitable. Although trace analysis may be done quite well by spectroscopic or photometric methods, electroanalytical methods offer ease of operation and relatively lower costs of purchase and maintenance.

Potentiometry

Potentiometry involves an electrode that responds to the activity of a particular group of ions in solution. Potentiometric methods correlate the activity of an ion with its concentration in solution.

In potentiometric titrations, titrant is added to a solution and the potential between an indicator and reference electrode is measured. The reaction must involve the addition or removal of an ion for which an electrode is available. Acid-base titrations are performed with a glass indicator electrode and a calomel reference electrode. The endpoint corresponds to the maximum rate of change of potential per unit volume of titrant added.

Advantages of potentiometric titrations include its applicability to colored, turbid, or fluorescent solutions. It is also useful in situations where indicators are unavailable.

The sensitivity of potentiometric titrations is limited by the accuracy of the measurement of electrode potentials at low concentrations. Solutions that are more dilute than 10^{-5} N cannot be accurately titrated potentiometrically. This is because the experimentally measured electrode potential is a combined potential, which may differ appreciably from the true electrode potential. The difference between the true and experimental electrode potentials is due to the residual current, which arises from the presence of electroactive trace impurities.

The direct potentiometric measurement of single ion concentrations is done with ion selective electrodes (ISEs). The ISE develops an electric potential in response to the activity of the ion for which the electrode is specific. ISEs are available for measuring calcium, copper, lead, cadmium, ammonia, bromide, nitrate, cyanide, sulfate, chloride, fluoride, and other cations and anions.

Cation ISEs encounter interferences from other cations, and anion ISEs encounter interferences from other anions. These interferences can be eliminated by adjusting the sample pH or by chelating the interfering ions. ISE instructions must be reviewed carefully to determine the maximum allowable levels of interferants, the upper limit of the single ion concentration for the ISE, and the type of media compatible with the particular ISE.

Some of the solutions that can be analyzed by potentiometric methods are:

Anodizing solutions: Al, H_2SO_4, $C_2H_2O_4$, CrO_3, Cl
Brass solutions: Cu, Zn, NH_3, CO_3
Bronze solutions: Cu, Sn, NaOH, NaCN, Na_2CO_3
Chromium solutions: Cr, Cl
Cadmium solutions: Cd, NaOH, NaCN, Na_2CO_3
Acid copper solutions: Cl
Alkaline copper solutions: NaOH, NaCN, Na_2CO_3
Gold solutions: Au, Ag, Ni, Cu
Lead and tin/lead solutions: Pb, Sn, HBF_4
Nickel solutions: Co, Cu, Zn, Cd, Cl, H_3BO_3
Silver solutions: Ag, Sb, Ni
Acid tin solutions: Sn, HBF_4, H_2SO_4
Alkaline tin solutions: Sn, NaOH, $NaCO_3$, Cl
Zinc solutions: Zn

Conductometry

Electrolytic conductivity measures a solution's ability to carry an electric current. A current is produced by applying a potential between two inert metallic electrodes (e.g., platinum) inserted into the solution being tested. When other variables are held constant, changes in the concentration of an electrolyte result in changes in the conductance of electric current by a solution.

In conductometric titrations, the endpoint of the titration is obtained from a plot of conductance against the volume of titrant. Excessive amounts of extraneous foreign electrolytes can adversely affect the accuracy of a conductometric titration.

Conductometric methods are used when wet or potentiometric methods give inaccurate results due to increased solubility (in precipitation reactions) or hydrolysis at the equivalence point. The methods are accurate in both dilute and concentrated solutions, and they can also be used with colored solutions.

Conductometric methods have been applied to the analysis of Cr, Cd, Co, Fe, Ni, Pb, Ag, Zn, CO_3, Cl, F, and SO_4.

Polarography

In polarography, varying voltage is applied to a cell consisting of a large mercury anode (reference electrode) and a small mercury cathode (indicator electrode) known as a dropping mercury electrode (DME). Consequent changes in current are measured. The large area of the mercury anode precludes any polarization. The DME consists of a mercury reservoir attached to a glass capillary tube with small mercury drops falling slowly from the opening of the tube. A saturated calomel electrode is sometimes used as the reference electrode.

The electrolyte in the cell consists of a dilute solution of the species being determined in a medium of supporting electrolyte. The supporting electrolyte functions to carry the current in order to raise the conductivity of the solution. This ensures that if the species to be determined is charged, it will not migrate to the DME. Bubbling an inert gas, such as nitrogen or hydrogen, through the solution prior to running a polarogram, will expel dissolved oxygen in order to prevent the dissolved oxygen from appearing on the polarogram.

Reducible ions diffuse to the DME. As the applied voltage increases, negligible current flow results until the decomposition potential is reached for the metal ion being determined. When the ions are reduced at the same rate as they diffuse to the DME, no further increases in current occur, as the current is limited by the diffusion rate. The half-wave potential is the potential at which the current is 50% of the limiting value.

Polarograms are obtained by the measurement of current as a function of applied potential. Half-wave potentials are characteristic of particular substances under specified conditions. The limiting current is proportional to the concentration of the substance being reduced. Substances can be analyzed quantitatively and qualitatively if they are capable of undergoing anodic oxidation or cathodic reduction. As with other instrumental methods, results are referred to standards in order to quantitate the method.

Advantages of polarographic methods include their ability to permit simultaneous qualitative and quantitative determinations of two or more analytes in the same solution. Polarography has wide applicability to inorganic, organic, ionic, or molecular species.

Disadvantages of polarography include the interferences caused by large concentrations of electropositive metals in the determination of low concentrations of electronegative metals. The very narrow capillary of the DME occasionally becomes clogged.

Polarographic methods are available for the following solutions:

Anodizing solutions: Cu, Zn, Mn
Brass solutions: Pb, Cd, Cu, Ni, Zn
Bronze solutions: Pb, Zn, Al, Cu, Ni
Cadmium solutions: Cu, Pb, Zn, Ni
Chromium solutions: Cu, Ni, Zn, Cl, SO_4
Acid copper solutions: Cu, Cl
Alkaline copper solutions: Zn, Fe, Pb, Cu
Gold solutions: Au, Cu, Ni, Zn, In, Co, Cd
Iron solutions: Mn
Lead and tin-lead solutions: Cu, Cd, Ni, Zn, Sb
Nickel solutions: Cu, Pb, Zn, Cd, Na, Co, Cr, Mn
Palladium solutions: Pd, Cr^{3+}, Cr^{6+}
Rhodium solutions: Rh
Silver solutions: Sb, Cu, Cd
Acid tin solutions: Sn^{4+}, Cu, Ni, Zn
Alkaline tin solutions: Pb, Cd, Zn, Cu
Acid zinc solutions: Cu, Fe, Pb, Cd
Alkaline zinc solutions: Pb, Cd, Cu
Wastewater: Cd, Cu, Cr^{3+}, Ni, Sn, Zn

Amperometry

Amperometric titrations involve the use of polarography as the basis of an electrometric titration. Voltage applied across the indicator electrode (e.g., DME or platinum) and reference electrode (e.g., calomel or mercury) is held constant and the current passing through the cell is measured as a function of titrant volume added. The endpoint of the titration is determined from the intersection of the two straight lines in a plot of current against volume of titrant added. Polarograms are run to determine the optimum titration voltage.

Amperometric titrations can be carried out at low analyte concentrations at which volumetric or potentiometric methods cannot yield accurate results. They are temperature independent and more accurate than polarographic methods. Although amperometry is useful for oxidation-reduction or precipitation reactions, few acid-base reactions are determined by this method.

Some of the reactions that can be analyzed by amperometric methods are given in Table II.

Electrogravimetry

In electrogravimetry, the substance to be determined is separated at a fixed potential on a preweighed inert cathode, which is then washed, dried, and weighed. Requirements for an accurate electrogravimetric analysis include good agitation, smooth adherent deposits, and proper pH, temperature, and current density.

Advantages of electrogravimetry include its ability to remove quantitatively most common metals from solution. The method does not require constant supervision. Disadvantages include long electrolysis times.

Some of the metals that have been determined electrogravimetrically are cadmium, cobalt, copper, gold, iron, lead, nickel, rhodium, silver, tin, and zinc.

SAMPLING

Analyses are accurate only when the sample is truly representative of the solution being analyzed. Each tank should have a reference mark indicating the correct level for the solution, and the bath should always be at this level when the sample

is taken. Solutions should be stirred before sampling. If there is sludge in the tank, the solution should be stirred at the end of the day and the bath allowed to stand overnight, taking the sample in the morning.

Solutions should be sampled by means of a long glass tube. The tube is immersed in the solution, the thumb is placed over the upper open end, and a full tube of solution is withdrawn and transferred to a clean, dry container. The solution should be sampled at a minimum of 10 locations in the tank to ensure a representative sample. A quart sample is sufficient for analysis and Hull cell testing, and any remaining solution can be returned to its tank.

STANDARD SOLUTIONS, REAGENTS, AND INDICATORS FOR WET METHODS

Standard solutions, reagents, and indicators can be purchased ready-made from laboratory supply distributors. Unless a laboratory has the experience and high degree of accuracy that is required in preparing these solutions, it is recommended that they be purchased as prepared solutions. Preparations for all the solutions are given here to enable technicians to prepare or recheck their solutions.

A standard solution is a solution with an accurately known concentration of a substance used in a volumetric analysis. Standardization of standard solutions requires greater accuracy than routine volumetric analyses. An error in standardization causes errors in all analyses that are made with the solution; therefore, Primary Standard Grade chemicals should be used to standardize standard solutions.

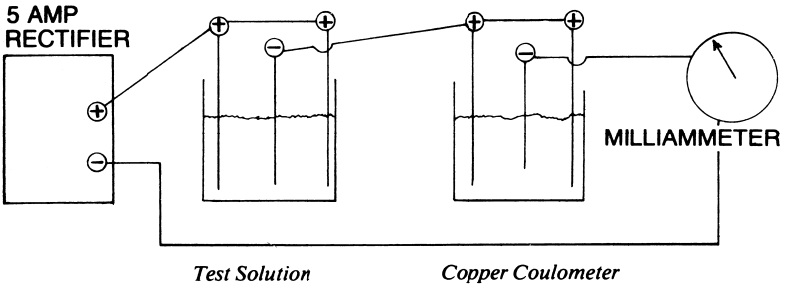


Fig. 1. Test setup for determination of cathode efficiency. Use 500-ml beakers and 1 ´ 2-in. brass cathodes. The anodes for the test solution should match that used in the plating bath. Use copper anodes for the coulometer.

The strengths of standard solutions are usually expressed in terms of normality or molarity. Normalities of standard solutions and their equivalent molarities are listed in Table III. The methods to standardize all the standard solutions required for the analysis of plating and related solutions are listed in Table IV.

Indicators are added to solutions in volumetric analyses to show color change or onset of turbidity, signifying the endpoint of a titration. The indicators required for all of the analyses and their preparations are listed in Table V. Analytical Grade chemicals should be used in preparing analytical reagents

(Table VI) and Reagent Grade acids should be used (Table VII). When chemicals of lesser purity are used, the accuracy of the results will be diminished.

Tables VIII through XII provide specific methods for testing the constituents of electroplating, electroless, and anodizing baths, as well as acid dips and alkaline cleaners.

SAFETY

As with any laboratory procedure, the accepted safety rules for handling acids, bases, and other solutions should be followed. Acids are always added to water, not the reverse. Mouth pipettes should not be used for pipetting plating solutions. Safety glasses should always be worn, and care should be exercised to avoid skin and eye contact when handling chemicals. A fume hood should be used when an analytical method involves the liberation of hazardous or annoying fumes. Laboratory staff should be well versed in the first-aid procedures required for various chemical accidents.

DETERMINATION OF CATHODE EFFICIENCY

The procedure for determining cathode efficiency, using the setup pictured in Fig. 1, is as follows:

1. Connect the copper coulometer in series with the test cell.
2. The copper coulometer solution should contain 30 oz/gal copper sulfate pentahydrate and 8 oz/gal sulfuric acid.
3. Use the same anodes, temperature, and agitation in the test solution that are used in the plating bath.
4. Plate at 0.4 A (30 A/ft^2) for a minimum of 10 minutes.
5. Rinse both cathodes, dry in acetone, and weigh.

$$\% \text{ Cathode Efficiency} = \frac{\text{weight in grams of test metal} \times \text{valence of test metal in bath} \times 3177}{\text{weight in grams of copper metal} \quad \text{atomic weight of test metal}}$$

**Editor's note: To view this article in its entirety, including corresponding tables, please consult the online Guidebook archive.*

THICKNESS TESTING

BY NORBERT SAJDERA
KOCOUR CO., CHICAGO; www.kocour.net

Coatings are applied to base materials to provide properties not inherent in the base. These include, but are not limited to, corrosion protection, wear resistance, conductivity, color, reflectivity, and solderability.

The amount of coating applied is critical to the final product's utility and cost. The determination of the amount of coating is, therefore, important in appraising its utility and assessing its cost.

Thickness is the most commonly used word to describe the amount of coating. A few of the methods used measure the linear depth of the coating directly. These include the micrometer, with variations using styluses attached to sensitive mechanical and electronic amplifiers, and the microscope, with various methods to expose the coating layers for measurement.

More commonly, gauges estimating the weight per measured area are used. The thickness is then calculated using the following equation:

$$T = m \quad 10/A \quad d, \tag{1}$$

where T = thickness (μm), m = mass of coating (mg), A = area tested (cm^2), and d = density (g/cm^3).

The instruments using the weight per unit area as the basis for their measurements are beta backscatter, coulometric, and X-ray.

The magnetic and eddy-current methods compare the magnetic and electrical properties of the base and coating materials to calibrated standards with similar properties. The drop test is based on the rate of attack of certain chemical solutions. With such a diversity of methods, it is useful to use the summary in Table I to help choose a measuring system for a particular requirement. The gravimetric, microscopic, and X-ray are not included in Table I, because they apply to almost all of the coating combinations listed. A convenient conversion table for different systems of units is given in Table II.

BETA BACKSCATTER

If a stream of beta particles is directed at matter, it will collide with the atoms in the matter. This results in a reduction of speed and a change in direction of the particles. Those particles that leave the matter through the same surface from which they entered are said to be backscattered. The number of particles backscattered is proportional to the number of atoms per unit area and, therefore, to the atomic weight. The penetration depth of the beta rays is dependent on the energy level of the radioisotope used as their source.

The backscatter can be measured with a Geiger-Müller counter placed in its path. In a measuring system, a radioisotope is placed between the Geiger-Müller counter and the coating to be measured. A stream of particles is directed from the isotope through an aperture and then to the coating. The backscatter radiates back through this stream, passes the radioisotope, and then is measured with the Geiger-Müller counter.

The isotope is chosen on the basis of its maximum energy and half-life. As the

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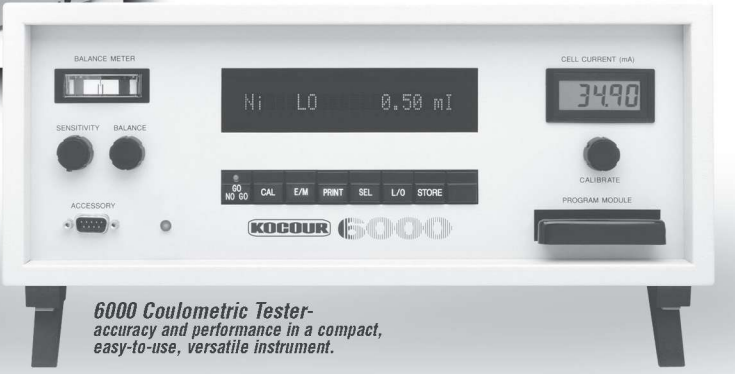
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Table I. Applicability of Coating Thickness Measuring Methods

Substrate	*Copper*	*Nickel*	*Chro-mium*	*Auto-catalytic Nickel*	*Zinc*	*Cad-mium*	*Gold*	*Palla-dium*	*Rho-dium*	*Silver*	*Tin*	*Lead*	*Tin-Lead Alloys*	*Non-metals*	*Vitreous and Porcelain Enamels*
Magnetic steel (including corrosion-resisting steel)	CM	CM[a]	CM	C[b]M[a]	CM	BCM	BM	BM	BM	BCM	BCM	BCM	B[c]C[c]M	BM	M
Nonmagnetic stainless steels	CE[d]	CM[a]	C	C[b]	C	BC	B	B	B	BCE[d]	BC	BC	B[c]C[c]	BE	E
Copper and alloys	C only on brass and Cu-Be	CM[a]	C	C[b]	C	BC	B	B	B	BC	BC	BC	B[c]C[c]	BE	E
Zinc and alloys	C	M[a]	—	—	—	B	B	B	B	B	B	B	Bc	BE	—
Aluminum and alloys	BC	BCM[a]	BC	BC[b]E[a,b]	BC	BC	B	B	B	BC	BC	BC	B[c]C$_c$	E	E
Magnesium and alloys	B	BM[a]	B	B	B	B	B	B	B	B	B	B	B[c]	E	—
Nickel	C		C	—	C	BC	B	B	B	BC	BC	BC	B[c]C[c]	BE	—
Silver	B	BM[a]	B	B	B	—	B	—	—	—	—	BC	B[c]	BE	E
Glass sealing nickel-cobalt-iron alloys UNS No. K94610	M	CM[a]	M	C[b]M[a]	M	BM	BM	BM	BM	BM	BM	BCM	B[a]C[c]M	BM	—
Nonmetals	BCE[d]	BCM[a]	BC	BC[b]	BC	BC	B	B	B	BC	BC	BC	B[c]C[c]	—	—
Titanium	B	BM[a]	—	BE[a,b]	B	B	B	B	B	B	B	B	Bc	BE	—

B = Beta backscatter; C = Coulometric; E = Eddy current; and M = Magnetic.
[a]Method is sensitive to permeability variations of the coating.
[b]Method is sensitive to variations in the phosphorus content of the coating.
[c]Method is sensitive to alloy composition.
[d]Method is sensitive to conductivity variations of the coating.
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thickness of the deposit increases, the energy needed to penetrate the deposit is increased. Metals with larger atomic numbers require higher energies for the same thickness.

As particles are emitted by the source, the number of active particles remaining is reduced. The half-life of an isotope is the time necessary to reduce the activity of the source by one half. As the activity decreases, the instrument requires recalibration for the new activity level.

Accurate placement of the part is essential for precise measurement. An aperture is provided to control the area exposed to the beta rays. The aperture is mounted in a probe together with the source to control the distance of the source to the sample.

The Geiger-Müller tube is part of a counting system that records the backscatter and then computes the thickness. A full line of accessories to store data and provide statistical information is available. Many systems provide computer prompting for both measuring and calibration procedures.

The beta backscatter method applies to coatings and substrates whose atomic numbers differ by at least 5. ASTM Standard Method B 567 details the consideration necessary for accurate measurement with this method.

COULOMETRIC METHOD

The coulometric method is based on Faraday's law. The law states that one gram-equivalent weight of metal will be stripped or deposited for every 96,500 coulombs (ampere-seconds) of electricity passed through the electrolyte. This law is so basic that it has been used to define the international ampere.

The international ampere is defined as the unvarying electric current that, when passed through a solution of silver nitrate, will remove 0.000118 gram of silver per second from the anode. This figure (0.000118 gram of silver per second) is called the electrochemical equivalent of silver.

The following equation defines the weight of metal deposited according to Faraday's law:

$$M = eit, \tag{2}$$

where M = mass (g), e = electrochemical equivalent (g/ A-sec), i = current (A), and t = time (sec). To apply the coulometric method to thickness testing, four para-

Table II. Thickness Conversion Chart

Existing Unit of Measure	Desired Unit of Measure					
	Angstrom	Microinch	Micrometer	Mil	Millimeter	Inch
Angstrom	1	0.004	0.0001	0.000004	0.0000001	0.000000004
Microinch	250	1	0.025	0.001	0.000025	0.000001
Micrometer	10,000	40	1	0.04	0.001	0.00004
Mil	250,000	1,000	25	1	0.025	0.001
Millimeter	10,000,000	40,000	1,000	40	1	0.04
Inch	250,000,000	1,000,000	25,000	1,000	25	1

How to use:
1. Locate existing unit in vertical column (left).
2. Find multiplier on the horizontal line that is under the new desired unit of measure.
3. Multiply existing quantity times multiplier.
Result is the approximate equivalent measurement in the desired unit.
Example: 100 microinches = ? micrometers 0.025 is the multiplier 100 0.025 = 2.5 (micrometers).

meters must be controlled, namely, area, amperage, time, and anode efficiency. At 100% anode efficiency, by substituting the mass obtained from Faraday's law into the thickness formula, the thickness becomes

$$T = eit \quad 10/A \quad d. \tag{3}$$

The area to be measured is determined by a flexible rubber gasket. This area can range from 0.13 to 0.32 cm in diameter. The gasket is an integral part of the deplating cell, that holds the solution during the test. The gasket must be flexible so that it will prevent leakage of the solution, yet sufficiently rigid for precise maintenance of the area.A constant pressure device is included to aid in controlling the gasket pressure. Since this measurement yields weight per area, accurate control of this diameter is essential.

On most instruments, the current source and timer are included in a current supply package. This package provides a means for producing a specific constant amperage for each coating to be tested.

When the coating is penetrated, there is a voltage change. The rate of change of this voltage is monitored and used to terminate the test. An electronic timer is used to record the time elapsed. A computer processes the time and amperage, then displays the thickness. Also included in the package are electronic controls to modify the current and termination sensitivity. These controls are provided to compensate for minute changes in anode efficiency and area.

It is necessary to use a specific electrolyte for each combination of coating and substrate. The electrolyte must satisfy three conditions:

1. The solution must not chemically attack the coating.
2. Anodic dissolution of the coating should be at constant efficiency, ideally 100%.
3. The voltage change on penetration of the coating should be significant.

This method is capable of consistently measuring the thickness of a variety of metallic coatings to ±10% of their true value. For certain coating and substrate combinations, the accuracy can be higher. The most accurate measurements are in the range of 40 to 2,000 microinches; however, chromium can be measured in thicknesses as low as 3 microinches. The accuracy of measurement in a specific thickness range may be increased by calibrating the instrument with standards in that range.

Coatings on wire are measured by means of an auxiliary cell. Tests are performed on sample lengths from 0.5 to 4.0 in. in length.

One advantage of this method is the ability to measure combination coatings such as copper/nickel/chromium and copper/tin. The instrument manufacturer's instructions should be followed precisely for accurate results. Additional guidelines for achieving accurate measurements are contained in the following ASTM methods:

1. ASTM B 504, standard method for coulometric thickness.
2. ASTM B 298, for silver coatings on copper wire.
3. ASTM B 355, for nickel coatings on copper wire.

The coulometric instrument has found application in measuring other qualities of metallic coatings. ASTM B 764 describes a procedure for simultaneous thickness and electrochemical potential (STEP) determination for the layers of multilayer nickel deposit.

DROP TESTS

The drop test for measuring plating thickness is based on the rate of attack of specially prepared corrosive solutions on a metal coating. For consistent results, the drop size, drop rate, temperature, time, and solution composition must be controlled.

The test is performed by allowing the solution to drop on a particular spot at a rate of 100 drops per minute. The operator then observes the time at which the coating is penetrated. For the most common thicknesses, the elapsed time is less than one minute.

Reproducibility of the test is dependent on the skill of the operator. The operator must detect the point at which the base metal is exposed and record the time. An experienced operator can reproduce his readings within ±5%. For best accuracy, the operator should standardize his technique with a standard of known thickness.

The accuracy of the system is generally considered to be ±15%, because the operator cannot control some of the factors that affect the test. These factors include drainage of the solution, alloying at the coating/substrate interface, and composition of the coating.

Low cost and the ability to measure thickness quickly on irregular shapes are the chief advantages of the drop test. The greatest disadvantages are destruction of the coating and objections to the use of corrosive solutions in some areas. The largest application is in the fastener industry.

Standard guidelines for the use of this test are contained in ASTM B 555. Some

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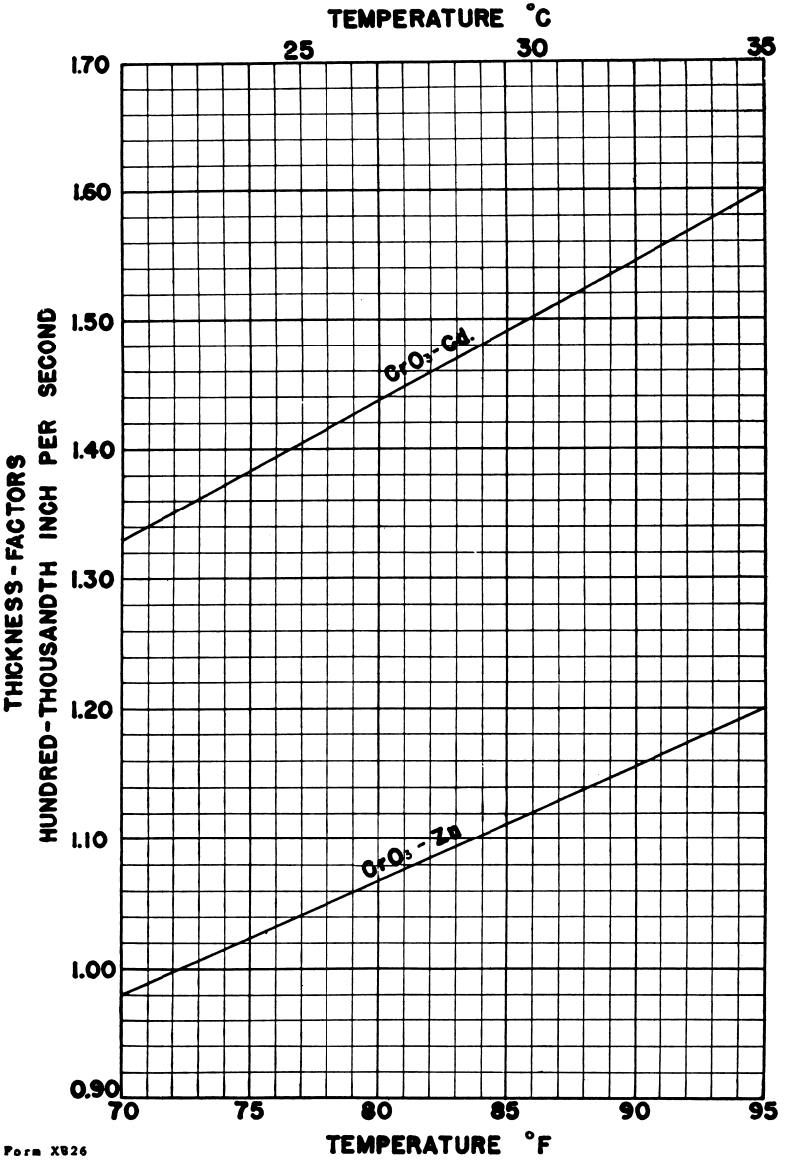


Fig. 1. Time, temperature, and thickness relation for chromic acid drop test on zinc and cadmium.

typical procedures are provided below.

Reagents

1. Cadmium deposits:
   Ammonium nitrate, 110 g/L
   Hydrochloric acid, 10 ml/L
2. Zinc deposits:
   Ammonium nitrate, 100 g/L
   Nitric acid, 55 ml/L
3. Zinc and cadmium deposits:
   Chromic acid, 200 g/L
   Sulfuric acid, 50 g/L
4. Tin deposits:
   Trichloroacetic acid, 100 g/L
5. Copper deposits:
   Ferric chloride ($FeCl_3 \cdot 6H_2O$), 450 g/L
   Antimony trioxide, 20 g/L
   Hydrochloric acid, 200 ml/L
   Acetic acid (CP, glacial), 250 ml/L

Operating Conditions

Drop rate: 90 to 110 drops per minute (100 preferred).

Temperature: 20 to 30°C (70 to 90°F).

Penetration rate: For zinc and cadmium (using separate reagents listed above), each second = 0.00001 in. For copper deposits, two seconds = 0.00001 in. Figure 1 shows the penetration factor as a function of temperature for testing zinc and cadmium deposits with the chromic acid/sulfuric acid reagent.

Lacquer or other films are removed from the area to be tested, which is then cleaned with a suspension of magnesium oxide in water. The specimen is held at an angle of 45° below the dropping tip. To ensure that the reagent impinges on the same spot throughout the test, it is preferable to clamp the specimen in place rather than to hold it by hand.

The apparatus may consist of a separatory or dropping funnel, which is fitted with a short length of tubing terminating in a drawn-out tip. Special funnels are available with two stopcocks. One of these is fully opened and the other used to set the desired drop rate. An automatic drop-test apparatus is available in which the drop rate is automatically maintained at 100 drops per minute by means of a synchronous motor-driven mechanism.

EDDY CURRENT

Eddy current thickness gauges are electromagnetic instruments designed to measure the apparent change in impedance of the coil that induces the eddy current into the base metal. They are calibrated by comparing the apparent change in impedance to known thickness of coatings on selected base materials.

It is the difference between the conductivity of the base material and the coating that influences the change in impedance; therefore, the instrument has its greatest accuracy when testing nonconductive coatings on conductive base materials and vice versa. The test can be applied to poor electrical conductors over good electrical conductors with some loss in accuracy.

The thickness test is performed with the aid of a specially designed probe. Measurements are made by holding the probe perpendicular to the surface and with the probe point in contact with the area to be measured. The measurements are rapid and nondestructive; therefore, some problems with accuracy may be resolved by statistical evaluation of many readings. Thickness gauges are available with digital display, memory, hard-copy printout, and computer prompting of the calibration procedure.

In the range of 5 to 50 μm, the thickness can be determined to within 10% or 1 μm, whichever is greater, of the true thickness. This test is sensitive to marked differences in the surface contour of the test specimen. Particular attention should be paid to the distance from an edge, surface roughness, and curvature at a test point.

Erroneous results may be avoided by calibrating with standards that approximate the surface condition and curvature of the specimen to be tested. The type of electroplating solution used can influence the electrical conductivity of the deposit and, therefore, the thickness measured.

Zinc plated in cyanide, chloride, or alkaline baths is the most prominent example of this problem. Calibrating the instrument with standards from the same or similar solutions can greatly reduce error.

Eddy current thickness testing is widely applied to anodic coatings on aluminum, nonmetallic coatings on nonmagnetic base metals, and to a lesser extent, to metallic coating/substrate combinations that have different electrical conductivities. The instrument manufacturers' instructions should be followed precisely for best results. A standard method for the application and performance of this test is available in ASTM B 244.

MAGNETIC METHOD

The magnetic method uses the magnetic influence of the coating and substrate on a probe as the basis of a measuring system. Two types of probe systems are in common use. The first to be developed makes use of a mechanical system to measure the influence of the coating thickness on the attractive force between a magnet and the base material.

An electromagnetic probe was later developed that measures the influence of the coating thickness on the reluctance of a magnetic flux path through the coating and base material.

Three types of coatings can be measured with this system:

1. Nonmagnetic coatings on ferromagnetic base metals.
2. Nickel coatings on ferromagnetic base metals.
3. Nickel coatings on nonmagnetic base materials.

The test is performed with the aid of specially designed probes. With the permanent magnet type, measurements are made by placing the probe perpendicular to the surface to be measured and observing the force necessary to remove the probe.

The electromagnetic-type probe requires placing the probe perpendicular to the surface to be measured and observing the reluctance measurement. The measurements are rapid and nondestructive; therefore, some problems with accuracy may be resolved by the statistical evaluation of many readings.

Commercial instruments are available with analog and/or digital thickness display, memory, hard copy printout, and computer prompting of calibration procedures.

The effective thickness range is dependent on the choice of probe system (magnet or reluctance) and the coating/substrate combination. The ranges for the magnet type are:

1. Nonmagnetic coating on magnetic base, 5 to 25 μm.
2. Nickel coating on magnetic base, 5 to 50 μm.
3. Nickel coating on nonmagnetic base, 5 to 25 μm.

The ranges for the reluctance type are from 5 μm to 1 μm for all three coating/substrate combinations. Both types of instruments are sensitive to marked differences in the surface contour of the test specimen.

Particular attention should be given to the distance from an edge, surface roughness, and curvature at the testing point. Erroneous results may be avoided by calibrating with standards that approximate the surface condition and geometry of the specimen to be tested. When properly calibrated, the magnetic system can determine the actual thickness within 10%. The instrument manufacturer's instructions should be carefully followed for the most accurate results. Two standard methods have been developed for additional guidance to more reliable readings. They are ASTM B 499 and ASTM B 530.

GRAVIMETRIC

This method requires the measurement of the area to be tested and the determination of the mass of the coating in that area. The area may be determined by standard measuring techniques. The coating mass may be determined by one of the following procedures:

1. Weigh coating directly after dissolving the base material without attacking the coating.
2. Determine coating mass by analyzing the solution used to dissolve the coating and all or a portion of the base material.
3. Determine coating mass as the difference between the weight before and after dissolving the coating without attacking the base material.
4. Determine coating mass as the difference between the weight before and after coating.

Usually this method is assigned to a laboratory equipped to handle the corrosive solutions and to measure the mass and area with sufficient accuracy. After the area and mass have been determined, the thickness may by determined by using Equation (1).

Procedures 1, 2, and 3 are destructive; procedure 4 is nondestructive. This method has the capacity to yield extremely accurate results and is frequently used to determine the exact mass of metal used for cost purposes, particularly with the more precious metals. This method (procedure 4) is used as a technique for making thickness standards.

ASTM has developed procedures for several specific coatings. They are Method A 90 for zinc, Method A 309 for terneplate, Method A 630 for tin plate, and Method B 137 for anodized aluminum. ASTM B 767 serves as a guide for use of this procedure for a variety of plating and substrate combinations.

MICROMETRIC

A micrometer may be used to check the thickness of coatings over 0.001 in. If the micrometer is equipped with a dial indicator, thicknesses of 0.0005 in. may be measured on uniformly coated cylindrical parts. It is necessary to measure the same spot before and after plating. Measurements may be obtained by masking the deposit and dissolving the unmasked coating, then measuring the step produced by this procedure.

MICROSCOPIC

The microscope can be used as a length measuring instrument when it is equipped with a filar eyepiece. The specimen must be carefully polished to prepare a smooth reflective surface and then etched to reveal the various metals exposed. This generally requires the services of an experienced metallographer.

The measurements are generally made on a transverse section of the deposit so that the various layers of plating are exposed for viewing. Measurements are also made on tapered sections to increase the length to be measured. The thickness is then calculated by correcting the observed length for the taper angle.

This method is destructive and time consuming. The thickness results have a precision of ±2%; however, the accuracy has a constant uncertainty of about 0.8 μm (30 microinches). Therefore, despite the precision of the method, it should not be considered as a reference to resolve questions about thicknesses less than 8 μm (300 microinches).

The filar eyepiece is calibrated by comparing the divisions on the filar micrometer to the known distance between divisions on a stage micrometer. This method is a true measure of length and does not require a plated standard for calibration.

Due to the high cost of this technique, its use has been reserved for those occasions that require more information than may be obtained from other thickness-gauging methods. Information concerning porosity, surface roughness, grain structure, and adhesion may be gathered from the specimen prepared for a thickness test.

ASTM B 487 is a standard method outlining the conditions for accurate results.

The wavelength of light limits the resolution of the light microscope to about 10 microinches. The scanning electron microscope utilizes the shorter wavelength of electron waves to measure metallurgical specimens with a 4 microinch resolution. ASTM B 748 is the standard test method for this procedure.

Attachments are available for the metallurgical microscope that allow it to be used as an interferometer. The method is mentioned, because its accuracy with thin coatings can be within ±5% of the true thickness. Conditions necessary for this procedure are contained in ASTM Standard Method B 588.

THE SPOT TEST

This test was developed as a rapid and inexpensive thickness test for chromium coatings on nickel and stainless steel. The test has an accuracy of ±20% for coatings up to 1.2 μm thick. A wax ring is outlined on the part to be tested. A drop of hydrochloric acid is placed in the ring, and the time between the onset and cessation of gassing is recorded. ASTM B 556 provides a standard guide for the performance of this test.

X-RAY FLUORESCENCE

This method is similar to beta backscatter in that the area to be tested is the target of radiation, and the energy emitted from that surface is measured. In this method, the radiation used is X-rays produced by an X-ray tube. The radiation measured is secondary emissions from the interaction of the X-rays with the coating and substrate. Unlike beta backscatter, the emissions measured are specific for each metal.

Among the unique characteristics of this method are the following:

1. No physical contact with the measured surface is required, thereby protecting that surface.
2. Extremely small areas may be measured.
3. Since the emissions are specific for each metal, alloy compositions may be determined.
4. With proper calibration, intermediate coatings may be measured in a multilayer system.

Thickness may be measured in the range 0.25 to 10 μm, depending on the metal being measured. With proper calibration, the thickness may be determined to within 10% of its true value. ASTM B 568 outlines a standard method for this measurement system. Due to the noncontacting characteristic and the rapid test time, this procedure is used to continuously monitor thickness on continuous-coil plating machines and automated plating machines.

STANDARDS

Thickness standards are required for calibrating thickness gauges. In most cases, the standards should be plated from a similar plating solution and on the same base metal as the product to be tested.

After receipt, it is important to have a system to ensure the standard's reliability after use. One system makes use of primary, secondary, and working standards. The working standards are used for calibrating the thickness gauge daily.

Once a week, the working standards are calibrated against the secondary standards. The secondary standards are then calibrated against the primary standard once a month. The time between calibrations can be varied based on experience with the expected life of the standard. When a new standard is purchased, it becomes the primary standard, and the remaining standards are lowered in rank.

SUMMARY

To measure the thickness of a coating, many properties have been utilized. Measurements have been described that use the atomic configuration, electrochemical equivalent, corrosion rate, electrical conductivity, magnetic properties, density, and actual linear measure of the coating.

In addition to these methods, tests have been successfully performed by using the electrical resistance and transparency of the coating. Each of these methods has its proper application.

It is obvious that one system is not capable of satisfying the needs of every plater. Certainly, a plater coating 10,000 fasteners per barrel load at a rate of 50 barrel loads per shift has a problem that is substantially different from a plater that hard chromium plates printing rolls. Experience and judgment are required, and the responsibility for choosing the most economical thickness-measuring system adequate for a particular problem is not a simple task.

CHOOSING AN ACCELERATED CORROSION TEST

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Accelerated corrosion tests are typically used to determine if a coating/substrate combination has been produced to yield a satisfactory service based on historical data from previous testing and field exposures of similar coating/substrate combinations. The intent is to find out, in a relatively short amount of time, what the appearance or performance of the product will be after several years of service.

Real-life exposures are complicated events that may involve several factors including geometric configuration, porosity/adherence of corrosion product, soiling, abrasion, frequency of cleaning, cleaning procedures, cleaning chemicals, sun exposure, and temperature variations. Because of this, it is critical that the accelerated test chosen simulates "real-life" corrosion mechanisms as much as possible. The following guidelines were prepared to assist in choosing the best accelerated corrosion test for a given application.

CORROSION MECHANISMS

Coated metallic products are subjected to two basic corrosion mechanisms during their service life: (1) electrochemical (galvanic) and (2) chemical attack.

Electrochemical (Galvanic)

Electrochemical corrosion can be caused by dissimilar metals contacting an electrolyte. This is the common "battery" effect. Detrimental galvanic corrosion effects occur when the substrate is electrochemically more active than the protective coating, or when the corrosive environment contains a metal that is less active than the coating and substrate. The electrolyte (water, salt solution, acid, etc.) must be in contact with both metals for this mechanism to occur.

Examples of the beneficial use of this corrosion mechanism include galvanized or electroplated zinc over steel, where the zinc, being electrochemically more active than steel, will corrode in preference to the steel when exposed to a corrosive environment (electrolyte). This protection is extended even if large scratches are present through the zinc and into the steel. Another example is duplex nickel. Nickel containing sulfur (~0.02%) from the addition of brightening agents is electrochemically more active than nickel without sulfur. A two-layer system, consisting of semibright nickel (no sulfur) followed by bright nickel, yields a galvanic couple wherein the bright nickel corrodes in preference to the semibright, providing galvanic protection to the second nickel layer, thereby delaying corrosion of the basis metal (and failure).

The electrochemical mechanism can also involve a difference in the quantity of oxygen contacting the surface of the exposed specimen in the presence of an electrolyte. Two dissimilar metals are not required. The area of the specimen that is oxygen deficient becomes anodic to the area that contacts the larger quantity of oxygen. The anodic area dissolves into the electrolyte, leaving a corrosion pit. Hydroxides (alkali) are deposited at the cathodic (oxygen-rich) area.

The physical variations of the oxygen concentration cell mechanism are given various names.

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Crevice corrosion: When specimens with complicated geometric shapes are allowed to contact corrosive liquids (water, salt solution), the sharply recessed areas (pores) in the surface of the specimen contact less oxygen than the remaining surface due to differences in oxygen diffusion. The metal inside the pores becomes anodic to the bulk. An example would be the crevice underneath the head of a bolt or screw when these are tightened to a nut or other surface.

Sandwich corrosion: The gap between joining flat surfaces becomes anodic to the exterior surface. The corrosion products tend to push the joined surfaces apart. An example is the gap between riveted aluminum sheets comprising an aircraft wing or body panel.

Poultice corrosion: Accumulated soil on a corrodible surface acts as a "poultice," holding thousands of pockets of electrolyte (water, salt, etc.) onto the surface. Differences in oxygen concentration then act to corrode the surface. An example is the dirt that accumulates on the underside and wheel wells of an automobile.

Filiform corrosion: This type of oxygen cell corrosion is peculiar to organic coatings (paints, lacquers, etc.) that are subjected to chipping. The chipped area contacts more oxygen than the metal covered by coating. As the covered metal that is some distance from the chip corrodes and precipitates hydroxides under the paint, a wormlike appearance in the coating develops as the coating is lifted off the base metal. The "worm" traces take straight lines under constant temperature and twist under variant temperature.

Chemical Attack

The chemical nature of acids and certain chemicals is that they attack (dissolve) metals. The performance of a coating in resisting attack is determined by subjecting the test specimen to varying concentrations of acids, acid-forming gases, or chemical solutions.

Acid attack, chemical attack, and electrochemical techniques can also be used to determine the porosity of a coating, which can sometimes be related to service life. Examples of such techniques are the ferroxyl test, electrographic printing, and the copper sulfate test (on hard chrome over steel).

TEST METHODS

The following are commonly performed accelerated corrosion and porosity tests. Table I summarizes applicability and denotes the most common test used on a given coating/substrate combination.

Salt Spray (ASTM B 117)

This is the most widely specified corrosion test. It has broad applicability. The salt solution that is utilized closely simulates the corrosive effects of outdoor exposure on automotive hardware (except some decorative nickel-chromium applications; see CASS and Corrodkote in Table I).

Test results normally are obtained in a few hours for lesser protective systems (phosphate, oil, hard chromium plating) and it may take many days (40-80) for superior systems such as tin-nickel plating, heavy galvanize, and galvanize/paint combinations.

The corrosion mechanisms employed are oxygen concentration cell and galvanic effects, accelerated by use of an electrolyte with a chloride content of 5% weight (more has been shown to be unnecessary); elevated temperature; inclination of test specimen; and utilization of a fine-fog mist.

Table I. Applicable Corrosion Test for Various Coatings/Substrates

		Applicable Test(s), Most Commonly Performed Test in Parentheses (X)												
Coating	Substrate	AA	CASS	CDK	EG	F	FACT	HUM	K	LA	SS	SO_2	TS	W
Anodize (chromic)	Aluminum	X	–	–	–	–	X	–	–	–	(X)	–	–	–
Anodize (hardcoat)	Aluminum	(X)	–	–	–	–	X	–	–	–	X	–	–	–
Anodize (sulfuric)	Aluminum	–	–	–	–	–	X	–	–	–	(X)	–	–	–
Black chrome	Steel	–	–	–	–	–	–	(X)	–	–	X	–	–	–
Black oxide	Steel	–	–	–	–	–	–	(X)	–	–	X	–	–	–
Bronze plate	Ferrous	(X)	–	–	–	–	–	–	–	–	(X)	–	–	–
Cadmium plate	Ferrous	X	–	–	–	–	–	–	–	–	(X)	–	–	–
Chromated cadmium	Ferrous	X	–	–	–	–	–	–	–	–	(X)	–	–	–
Chromated zinc	Ferrous	X	–	–	–	–	–	–	–	–	(X)	–	–	–
Copper plate	Nonconductor[a]	–	–	–	–	–	–	X	–	–	–	–	–	–
Copper/nickel/chromium	Ferrous	X	X	(X)	X	X	–	–	–	–	X	–	–	–
Copper/nickel/chromium	Nonferrous	X	X	(X)	X	–	–	–	–	–	X	–	–	–
Copper/nickel/chromium	Plastic	(X)	–	–	–	–	–	–	–	–	X	–	–	–
Electroless nickel	Ferrous	X	–	–	–	–	–	–	–	–	(X)	–	–	–
Electroless nickel	Nonferrous	X	–	–	–	–	–	–	–	–	(X)	–	–	–
Galvanize	Ferrous	X	–	–	–	–	–	–	–	–	(X)	–	X	–
Hard chrome plate	Ferrous	–	–	–	X	–	–	–	–	–	(X)	–	–	–
Hard chrome plate	Nonferrous	–	–	–	–	–	–	–	–	–	X	–	–	–
Iron phosphate	Ferrous	–	–	–	–	–	–	(X)	–	–	X	–	–	–
Lacquered brass/nickel	Ferrous	–	–	–	–	–	–	X	–	(X)	X	–	–	–
Manganese phosphate	Ferrous	–	–	–	–	–	–	(X)	–	–	X	–	–	–
Nickel plate	Ferrous	–	–	–	–	–	–	X	–	–	(X)	–	–	–
Oils/greases	Ferrous	–	–	–	–	–	–	X	–	–	–	–	–	–
Paint	Ferrous	X	–	–	–	–	–	X	–	–	(X)	–	–	X
Paint	Nonferrous	X	–	–	–	–	–	X	–	–	(X)	–	–	X
Passivate	Stainless steel	–	–	–	–	–	–	–	–	–	(X)	–	–	–
Tin plate	Ferrous	(X)	–	–	–	–	–	–	–	–	X	–	–	–
Tin-nickel plate	Ferrous/nonferrous	–	–	–	–	–	–	–	(X)	–	–	X	–	–
Zinc phosphate	Ferrous	–	–	–	–	–	–	(X)	–	–	X	–	–	–
Zinc plate	Ferrous	X	–	–	–	–	–	–	–	–	(S)	–	–	–

AA, acetic acid-salt spray; CASS, copper accelerated salt spray; CDK, Corrodkote; EG; electrographic; F, ferroxyl; FACT; Ford accelerated corrosion test; HUM, humidity; K, Kesternich; LA, lactic acid; SS, salt spray; SO_2, Sulfur dioxide; TS, triple spot; W, weatherometer.

[a]Printed circuit boards.

100% Relative Humidity (ASTM D 2247)

This test has wide applicability for protective coatings that are exposed indoors, in sheltered areas, or in areas where water (condensation) can accumulate on the surface of the specimen.

Many variations of this test are employed to more accurately reflect service conditions. These include varying humidity levels from 60 to 95% relative humidity; cycling humidity with periodic dips into corrosive liquids (ASTM G 60); cycling humidity with drying cycles for coatings on wood (ASTM D 3459); and combining humidity with severe temperature fluctuation (ASTM D 2246).

The corrosion mechanism employed is oxygen concentration cell, accelerated by high humidity level, elevated temperature, and inclination of test specimen.

ASTM B 287 (Acetic Acid-Salt Spray)

This test is intended for coating systems that provide excellent corrosion-protection results in long-term salt spray (B 117) exposure. This test is approximately twice as severe as the salt fog (B 117) test, although this may vary significantly with each application.

The corrosion mechanism employed is oxygen concentration cell accelerated by operation at lowered pH (3.1-3.3 vs. 6.5-7.2 for the salt fog test); use of an electrolyte with a chloride content of 5% weight (more has been shown to be unnecessary); elevated temperature; inclination of test specimen; and utilization of a fine-fog mist.

Copper Accelerated Salt Spray (CASS) (ASTM B 368)

This test was developed for use on copper-nickel-chromium coatings over ferrous and nonferrous substrates.

The oxygen concentration cell corrosion mechanism is accelerated by operation at lowered pH (3.1-3.3 vs. 6.5-7.2 for the salt fog test); use of an electrolyte with a chloride content of 5% weight (more has been shown to be unnecessary); elevated temperature; inclination of test specimen; utilization of a fine-fog mist; and the addition of cupric chloride to provide galvanic effects.

Corrodkote (ASTM B 380)

This test was also developed for specific use on copper-nickel-chromium coatings on ferrous and nonferrous substrates.

The corrosion mechanisms employed are oxygen concentration cell and galvanic effects produced by cupric and ferric ions, plus complicated chemical effects produced by the nitrate, chloride, and ammonium ions.

The test utilizes a kaolin paste that holds the corrosive ions to the surface of the test in a "poultice" fashion, similar to accumulated dirt and scale on exterior automotive parts.

FACT (ASTM B 538)

This test is limited to anodized aluminum coatings and is basically a porosity test used to obtain rapid corrosion protection results based on the porosity level found. Substantial service background is needed to correlate test data with service life for any specific application.

The test consists of an electrolytic cell with salt spray (ASTM B 117) or CASS (ASTM B 368) solution as an electrolyte.

The cell is placed onto the test specimen with a gasket to prevent leakage. A potential is applied between a platinum anode and the test specimen (cathode). As hydrogen is discharged from the cathodic sites (pores), alkalinity is developed,

attacking the coating and decreasing the cell voltage. The decreasing cell voltage is integrated over time, yielding a comparative result.

Weatherometer (ASTM G 23)

This test is utilized to evaluate the performance of paint and lacquer systems under simulated outdoor exposure. The test yields data on the resistance of the coating system to condensation effects (rain) and the stability of the pigment in the paint (colorfastness) when exposed to sunlight. Intense ultraviolet radiation from twin carbon arc lamps and variant humidity levels (cycling from approximately 70 to 100% relative humidity) provide long-range test results in a short time frame (100-2,000 hr).

Lactic Acid

Lacquered brass- and copper-based alloys are tested for porosity and resistance to tarnishing by everyday handling (perspiration), using this test. Although not ASTM standardized, the procedure is gaining industrial acceptance. The principal mechanism is chemical attack.

The procedure is as follows:

1. The item is dipped in a room-temperature solution of lactic acid (85%) saturated with sodium chloride.
2. The item is air dried for 2 hr in a convection oven at 120°F.
3. The item is suspended in the air above 100 ml of 30% acetic acid in an airtight chamber (desiccator). An acceptable substitute is the vapor

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produced by 100 ml of a 50% solution of acetic acid in water over a small, open dish.

A typical successful exposure is 20 hr above the acetic acid without the appearance of green (nickel) corrosion, loss of adherence of the organic coating, or tarnishing of the brass or copper plate.

Sulfur Dioxide/Kesternich (ASTM B 605)

A few coatings are so stable that normal corrosion-resistance testing results in unwieldy exposure hours. To yield results in a realistic amount of time, an acidic attack mechanism is used. Two of these tests are the sulfur dioxide (ASTM B 605) and the Kesternich (Volkswagen) test, Volkswagen specification DIN 50018. These procedures normally are limited to tin-nickel and similar inert coatings, or to coatings where a quick detection of a fault or surface imperfection is required.

Both procedures use sulfur dioxide gas at elevated temperatures and humidity levels, forming sulfurous acid on the surface of the test specimen.

Triple Spot (ASTM A 309)

Galvanized steel is protected from corrosion by the sheer thickness of the zinc coating. An estimate of the corrosion resistance can, therefore, be obtained by measuring the average thickness of the zinc coating on the steel. The thickness is measured using the "weight-area method" and an inhibited acid for stripping.

This indirect method for measuring corrosion resistance of galvanically protected steel is limited to thick coatings (galvanize). Relatively thin coatings, such as electroplate, are not as easily correlated to corrosion performance, because local variation in thickness will yield service failures that are not "predicted" by this method.

Electrographic and Chemical Tests for Porosity

Pores and cracks in chromium over nickel or nickel over steel can be detected using absorbent paper soaked in chemicals that react with the substrate, such as dimethylglyoxime for nickel substrates and potassium ferricyanide for steel substrates (commonly called the ferroxyl test).

The test specimen is covered by the soaked paper and, with pressure from a stainless steel cathode, a small current is passed (the test specimen is anodic). The chemicals react with the substrate at cracks and pores, thereby forming colored traces in the paper. Correction to actual service life is difficult.

Pores in hard chromium deposits over steel can be detected by applying an acidified copper sulfate solution (50 g/L with a pH $\leq$ 2) for approximately 30 seconds. Galvanically deposited copper will appear at areas with pores present.

pH AND ORP

BY MICHAEL BANHIDI
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PH

The term "pH" is used to express the degree of acidity or alkalinity of a solution. Although many different ions may be formed in solution those that establish whether the solution is acid or alkaline are the hydrogen (H^+) and the hydroxyl (OH) ions, respectively. When the hydrogen ions exceed the hydroxyl ions in number, the solution is acid. When they are equal, the solution is neutral. Alkalinity (or basicity) denotes that the hydroxyl ions exceed the hydrogen ions.

Acids and alkalis vary in the degree to which they form ions in solution. Those that almost completely ionize are called strong acids or bases. Hydrochloric acid and sodium hydroxide are examples. Other acids and bases ionize to only a small degree and are called weak acids or bases. Acetic acid and ammonium hydroxide are typical examples. Acids and bases may also be classified according to the number of H+ ions they can donate per molecule. If an acid can donate only one H+ ion it is known as monofunctional. If the available H^+ ions are more than one a di- (two) or tri- (three) classification is used.

Even pure water dissociates to a minute degree into hydrogen and hydroxyl ions. Pure water at 25°C always contains 0.0000007 or, in simple form, 1×10^{-7} gram-equivalents per liter of hydrogen ions and, since pure water is neutral, an equal concentration of hydroxyl ions.

The product of these concentrations is a constant equal to 1.0×10^{-14} at 25°C. Thus, if the hydrogen-ion concentration of a solution were 1.0×10^{-4} gram-equivalents per liter, the hydroxyl-ion concentration would be equal to 1 10-10 gram-equivalents per liter. Because, in this case, the hydrogen-ion concentration is greater than the hydroxyl-ion concentration, the solution is acidic.

To express hydrogen-ion concentration more conveniently than by the use of decimals or by negative exponents, the term "pH" was adopted. Expressed mathematically, pH is equal to the negative logarithm to the base of 10 of the hydrogen-ion concentration. This is expressed as follows: hydrogen-ion concentration = 1×10^{-7} gram-equivalents of hydrogen ion per liter or has a pH value of 7. Since acid solutions contain more than 1×10^{-7} gram-equivalents of hydrogen ion per liter, the pH values of these solutions are less than 7. Conversely, alkaline solutions have pH values greater than 7.

It is also helpful to remember that a unit change in pH represents a tenfold change in acidity or alkalinity. Thus, compared with a solution of 5 pH, a solution of 4 pH is ten times as acidic—of 3 pH, a hundred times as acidic—and 2 pH, a thousand times as acidic.

The commonly accepted range within which pH values are expressed covers the scale 0 to 14. In plating solutions pH determinations below 1 and above 12 are of little or no value. Outside these limits acidities or alkalinities are more conveniently expressed as percent concentrations.

Nonaqueous solvents may provide a pH outside the 0 to 14 range normally encountered in aqueous solutions. Many digital meters are capable of -19.99 to

Table I. Components of Common Buffers

Components	Concentration		pH
Hydrochloric acid	0.365 g/L	1:1 mixture	2.08
Potassium chloride	6.7 g/L		
Potassium hydrogen tartrate	5.64 g/L		3.57
Potassium hydrogen phthalate	10.2 g/L		4.00
Acetic acid	6.0 g/L	1:1 mixture	6.9
Sodium acetate	8.2 g/L		
Borax	19.06 g/L		9.2

+19.99 pH. In other meters, such as the analog meters, the scale is limited. In this case the millivolt range of the pH meter provides greater range, such as ±1,400 mV, than the normal 0 to 14 pH range, which is ±421 mV at 25˚C; therefore, the pH value can be calculated by comparing the millivolt values obtained in a sample. Of course there is reduced readability with the larger millivolt range. Relating pH and millivolt values observed on the pH meter, the pH value can be calculated using the following formula:

$$pH_x = pH_s - (E_x - E_s)/S$$

where pH_x is the pH of the sample (x); pH_s is the pH of the standard (s); E_x is the millivolt value of the sample as read by the pH meter; E_s is the millivolt value of the standard as read by the pH meter; and S is the slope, normally 59.16 mV/pH unit at 25˚C. The pH can be determined colorimetrically or electrometrically.

Colorimetric Method

For a visual indication of the pH a so-called acid-base indicator or mixture of indicators is employed. Such an indicator is a weak organic acid (or base) having the special feature that it changes color within a definite pH range.

The standard colorimetric method is carried out by placing a given quantity of solution to be tested in a glass tube. A set amount of indicator is added and compared with standards, in which a solution with known pH has been prepared with the same amount of indicator. This method is cumbersome and rarely used today.

The derivative of the standard colorimetric method is the pH test paper. The indicator is impregnated on an absorbent paper strip. A color chart with the appropriate pH values is printed on the strip or a card. After immersion in the solution the strip is compared with the standard color. Reliable pH papers are accurate ±0.3 units from the electrometric value. In the case of a strong oxidizing or reducing solution the pH papers are not reliable.

Electrometric Method

Certain electrodes, such as hydrogen, quinhydron, antimony and others, when immersed in a solution, develop voltages (called electrical potential), which depend upon the pH of the solution. As a result a pH meter is basically a millivolt meter. The glass bulb electrode is the key to making a pH measurement. The special composition glass used is very selective and sensitive to hydrogen ions. The potential that is developed at the glass membrane can be related to the pH of the solution. To complete the circuit and provide a stable and reproducible referencing potential, another electrode is required. The "reference" electrode makes contact with the solution through a junction, which allows slow leakage of the filling solution into

Table II. Standard Potential (E^0)

Electrode Reaction	E0 (V)
$Na^+ + e^- = Na$	-2.714
$CNO^- + H2O + 2e^- = CN^- + 2OH^-$	-0.97
$Zn2^+ + 2e^- = Zn$	-0.763
$2H^+ + 2e^- = H_2$	0.000
Ag/AgCl electrode, 4N KCl	+0.199
Calomel electrode, sat KCl	+0.244
$(Cr_2O_7)^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	+1.33

the sample. When the glass (pH) and reference electrodes are paired, or built together as a combination electrode, and connected to a pH meter, the voltage developed at the electrode pair is amplified and displayed on a meter or a digital readout. The meter is standardized with a known solution called a buffer. A buffer is a specially prepared solution that resists changes in pH and has a specific pH value at a specific temperature. In Table I the component of the most common buffers is shown.

When highly accurate pH measurements are required, temperature, meter standardization, and electrode technique should be considered. Temperature has two effects on the accuracy of pH readings. The first effect is on the electrodes, which is corrected by either automatic temperature compensation (ATC) or by manually adjusting the temperature control on the pH meter. Temperature also effects the pH value of the buffer (which is used for standardization). Because samples do not change pH with temperature in the same way, the relationship between temperature and pH must be determined experimentally. Most buffer bottles have a chart on their labels that gives the pH as a function of temperature.

The pH meter should be standardized with accurate buffers, which have pH values close to the pH values of the samples. Use of the slope control corrects for nonideal electrode behavior associated with aging of the electrodes.

Proper storage of the electrodes increases their life and provides faster response and less drift when making pH measurements. The electrodes should be carefully rinsed between each measurement to prevent contamination. Do not wipe the glass electrode, which could transfer a charge to the glass bulb resulting in a long stabilization time. The rinsed glass electrode should be stored in distilled water. Finally, the consistency of the measuring technique is important, whether the samples are measured in static or stirred condition; however, the standardization buffer and the sample solution should be treated the same.

OXIDATION-REDUCTION POTENTIAL

Oxidation-reduction potential (ORP) measurements are used to monitor chemical reactions, quantify ion activity, or determine the oxidizing or reducing properties of solutions. Although ORP measurements are somewhat similar to those of pH, the potential value must be interpreted carefully for useful results. An ORP measurement is made using the millivolt mode of the pH meter. Consequently, by substituting a metallic electrode for the pH glass electrode, many other ions besides the hydrogen ion can be detected with the same pH meter.

In many chemical reactions electrons are transferred from one substance to another. By definition a substance gains electrons in a reduction reaction and loses electrons in an oxidation reaction. Oxidation and reduction reactions occur

together. The available electrons from an oxidized substance are taken up by the reduced substance until an equilibrium condition is reached.

Since it is impossible to measure absolute potentials, an arbitrary standard, the hydrogen electrode, is chosen. ORPs are defined relative to this standard. The electrode reaction

$$2H^+ + 2e^- = H_2$$

is assigned a potential of 0.000 V when the hydrogen activity is 1 M (concentration of 1 mole/L), and the partial pressure of hydrogen is 1 atm.

When reactions are written as oxidation (e.g., $Na = Na^+ + e^-$), potentials have the opposite polarity. The standard potential E0 of any oxidation-reduction reaction is referenced to the standard hydrogen electrode and refers to the condition of the oxidation-reduction reaction where temperature is 25°C, ion activity is unity, and gases are at 1 atm pressure. Table II shows the standard potential E^0 associated with various reactions.

The ORP is characteristic of reactions involving both oxidation and reduction and varies as a function of (1) the standard potential, (2) relative ion concentration, (3) temperature, and (4) the number of electrons transferred in the reactions.

ORPs are usually displayed as millivolts (mV). When measured with a pH meter (set to read in mV), this ORP is generally the electromotive force (EMF) difference developed between the ORP electrode and a constant voltage reference electrode (saturated calomel, instead of a normal hydrogen electrode) that is immersed in the solution. Any one of three different types of metallic electrodes may be used. There are three types of metallic electrodes used in ORP measurements that differ in construction but are based on the same principle that an oxidized and a reduced state must be present.

The first type of metallic electrode to be considered consists of a metal contact with a solution of its own ion. The metallic electrode is in a reduced state and its ions are in an oxidized state. An example of this type is silver in a silver nitrate solution. It is used mainly on the analytical field.

The second type of metallic electrode consists of a metal coated with a sparingly soluble salt of this metal in a solution of soluble salt with the same anion (e.g., silver-silver chloride in a solution of potassium chloride). The third type of metallic electrode consists of an inert metal in contact with a solution containing both the reduced and oxidized state of an oxidation-reduction system. An example would be platinum in contact with ferric-ferrous ions. Platinum and gold are the most common ORP electrodes.

The nature of the test solution and the method to be used will determine the choice of the electrode. The reference electrodes can be identical, but a noble metal electrode replaces the glass pH electrode. The signal from the ORP electrodes must be fed into an amplifier with high-input resistance.

If one or both reactions pair hydrogen ions the ORP measurement becomes pH dependent. Consider the following reaction, which occurs in the reduction of hexavalent chromium:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$$

The reaction depends on solution pH. Potential changes measured by the ORP electrode will continue to vary with the redox ratio, but the absolute potential will also vary with pH. In the first step the pH is lowered to 2 to 2.5. Sulfur dioxide or sodium sulfite solution is used as the reductant. The overall reaction is

Table III. ORP Values of Quinhydrone-Buffer Standards

	pH 4			*pH 7*		
	20°C	*25°C*	*30°C*	*20°C*	*25°C*	*30°C*
Reference						
Ag/AgCl	+268	+263	+258	+92	+86	+79
Calomel	+233	+218	+213	+47	+41	+34

$$Cr_2O_7^{2-} + 2H^+ + 3H_2SO_3 = 2Cr^{3+} + 4H_2O + 3S0_4^{2-}$$

In the second part of the process the waste liquors are neutralized to a pH level of 7 to 8. At this pH the chromic ion precipitates as a sludge and is sent to clarifiers for ultimate disposal or recovery. All these reactions will take place in a definite pH and in a specific millivolt range.

Although applications for ORP measurement are not as widespread as for pH one of the most important applications in the metal-finishing industry is the oxidation of cyanide wastes. Oxidation converts the toxic cyanides to harmless compounds. Typically, chlorine gas or sodium hypochlorite are the oxidants. In the first step caustic or lime is added to make the cyanide-bearing waste alkaline to a pH of 9 to 10. An acid solution would release deadly cyanide gas; therefore, the system generally incorporates pH control. The first stage reactions are

$$Cl_2 + CN^- + 2OH- = 2Cl^- + OCN^- + H_2O$$

The second step in cyanide oxidation takes place at a controlled pH in the 7 to 8 range. The reaction is:

$$3Cl_2 + 2OCN^- + 4OH^- = 6Cl^- + 2CO_2 + N_2 + 2H_2O$$

In industrial plants ORP is rarely applied to nice clean reactions where potentials can be estimated easily. In waste treatment or sewage plants, for instance, solutions contain a host of constituents that the reagent oxidizes and reduces simultaneously. ORP relates to the concentrations and activities of all participating reactions. It frequently becomes necessary to determine the control points experimentally.

If day-to-day relative potential values are to be compared, the pH meter must be standardized to the same starting point. Short the meter glass and reference inputs and adjust the standardization control until zero millivolt is displayed using the "absolute millivolt" mode to set the potential to some arbitrary value when the electrodes are reading the potential in a repeatable standard solution.

Because ORP is a characteristic measure of redox equilibrium it should not require standardization or calibration. The measured potential is absolute in a sense. Yet, frequently, it is desirable to check systems for proper operation and electrode poisoning. Solutions of known potential can be developed by saturating buffer solutions with quinhydrone. The reaction is such that the measured potential will vary only along with the solution pH and temperature. The procedure is as follows: (1) Saturate the buffer with quinhydrone, made up fresh for each test. Quinhydrone is not readily soluble so a few crystals stirred into the buffer are sufficient. The solution will be amber colored. (2) Clean the platinum electrode. (3) Place the platinum and reference electrodes in a quinhydrone-buffer solution and measure the potential and temperature. Measured potential will generally be within ±10 mV of theoretical value. The ORP values of quinhydrone-buffer solution can be seen in Table III.

MICROHARDNESS TESTING OF PLATED COATINGS

BY JOHN D. "JACK" HORNER
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Hardness has been defined simply as the resistance to penetration. In order to measure this resistance to penetration a testing machine is used to push a specific indenter into the test material with a specified force, and either the depth of penetration or the area of the "footprint" left by the indenter is used to derive a hardness "number." Hardness as measured by indentation is not a single fundamental property but a combination of properties, and the contribution of each to the hardness number varies with the material and the type of test. Variously shaped indenters have been developed and are in use in different industries. The hardness number varies with the size and shape of the indenter and the force used, among other variables, which results in several different hardness scales. The metalworking industry uses several with one or more of the many Rockwell scales being among the more common. Unless the coatings are extremely thick Rockwell methods cannot be used for plated parts.

The results of hardness testing of plated coatings have been the subject of disagreements for several years. Standardized methods such as ASTM E 384 (Standard Test Method for Microhardness of Materials), which had been developed to measure the hardness of solid materials, were found to need certain modifications to be adapted to relatively thinly plated coatings. This problem was recognized with ASTM B 578 (Standard Test Method for Microhardness of Electroplated Coatings). The term microhardness is used to describe hardness as measured with small indenters and comparatively lower forces. (Some have proposed that microhardness would be more accurately described as microindentation.) Generally, the term microhardness is used for hardness testing when the forced used is 1,000 grams or less.

WHICH HARDNESS SCALE TO USE

There are two indenters commonly used for testing plated coatings. The Vickers indenter has been in use longer and is a small, pyramid-shaped diamond that produces a square footprint or impression. The Knoop indenter was developed by the National Institute of Standards and Technology (NIST) and is a small, rhomboid diamond that produces a longer, thinner, less-penetrating impression. This feature makes it more adaptable for thinly plated coatings. Currently, the ASTM specification specific for microhardness testing of plated coatings is B 578 and covers only the Knoop indenter. It is expected that future revisions of this specification would include the Vickers indenter. It is important to know that these two indenters are not the same and microhardness numbers, although fairly close, are not interchangeable. There are some advantages to using each method. Generally, Knoop is preferred for thinner coatings because of its narrower indent and because it penetrates only about one-half as deep as the Vickers indenter. The Vickers indenter is reported to be more tolerant of slight surface irregularities. Modern testing machines permit the use of either indenter. If necessary to cite an ASTM Standard Test Method the Knoop indenter has the advantage currently.

WHAT LOAD (FORCE) TO USE

It is important to recognize that microhardness numbers can vary with the force used. This is more pronounced at the lower forces. For the harder plated metals, such as hard copper, nickel, or chromium, 100-gram force (0.981 N) should be used. Higher loads of 200-gram force generally show less variance of readings between operators and laboratories but can produce cracking, not always apparent, with the harder, more brittle deposits. At loads of 50-gram force or less, higher values are obtained with considerably more variance, especially with harder materials. Many specifications recommend against using 50-gram loads with these harder materials. Lower forces of 25-gram force or less should be used only for the softer metals such as gold or lead.

HOW MICROHARDNESS IS EXPRESSED

The correct way to express microhardness is to place the microhardness number first, followed by the term for the scale (indenter) as either HK, for hardness Knoop, or HV, for hardness Vickers, with the force used as a subscript. ASTM B 578 specifies this in grams force. The international ISO 4516 specification expresses the force in kilograms force. Both specifications agree that the system of designation of hardness shall be such that the numerical value of the hardness number remains unaffected by the introduction of the SI unit of force, the newton, in place of the old unit. (The force, in newtons, divided by 0.00981 is equal to gram force.) Thus, a microhardness of 550 using a 100-gram force (0.981 N) and a Knoop indenter should be expressed as 550 HK_{100}.

RECOMMENDED PROCEDURE

Preparation of the Sample

Adequate plate thickness is necessary to achieve good results. Minimum plate thicknesses of 0.002 in. (about 50 mm) are preferred. Using the Knoop indenter an absolute minimum of 0.001 in. (25 mm) is sometimes used, although considered too thin by some. When production parts have insufficient plate thickness, it will be necessary to continue the plating of a sample part under constant conditions until minimum thickness is obtained. The use of test panels plated under the same conditions as the work is a common practice.

Except in rare instances, hardness is measured on a cross-section of the plated part. Cut the sample using adequate cooling to avoid any accidental heat treating of the specimen. Overplate the specimen with another metal to protect the edge and provide a visible contrast; e.g., use copper to overplate nickel or vice versa. The hardness of the overplate should be in the same range of hardness as the plate to be tested. Usually, an overplate thickness of about 0.001 in. (25 mm) is satisfactory. Mount the specimen in a plastic medium suitable for metallographic work. If the hardness of the specimen may be affected by the time at temperature involved in the mounting operation use low-temperature-setting plastics.

Grind and Polish the Mount

Avoid heat and "buffing" or work hardening the surface. Normal metallographic techniques require using successively finer grinding and polishing media, rinsing carefully between steps. The mount is rotated 90° at each step to help keep the surface of the mount flat and parallel with the bottom of the mount. The final finish should show few, if any, scratches when viewed at 400× magnification. The final polishing step is often a fine-grit diamond paste.

Calibrate With a Stage Micrometer

Take several readings and average the results to determine any correction factors that need to be used in measuring the indents on test pieces. Magnification of the testing machine should be a minimum of 400×; higher magnification can be a benefit. This correction factor can be different for different people using the same machine, but it should not change for each individual as long as nothing is changed in the equipment. This calibration should be repeated every few months or whenever there is any reason to expect that there has been a change.

Calibrate by Checking a Standard Test Block

It is preferred that the test block be of the same general hardness as the deposit being tested, within reason. (Avoid using a hard nickel or steel test block when the deposit is to be soft gold.) Standard hardness test blocks are available from various laboratory and testing equipment supply houses. Certified standards for microhardness made from electroformed, hard nickel are available from the NIST Office of Reference Materials (Gaithersburg, MD 20899). Using standard test blocks of the same general material as the deposit may minimize potential errors due to differences in resilient properties possible with some metals. (To verify the testing machine, ASTM E 384 calls for 20 indentations on the standard test block.)

Measure the Microhardness of the Sample

Following the instructions of the testing machine manufacturer, make the indentations with the long axis of the indenter parallel to the test surface when using the Knoop indenter. The Vickers indentation should be placed so that one diagonal is perpendicular to the edge of the coating. Indentations should be made in the center of the deposit and spaced at least about one and one-half times the length of the diagonal from each other. For best results, indentations should be symmetrical. When using the Vickers scale, both diagonals are measured and averaged; each diagonal should be of equal length within 5%. Knoop indentations only require measurement of the long diagonal; however, each leg should be of equal length within 20%. (Less than 20% would be better.)

Report the Results

ASTM B 578 asks that results be based on at least five measurements and that the report include range of hardness units, average (arithmetic mean), estimated standard deviation, and coefficient of variation. ISO 4516 asks that the report include the range, with the average optional, whether the tests were done on the surface or a cross-section, and any deviations from normal conditions such as temperature or force-retention time.

HOW MANY READINGS SHOULD BE TAKEN

ASTM B 578 and ISO 4516 call for "at least five measurements." During an extensive series of round-robin tests done over several years, better results were obtained taking five measurements on each of five indentations. This work was done by a section of Committee BO8 in ASTM. From one series of some 6,500 test readings, covering both Knoop and Vickers indenters, it was found that the total average microhardness readings were very close to the certified readings of NIST, even though some ranges were somewhat broad. It is recommended that given the possible variables in the technique, this practice of taking five measurements of each of five indentations be used. Use this for calibrating the machine with the standard test block and when testing sample deposits.

SOURCES OF ERRORS

Vibration

During the indentation process, while the indenter is in contact with the test part, vibration may be a major factor, often underestimated. The slightest vibration during this period will give low, false readings. Running motors; fans; people walking near the machine; auto, truck, or train traffic nearby; even thunderstorms in the area can cause significant vibration, which affects the microhardness readings. It is important to place the microhardness testing machine in a fashion and location to minimize any vibration effects. The operator should be aware of this sensitivity to vibration and keep his or her motions smooth and maintain minimum movement during the indentation process. At lower test loads vibration is even more critical. ASTM E 384 limits vibration to less than 0.005 g (2 in/sec^2). Slight, sporadic vibration can be a major source of the wide ranges often encountered in microhardness readings.

Equipment Problems

Mechanical: Indentation process must be smooth, with a controlled velocity (slow) of the indenter. Full force should be applied for usually 10 or 15 seconds. Longer load-retention times can be more prone to the effects of vibration. ASTM E 384 contains information on verification and calibration of microhardness testing machines.

Optics: 400 magnification should be the minimum; higher magnification would be better. Electronically projected images are more easily measured. Results obtained with lower magnification have varied widely and not agreed with results at 400 and higher.

Indenters: Should be examined at about 100× periodically for defects. Any chipped indenter must be replaced.

Sample Preparation Problems

Surface not perpendicular to indenter: This results in unsymmetrical indents, which can be corrected by repolishing the mount or by the use of a stage-leveling device.

Excessive surface scratches: These can interfere with locating the exact start of the indentation. Repolish the sample.

Sample overheated or surface work-hardened during preparation: A thin layer of work-hardened material may be removed by repeated light etching and light polishing steps. If the sample has been accidentally heat treated a new sample must be prepared.

Measurement Problems

With a machine properly calibrated against a stage micrometer it has been determined that measurements should not vary more than 5%. The range of hardness numbers, however, increases substantially when testing harder materials (with the widest ranges found with the Vickers indenter), and measurement errors will exceed 5%. With microhardness numbers over about 800 HK100, considerable variance can be expected, and it is often recommended that a practical range be specified, rather than a single figure.

Other Common Errors

Reporting errors: Omitting force (load), not expressing hardness numbers properly, and not including the other data as required by the pertinent specifications.

Converting from one hardness scale to another: Most specifications advise against

doing this unless using conversation data actually obtained from the specific material being tested. Hardness numbers should be expressed in the scale that they were tested. Similarly, conversion from one test load to another is to be discouraged without actual data obtained with the same test material.

Measuring hardness of nonuniform deposits: Porous deposits, deposits that contain codeposited hard or soft particles (often termed composites) will produce unreliable readings and should not be tested for hardness in the composite form using microindentation methods.

Deposit too thin: Indentation made too close to the edge of the deposit.

Very brittle deposits: These often crack, which is not always visible, and given unreliable results. The temptation is to use less force, which produces much higher numbers and is not comparable to data obtained at the recommended load of 100-gram force. This is the minimum force required for harder materials by the pertinent hardness specifications.

Including "unusual indentations" in the averages: An indentation that is noticeably different, either in shape or size, from other indentations is probably the result of an unknown test variable and not a true reflection of the hardness and should be rejected.

CONCLUSION

Microhardness testing of plated coatings, or more properly, microindentation test methods for hardness of these materials, can be a good tool in the study of materials, development of improvements, process and quality control, and other applications. The standard test methods, when followed closely and with due attention to the procedures and variables contained therein and in this article can produce dependable and repeatable results within practical limits. In the real world, however, these procedures have not always been followed. The reader is cautioned that there are data in the literature, both old and recent, that are incompletely presented and difficult to duplicate or to compare with data from other sources. The reliability of the test method has been found to improve with the number of indentations and the number of measurements if all the necessary precautions are taken and if the operator is knowledgeable on the procedure and has adequate equipment. It appears inherent to the method that wider ranges are found with the harder materials. Of the two common indenters Knoop has the smaller range when testing the harder materials. Those writing specifications and setting limits on hardness should be well aware of these factors.

THE EFFECTS OF SOLVENT ENTRAPMENT

BY RICARDO J. ZEDNIK AND RON JOSEPH (1944-2011), EXPONENT FAILURE ANALYSIS ASSOCIATES, MENLO PARK, CALIF.

There is a common perception that a thicker coating will necessarily provide better protection to the substrate than a thinner coating. Specifications normally call for a minimum dry film thickness (DFT), but often may not mention a maximum. Practically, one of the considerations limiting the maximum coating thickness is often cost. In applications where a functional coating is intended to provide critical protection to prevent corrosion, abrasion, or chemical attack, it may be tempting to significantly exceed the minimum specified requirements in the spirit of "better too much than too little."

In this article, we discuss why this common misconception can lead to catastrophic failure of a coating system, including cracking and delamination, which can leave the underlying substrate exposed and vulnerable.

Paint manufacturers normally formulate their products with a blend of two or more solvents so that they evaporate gradually and uniformly. The most volatile solvents evaporate shortly after application. Less volatile solvents are designed to remain in the film until the coating has had an opportunity to properly wet the surface. When the coating has the recommended thickness and the application conditions are appropriate (relative humidity, ventilation, temperature, etc.), the solvents fully evaporate as the coating solidifies. This results in a solid, high-quality, and coherent coating that has no voids and fully protects the underlying substrate, as illustrated in Figure 1. If indicated by the manufacturer, additional coats can be applied to build toward the desired total dry film thickness.

In order to build a thick protective coating system, specifications often call for the application of two coats of the topcoat. The second coat helps to isolate the topcoat from the substrate and reduces the possibility that the environment (oxygen, moisture and chemicals) can diffuse to the substrate. Another reason for the second coat is that is often covers existing pin holes and voids in the first topcoat. Painters, however, are often tempted to apply the two coats wet-on-wet or, worse, still apply one thicker coat. This cannot always be blamed on the painters, since they are often pushed by supervisors or managers who want to get the job out of the spray booth quickly to meet production schedules.

The downside is that when the wet film thickness is excessive, not all solvents are able to evaporate. This is because an impermeable layer of dry paint forms on the surface while the bulk of the paint is still wet; solvents are, therefore, prevented from efficiently leaving the surface, as shown in Figure 2(a). Instead, these trapped solvents form bubbles that substantially weaken the coating, often along the substrate interface, as shown in Figure 2(b).

Although the solvents may eventually escape after the paint has fully dried, the bubbles are permanent, as shown in Figure 2(c). These voids result in a porous, noncoherent coating that directly compromises the integrity of the paint system. Pores significantly reduce the structural strength of the coating and form an easy pathway for fracture. Mechanical stress can lead to a delamination crack that propagates

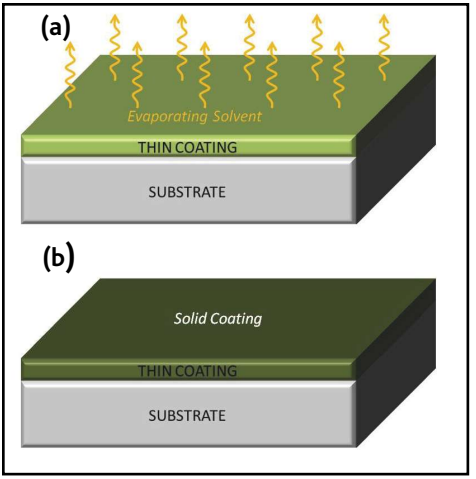


Figure 1. (a) Properly applied coating of the recommended thickness allows all the solvents to evaporate. (b) This results in a solid, coherent coating with no voids that effectively protects the substrate.

between voids, causing the entire coating to fail; the exposed substrate is now vulnerable to deterioration, including corrosion, abrasion, and chemical attack.

Figure 3 gives an example of a severe case of solvent entrapment that has led to a delamination failure of a single thick coat from an impervious substrate. In Figure 3(a) one can see that voids are absent near the smooth surface of the coating. Prior to the failure, a visual inspection of the coating's surface would have erroneously concluded that the coating was perfectly adequate. However, the delamination crack has propagated through multiple voids and resulted in complete failure of the coating system. As shown in Figure 3(b), the coating was severely weakened by the numerous voids, which permeate throughout the underside of the coating.

Solvent entrapment is often easily visible under a stereomicroscope because smooth rounded voids are produced. In fact, the surfaces of the voids appear to smooth and shiny, as can be seen in Figure 3.

The voids could also be air bubbles that were entrapped when the coating was mixed or applied. To differentiate between entrapped solvent and air bubbles, one can send a sample of the coating for analysis by Thermal Gravimetric Analysis (TGA) and / or Gas Chromatography Mass Spectroscopy (GC-MS). Even coatings that have been aged in the field for several years might still contain some entrapped solvents.

TGA measures the weight loss of a coating as its temperature is increased. Provided this test is conducted with a control sample that is fully cured it is often possible to determine if solvents are still present in the aged coating; however, it does not identify the solvents. On the other hand, GC-MS captures the solvents as they evaporate from the heated coating to both identify and quantify each solvent as it passes through the instrument. Accuracy of these measurements depends on several factors, including sample size.

Coating dry film thickness is not the only variable that needs to be carefully controlled: the environmental condition under which a particular product is applied is also important. Manufacturers typically specify these conditions, which include temperature and relative humidity. Nevertheless, applicators may seek ways to accelerate the drying process by blowing air across the surface or applying heat, particularly when multiple coats are required. Unfortunately, modifying the application environment to achieve this "acceleration" often comes at a price: for example, air movement or high temperature will increase the rate of

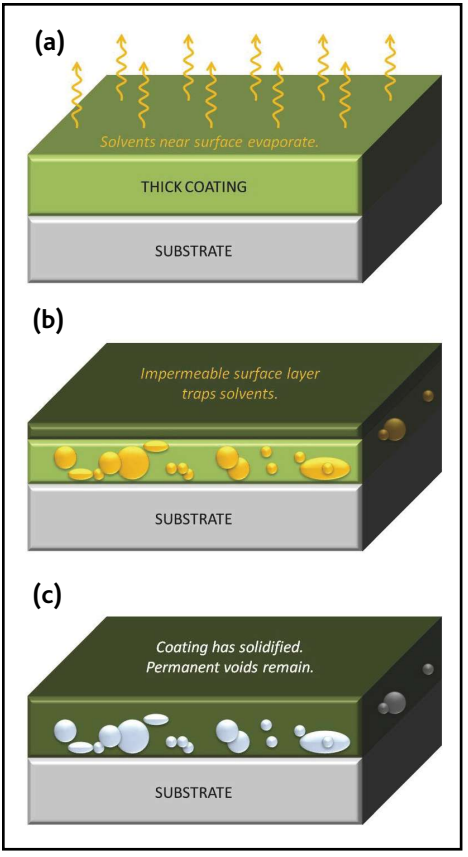


Figure 2. Coatings that are too thick can entrap solvents, leading to voids in the final coating. These voids jeopardize the integrity of the coating.

solvent evaporation. If solvents evaporate too quickly from the coating surface, once again, an impermeable dry "skin" will form. This thin layer will prevent further solvent evaporation; solvent entrapment caused by this mechanism will result in the same detrimental voids that jeopardize the coating strength.

In addition, delamination due to solvent entrapment can be exacerbated by environmental factors affecting the product after application. External effects, including contaminants such as air, moisture, or other environmental chemicals, can gradually diffuse through the product that has been damaged by solvent entrapment (regardless of the cause) and collect in the resulting voids. A relative pressure can build up inside the voids, which can cause them to grow in size; in an extreme case, leading to rupture and catastrophic failure of the coating. This mechanism, shown schematically in Figure 4, is further accelerated in applications where large temperature or pressure fluctuations are common, making it easier for the bubbles to "pop."

The two following case histories illustrate the effects of solvent entrapment.

CASE #1:

Early in his career, Ron Joseph was employed by a paint manufacturing company. He was asked to attend the inspection of a railcar that had been painted six years earlier with a new, untried coating system. Upon arriving at the site he was joined by the customer and several older and more experienced parties. The railcar was painted white (an automotive finishand) looked superb. Since the customer intended to evaluate this new coating system, he performed the standard ASTM D3359 "Standard Method for Measuring Adhesion by Tape Test – Method A." Using a sharp knife blade, he scribed a large "X" into the paint, ensuring that the cut penetrated down to the substrate.

The customer then lifted the apex of the "X" with his thumb and forefinger

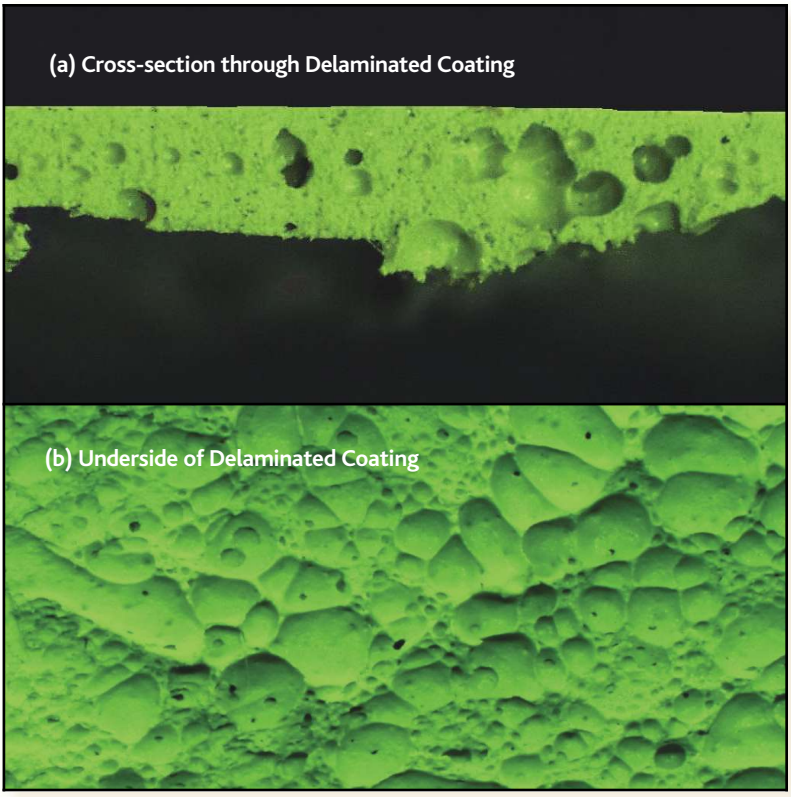


Figure 3. Example of solvent entrapment that has led to a delamination failure. Cross-section (upper image) and underside (lower image) of delaminated sample are shown at the same magnification.

and to everyone's horror the entire system lifted from the steel substrate. The coating delaminated like a sheet. Young Joseph was horrified—the paint had been supplied by his employer! One could clearly see the clean, un-corroded, abrasive blasted substrate shining like new under the coating system. Moreover, one could still smell solvents on the backside of the delaminated coating. Luckily, the customer was neither surprised nor upset. He had been present six years earlier when the railcar was first painted and he remembered the sequence:

1. **Steel abrasive blast cleaned with steel shot**
2. **Corrosion-resistant epoxy primer applied**
3. **Two coats of epoxy sanding primer applied**
4. **Primers sanded down using 240 and 320 grit paper until a completely smooth surface was achieved**
5. **Epoxy filler coat applied**
6. **Two coats of two-component aliphatic polyurethane applied**
7. **During inspection all dents and minor coating defects were circled using chalk**

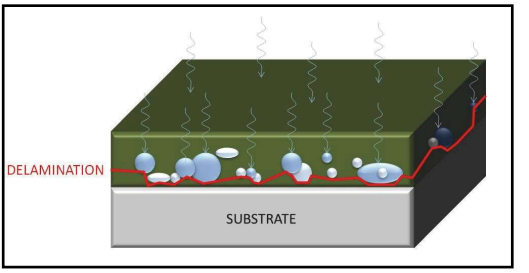


Figure 4. Environmental contaminants, such as moisture, can gradually diffuse through the damaged coating and collect in the voids. This can build up a pressure inside the voids and accelerate the delamination failure.

8. Areas with defects were sanded smooth and feathered
9.Additional coat of polyurethane was applied
10. Finally, glazing, adhesive labels, etc. were applied

The experimental railcar was then put into service for six years, during which it traveled many times through the desert, in tropical environments, along the coast, etc. The railcar experienced a wide range of environmental conditions. Nevertheless, sufficient solvent still remained in the coating to cause catastrophic delamination!

CASE #2:

A large multi-ton overhead crane had been fabricated for use in a steel mill. The crane had been freshly painted with an alkyd primer followed by three coats of a solvent-based acrylic-modified alkyd topcoat. Each coat had been applied wet-on-wet. Unbeknownst to the manufacturing manager, solvents in alkyds and modified alkyds of 1970s vintage evaporate slowly. At around 4p.m. on Friday afternoon the freshly coated crane was carefully lifted onto a special heavy-load transporter ready for a 300 mile drive to the steel mill. A few minutes before the truck driver was about to leave, the manufacturing manager quickly performed an adhesion test. To his horror he discovered that the entire paint system lifted off. Frantically, he called Ron Joseph, whose employer had supplied the paint. After some questioning and subsequent adhesion checks it was revealed that adhesion was good on one side of the crane but was catastrophically poor on the other. The "good" side had been exposed to the sun for the past week, while the "poor" side had been in the shade.

It was now too late for the manufacturing manager to take the crane off the transporter; therefore, Joseph recommended the crane be positioned so that the "poor" adhesion side would get the maximum amount of sunlight during its journey to the steel mill. Hopefully, by the time the site inspector would perform his adhesion check sometime during the following week, solvents would have evaporated and the coating would pass the adhesion test. As expected, the crane passed the test.

CONCLUSIONS:

- **It is poor practice to apply too many (or excessively thick) coats of paint without allowing the solvents to properly evaporate between coats.**
- **Beware of applying coats wet-on-wet, unless specifically recommended by the manufacturer.**
- **Thick coatings are not conducive to rapid solvent evaporation.**

- **In general, very high solids coatings (near 100% solids content) are not likely to experience solvent entrapment.**
- **Coatings that quickly form a surface film, or skin, after being applied are more likely to experience solvent entrapment.**
- **Solvent entrapment can also apply to waterborne coatings.**
- **Two-component coatings, such as epoxies, polyurethanes must not be applied after they reach their pot life.[1]**
- **If a two-component coating is close to its pot life and the painter needs to complete the job,[2] he must not add thinners to the coating with the expectation that this will extend the pot life. The addition of thinners will lower the viscosity of the coating, but the chemical reactions (cross-linking) that have already taken place cannot be reversed. Therefore, the coating will almost certainly entrap solvents during drying and curing.**

REFERENCES

1. When the coating approaches its pot life, the viscosity starts to increase rapidly and the painter can no longer achieve an acceptable finish because the paint can no longer be atomized.

2. Many painters are tempted to continue painting even after the coating has reached its pot life. In some cases, it may be possible to mix a small quantity of a new batch and add it to the current batch. This might extend the pot life sufficiently to allow the painter to complete the job.

THE VALUE OF OPTICAL MICROSCOPY IN FORENSICS OF PAINT FAILURES

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Many paint failures, especially in the architectural field, lead to litigation or insurance claims. Consequently, a paint consultant is often retained, usually by a law firm on behalf of an insurance company, to determine the root cause(s) of the problem(s). Based on the results of the investigation, the strength of the expert report, and other factors, the case will either settle or go to trial. This paper discusses one of the most fundamental tools in solving the paint problem—optical microscopy.

Microscopes. A stereomicroscope (Figure 1) is one of the most useful instruments in a forensics laboratory for paint. Depending on the model, the microscope should have the capability of magnifying an image through a range, such as 7X to 64X. How it works: light shines from the top down onto the sample and there is usually sufficient space to allow the operator to tilt the sample and observe it at a wide range of angles. Additionally, the angle of the light source can be changed possibly to see shallow defects (e.g., orange peel, dust, solvent popping, cratering, etc.) when looking at a paint failure.

A disadvantage of this instrument is the depth of field is shallow. This means while getting a sharp image at one location, the neighboring area(s) might be out of focus. Fortunately, for those who need excellent focus along the length of the sample, software packages are available that allow images of varying focal lengths to be blended together to form a perfectly focused image of the desired area.

For higher magnifications, other types of microscopes might be necessary. A calibrated optical inverted stage microscope capable of typical magnifications from 50X to 1000X can be useful (Figure 2). Because the depth of field is more limited than with the stereomicroscope, it is common to mount the sample in an epoxy resin and then polish the mount to an extremely smooth finish using 600 grit or higher abrasive paper, diamond abrasive pastes, or jeweler's rouge. The sample is placed upside down onto the microscope stage and incident light shines from the bottom up onto the sample surface. This differs from the stereomicroscope where the light shines from the top down on to the sample.

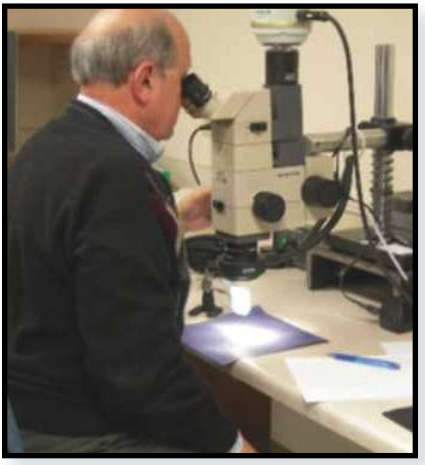


Figure 1. Typical stereomicroscope with 7X to 64X magnification.

Many analytical laboratories

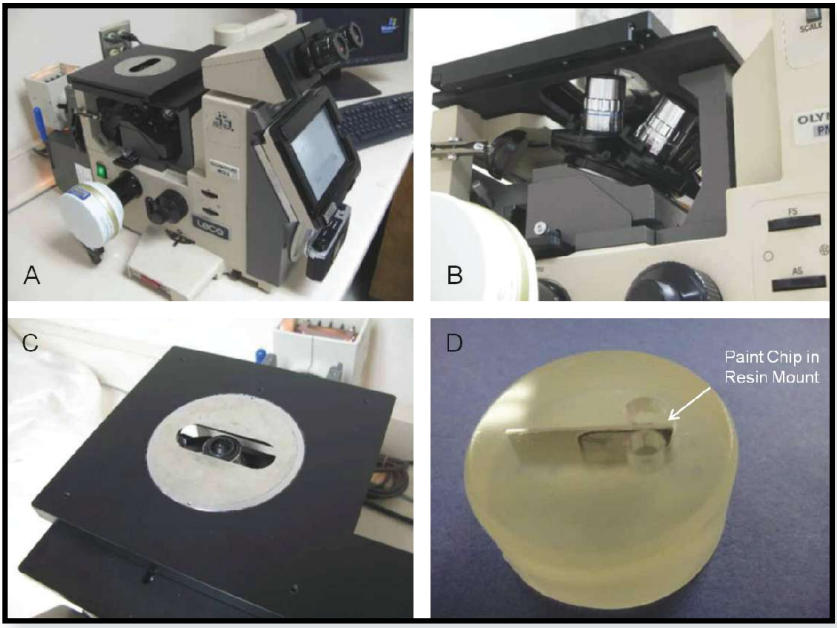


Figure 2. Metallographic microscope: overview (A); configuration of the lenses (B); inverted stage (C); and, epoxy-mounted paint film (D).

purchase microscopes that have the capability of taking digital micrographs and viewing the pictures on an adjacent monitor. In addition, microscopes have a built-in scale that allows one to immediately measure the length or width of any section of the micrograph. This is particularly valuable when measuring the dry film thickness (DFT) of paints on a variety of substrates, including non-flat surfaces, such as stucco, concrete, and weathered wood.

EXAMPLES OF FAILURE ANALYSIS

The following sections are some examples of failure analysis. Each question is immediately followed by a scenario setting the scene/tone for the question.

1. Did the contractor comply with the paint specification?

A Customer Specification calls for a fabricator to galvanize a steel product, apply an epoxy primer, and followed by a polyurethane top coat. The product was to be exposed to an aggressive marine environment, but after only a few years, the product failed prematurely due to extensive corrosion. The fabricator denied he had done anything wrong and insisted he had followed the Customer's Specification to the letter.

Samples of the failed steel were cross-sectioned and analyzed using a metallographic microscope. Figure 3 is a representative image. The microscopic analysis shows the fabricator had not followed the Customer Specification. The galvanizing was not a uniform, coherent layer of zinc, which may have been due to poor processing procedures. The organic coating system started by applying the

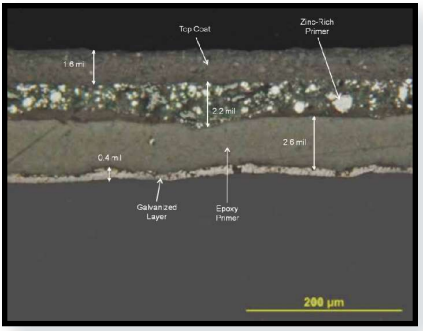


Figure 3. Various coating layers demonstrate whether the fabricator complied with the specification.

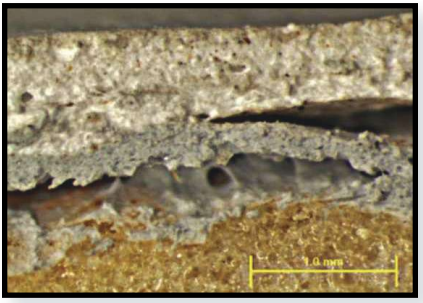


Figure 4. Solvent entrapment in the primer and delamination of the top coat from the primer.

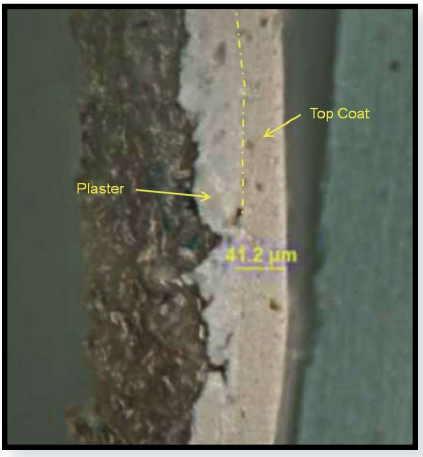


Figure 5. Acrylic latex top coat peeling away from the drywall compound.

epoxy primer and followed with a zinc-rich coating. Such a zinc-rich coating was not specified and did not provide significant corrosion protection as it had not been applied directly to the bare steel. Here is the absurdity: galvanizing means coating a steel product with zinc, which is used to protect the steel surface from corrosion by means of cathodic protection. Similarly, a zinc-rich primer provides cathodic protection, provided it is in direct electrical contact with the steel substrate. In other words, hot dip galvanizing and zinc-rich primers serve the same purpose! In this case, the fabricator and/or painting contractor applied two zinc coatings, when only one was required. More importantly, in order to provide maximum corrosion protection, the zinc-rich primer must be applied directly to the steel and not over an epoxy primer. Hence, the zinc-rich primer served no purpose other than to increase the thickness of the total coating system.

2. Roof coating peels off in sheets

A roof coating system was applied during the summer months to the top of a commercial building. Several weeks after completion, the building's owner noticed large sheets of roof coating peeling. A site inspection revealed the gray primer was pulling away from the underlying polyurethane foam, and in some instances, the top coat was pulling away from the gray primer as well (Figure 4).

An analysis by means of a stereomicroscope confirmed what the consultant anticipated. There was excessive solvent entrapped in the primer layer. This is seen by the large cavities in the gray coating and ex-

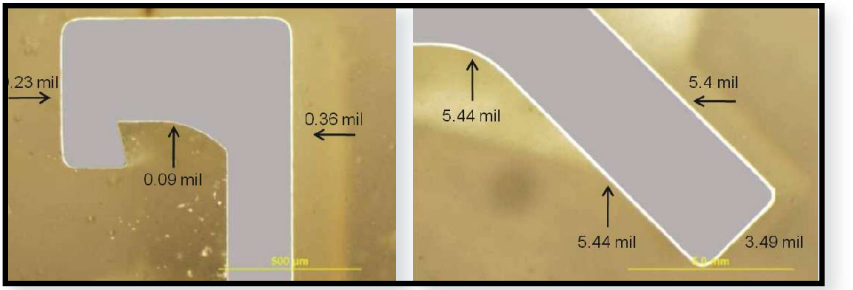


Figure 6. Two coating aluminum extrusions with non-uniform and uniform coating deposits.

plains why the primer lifted off the polyurethane foam. However, why did the top coat pull away from the primer? It was suspected the primer's top surface had started to oxidize in the strong ultraviolet (UV) light during the hot summer's day, and the oxidized surface was inert to the top coat layer.

Although microscopy provided hints of what might have gone wrong, additional analytical tests were conducted to confirm solvent was in fact present in the primer. The client had a limited budget and did not request the consultant prove the UV oxidation theory. However, a test such as x-ray photoelectron spectroscopy (XPS) could have determined if the epoxy had oxidized before the top coat was applied.

3. Acrylic Latex peels off school walls

Soon after occupying a new office building, while attaching drawings and other paper items to the walls, employees noticed the white acrylic latex wall paint peeling off. Blue painter's adhesive tape was used to mount the articles. Several classrooms exhibited the same problem, regardless of whether the wall was alongside a window or on the opposite side of the room. Was this the painter's fault? Was the paint itself defective? A microscopic analysis of some small paint samples that had peeled showed that the paint was well applied and at the manufacturer's recommended DFT. However, paint was not peeling off the wall; rather, a coating layer on the drywall, under the paint was coming off with the paint (Figure 5). Therefore, it was the under-coat (plaster) that had poor cohesion and broke away from itself: neither the painter nor the paint was at fault.

4. Coating of aluminum extrusions

Aluminum extrusions for architectural purposes are often coated with a polyvinylidene difluoride (PVdF) system. American Architectural Manufacturer's Association (AAMA) Specification 2605, "Voluntary Specification, Performance Requirement and Test Procedures for Superior Performing Organic Coatings on Aluminum Extrusions," is often specified for extrusions that will be exposed to a marine environment in which high humidity, salt-laden air, and fog are prevalent. A client wanted to ensure the extrusions he ordered would meet the section of the specification, which states:

> *4.3 ... Eighty percent of measurements on primary exposed surfaces shall meet or exceed 30 microns (1.2 mil) total film thickness. Paint process capability may result in readings below 25 microns (1.0 mil). No more than 5% of the total*

readings, on primary exposed surfaces, shall be below 25 microns (1.0 mil) (or, 85% of film thickness specified), assuming appropriate color and hide. [Under lining added]

Questions arose concerning the definition of "... exposed surfaces ..." and "*No more than 5% of the total readings, on primary exposed surfaces ...*" Is it adequate to assume that surfaces on the back side of the extrusion will not be exposed to the marine environment, especially fog? If the extrusion is part of a window opening, will it be exposed to fog?

Most paint consultants are aware initial paint and corrosion failures do not occur on the face of an extrusion, but rather on the edges and corners. Once these have been breached, corrosion tends to creep under the coating and penetrate onto the face. Therefore, when the specification allows no more than 5% of the exposed surfaces to be below 1.2 mil, does that consider the edges? Frankly, the focus should be on the edges rather than the faces and ideally, the specification should mandate the minimum DFT along the edges and corners to be 1.2 mil.

The micrographs in Figure 6 illustrate how microscopic analysis was valuable in assessing film thickness compliance with the specification. Also, notice how the coating thickness varies significantly throughout the aluminum part.

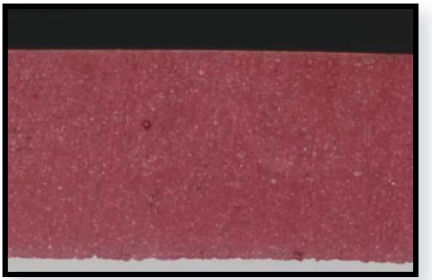


Figure 7. Thick, corrosion-resistant coating applied to mildly shot-blasted steel surface with low blast profile.

5. Surface preparation—abrasive blasting

A 100% solids coating was applied to a steel surface cleaned by abrasive blasting. Massive delamination of the coating occurred after the product was placed into service, and the client wanted to know if the contractor had followed the correct procedures when blast-cleaning the surface. By sectioning and polishing a sample of the coating and substrate, one could easily measure the blast profile even though the job had been conducted years before (Figure 7).

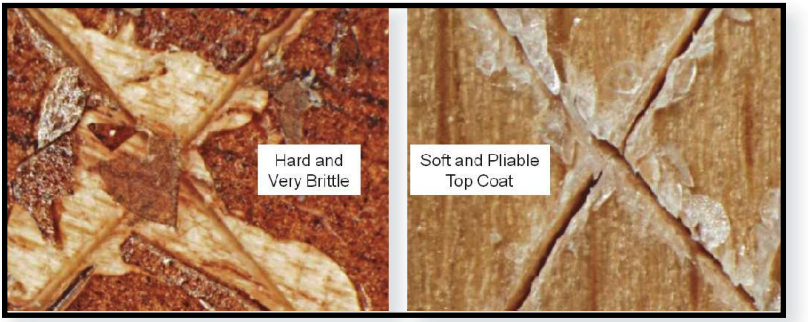


Figure 8. Hard brittle wood cabinet coating compared with a softer and more ductile replacement product.



Figure 9. Extensive solvent entrapment on the underside of an epoxy coating, resulting in poor wetting and inadequate adhesion to the substrate.



Figure 10. Top of epoxy coating showing extensive pinholes and craters.



Figure 11. Top coat blistering due to extensive solvent entrapment in the under coat.

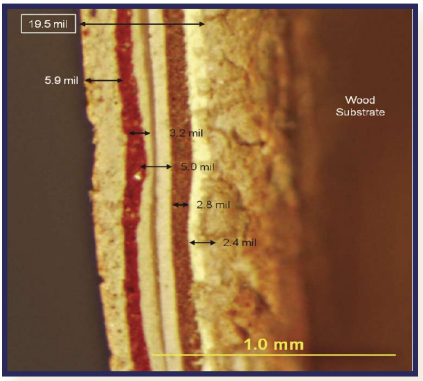


Figure 12. Multiple layers of paint leads to tremendous internal pressures.

6. Wood Coatings

A cabinet maker applied a lacquer from Company A for finishing kitchen cabinets. After the cabinets were installed, several customers complained the coating easily chipped off when something was dropped onto the wood. The problem was exacerbated when someone bumped into the corners or edges of the wood.

The cabinet maker then changed to a different lacquer and clear coat from Company B and the results appeared to be fine. Upon microscopic investigation, it was clear that the original finish was so brittle that when the paint consultant touched it with the tip of an X-Acto® knife, the coating shattered into small pieces and there was essentially no adhesion between the lacquer and the wood (see Figure 8). When the replacement coating was examined, some of the clear coat broke away from the underlying lacquer, but the coating system remained in good condition. There were no complaints that the new coating system failed in the field.

7. Delamination of epoxy primer

One of the most common reasons for paint delamination is solvent entrapment. Figure 9 illustrates a micrograph taken with a stereomicroscope showing extensive solvent entrapment on the underside of the coating. Although this was barely visible with the naked eye, it became obvious under approximately 15X magnification. To highlight the cavities, the paint consultant chose to illuminate the sample paint chip at a shallow oblique angle of approximately 10 to 15 degrees. Using oblique lighting, the top of the coating clearly showed pinholes filled

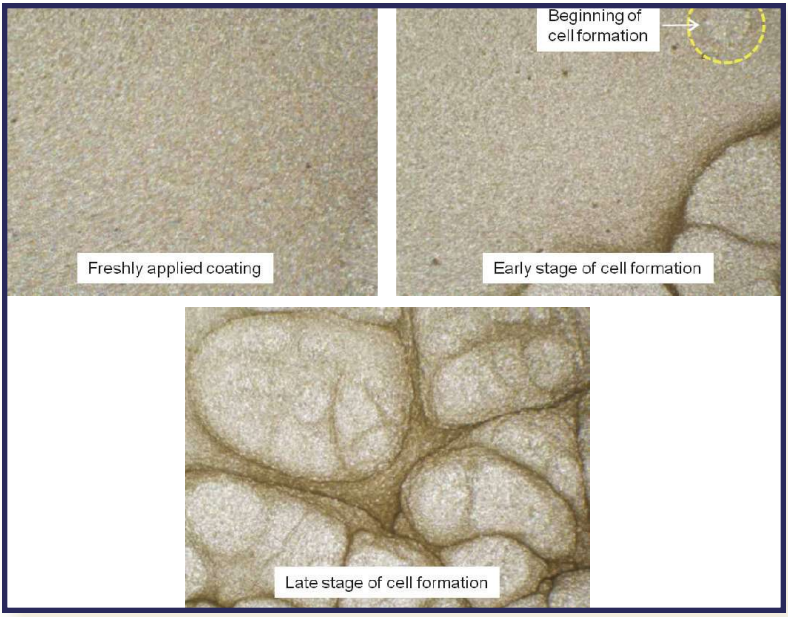


Figure 13. Metallic coating shows separation into cells structures as the paint starts to dry and cure.

in, but nevertheless, left small craters on the surface (Figure 10).

8. Paint blistering

Figure 11 illustrates what one might typically see under a large paint blister. In this micrograph, a large blister formed between the green top coat and the epoxy under coat. Severe solvent entrapment in the gray epoxy probably caused solvents to attempt to escape through the top coat. If the top coat was set up and cured, it would have been impermeable to some degree to the solvents lead to blisters. Elsewhere on the painted equipment, the top coat had already ruptured and peeled.

9. How many coats?

Paint was peeling from exterior wood siding. Upon closer examination, it was clear the coating was pulling the wood apart but that the paint itself was intact. The upper surface of the wood was aged so it could not withstand stresses applied by paint. How could one or two coats of acrylic latex paint apply such stress on wood? When a sample of the painted siding was examined under a stereomicroscope, it was evident the building had been painted five times (Figure 12). Every time a new coat of paint was applied, additional internal stresses built up. In fact, the total DFT of the system was 19.5 mil. It is understandable how so many layers could generate sufficient stress that the aged fibers of wood would lose cohesion and tear apart.

10. Watching metallic flakes separate.

The owner of a paint shop complained that no matter how his painters applied a particular pearlescent metallic paint, the final finish always appeared mottled.

One of the more curious and possibly exciting observations is to watch metallic paint to dry. In this case, a few drops of a pearlescent metallic paint were applied to a glass microscope slide. Viewing these drops through the microscope, you can immediately see the metallic particles flow along the surface of the paint toward discontinuities, such as small air bubbles, tiny dust particles, etc. The flow of pigments looked much like large quantities of debris flowing down a fast-moving river. In this case, over a period of a few minutes the metallic pigments started to form cells (as shown by the arrow in Figure 13), which kept growing over time. By the time the paint had dried, the entire surface was covered with large cells, resembling Bénard Cells. When looking at the painted panel from a distance of approximately 2 to 3 feet, the surface had a mottled appearance and did not meet the client's requirements.

Because separation occurred so quickly after the paint was applied, this investigation highlighted the importance of agitating the paint aggressively during paint application. Therefore, the use of a gravity-fed or cup spray gun would probably not be able to prevent such separation. Even the common air-driven agitators, used in most pressure pots, likely turn too slowly to prevent separation. On the other hand, a squirrel cage mixer may suffice.

If the painter stops triggering for more than a few seconds while moving from one part to another, the pigments might already start to separate in the fluid hose. To prevent separation after the paint has been deposited, it would behoove the painter to use a higher-than-usual atomizing air pressure and achieve a dryer rather than wetter finish. The goal should be to flash off the solvents quickly, thereby preventing the pigments from having too much mobility.

When one encounters a problem such as this one, the paint manufacturer and painter should work together to ensure that when the painter follows the best application practices, the pigments do not have time to separate. The manufacturer might be able to reformulate his product using faster drying solvents, or perhaps by selecting pigments more compatible. The painter has several tools at his disposal to apply a dryer finish, thus helping to prevent pigment separation.

CONCLUSION

This paper used illustrated examples to demonstrate the usefulness of tabletop optical microscopes. Such microscopes enable a paint consultant to better understand why a paint failed, if specifications were followed, and often explain any unacceptable appearance.

ACCELERATED CORROSION TESTING

BY RAYMUND SINGLETON
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Accelerated corrosion testing of metals and coatings was first developed in the late 1890s and early 1900s for testing products to increase their useful performance and service life. This method of testing the corrodibility of ferrous and nonferrous metals and organic and inorganic coatings has since been improved and variations added to better test new materials and help operators understand how they may perform in, and withstand, a wider range of real world environments.

Accelerated corrosion testing has also evolved from providing information to help determine durability of products, and their quality assurance during manufacturing, to use in product research and development. Professional trade, industry, military and standards organizations, such as: ASTM International (American Society for Testing and Materials), the Society of Automotive Engineers (SAE), the Federation of Societies for Coatings Technologies (FSCT), NACE International (National Association for Corrosion Engineers), Society for Protective Coatings (SSPC) and others have developed a number of accelerated corrosion tests to meet the demands of changes, and advances, in technology, materials, and other performance requirements and environmental regulations. For instance, water-based coatings have been developed as replacements for solvent-based liquid coating materials in response to environmental concerns. Some powder coatings and their application methods reduce the use of solvents and ease application. In addition, the automotive industry has improved coatings and increased the number of surfaces coated as part of the response to market pressures for longer warranties. Some of the more widely used tests are the representative ASTM Standards detailed in this article and well known industry cyclic corrosion tests such as: General Motors GMW14872 (formerly GM9540P), and SAE J2334. There are many other tests in use; however, those mentioned also exhibit wider applicability and versatility and are, therefore, some of the more popular procedures. Other than the ASTM B117 Salt Fog test, most widely used for on-line process and product quality control, no other single corrosion test is as dominant because of the wide variety of service conditions, product industries and specific issues such as various materials, applications methods, properties, and varying surfaces. Other considerations to consider when choosing or specifying a particular accelerated corrosion test include the multitude of environments and customer demands faced by a product and industry. A variety of standard tests has been developed to address these issues.

One of the first—and still most widely utilized—accelerated corrosion tests developed is ASTM B117 Operating Salt Spray (Fog) Apparatus. Early development of corrosion tests was initiated in order to evaluate the corrodibility of metals and protective properties of coatings in a marine or "near shore" environment. As corrosion testing was increasingly used also to evaluate product quality and materials used in product development, variations on the basic, or original, corrosion test standards have been added to increase their usefulness for a wider range of environments and materials. This process has resulted in the development of the various representative accelerated corrosion tests to be discussed in this article.

The usefulness of testing coatings for resistance to water, or high humidity, as a good indicator of their service life in service environments of that type resulted in the ASTM D1735 Standard Practice for Testing Water Resistance of Coatings Using Water Fog Apparatus and the ASTM D2247 Standard Practice for Testing Water Resistance of Coatings in 100% Relative Humidity. Demand for improved evaluation of decorative copper/nickel/chromium or nickel/chromium coatings on steel, zinc alloys, aluminum alloys, and plastics designed for severe service resulted in the ASTM B368 Standard Test Method for Copper Accelerated Acetic Acid-Salt Spray (Fog) Testing, widely known by its acronym as the "CASS" test. Additional needs for testing of product resistance to harsh industrial environments led to the development of the ASTM G85 Standard Practice for Modified Salt Spray (Fog) Testing with its 5 included corrosion test variations and the ASTM G87 Standard Practice for Conducting Moist SO2 Tests. The ASTM G85 variations (tests): Annex 2, Annex 3, Annex 4, and Annex 5 along with ASTM G87 were developed to subject test pieces to cycles of differing environments to more closely resemble the changes occurring in pertinent real-world environments. See Table I for information on "static" versus "cyclic" environment tests. With the wide variety of materials and coatings, their uses, and the service environments

Table I. Static Versus Cyclic Tests

Static Corrosion Tests
- In static corrosion tests the exposure zone conditions of the test chamber stay the same (within defined tolerance limits) throughout the duration of the test.
- The test duration (length of exposure) is the *only* variable.

Examples of Static Condition Corrosion Tests
- ASTM B 117 Salt (Fog) Spray
- ASTM B 368 Copper Accelerated Salt Spray
- ASTM D 1735 Water Fog Humidity
- ASTM D 2247 Condensing 100% humidity
- ASTM G 85, Annex 1 Acetic Acid Salt Fog

Cyclic Tests
- In cyclic corrosion tests the conditions in the exposure zone change for each step in the cycle in an ordered, predefined sequence. The changeable conditions can include temperature, various types of moisture application, different levels of humidity, different types of pollutant or electrolyte such as various salts, gases, etc., and various lengths of exposure for each.
- Cycle Type A tests
  - Temperature is constant
  - Various types of moisture application, different levels of humidity, different types of pollutant or electrolyte such as various salts, gases, etc., and various lengths of exposure for each step.
  - Total test duration (length of exposure) is also a variable

Examples of Cyclic Type A Condition Corrosion Tests
- ASTM G 85
  - Annex 2 Acetic Acid
  - Annex 3 Acidified SF
  - Annex 4 Salt/SO_2 Spray
- Cyclic Type B Tests
  - Temperature is different for at least some steps in the cycle
  - Various types of moisture application, different levels of humidity, different types of pollutant or electrolyte, such as various salts, gases, etc., and differing lengths of exposure for various steps.
  - Total test duration (length of exposure) is also a variable.

Examples of Cyclic Type B Condition Corrosion Tests
- ASTM G 85
  - Annex 5 Modified SF (DEC) Dilute Electrolyte Cyclic Fog/Dry Test
  - ASTM G 87 Moist SO_2
  - GM 9540P
  - SAE J-2334

in which they may be used, manufacturers and product development personnel now can select an accelerated corrosion test that best suits their particular product and applicable environmental conditions. Table I is provided to give a guide to which ASTM test standard can be used for the representative situations listed. Along with the development of new accelerated corrosion tests ASTM Standards have been developed to give direction and resources for the preparation of test pieces prior to testing and evaluation of post test results. A good example is ASTM D609 Standard Practice for Preparation of Cold-Rolled Steel Panels for Testing Paint Varnish, Conversion Coatings and Related Coating Products. This standard provides guidelines for the preparation of test pieces before they are introduced into the accelerated corrosion test. ASTM Standards: D1654 Standard Test Method for Evaluation of Painted or Coated Specimen Subjected to Corrosive Environments; D610 Standard Practice for Evaluating Degree of Rusting on Painted Steel Surfaces, and; D714 Standard Test Method for Evaluating Degree of Blistering of Paints were developed to provide common standards for analyzing and reporting the results obtained from the corrosion tests and observed on the tested specimens. These standards are summarized below.

ISSUES

Primary issues that arise when discussing the usefulness of accelerated corrosion tests are comparison to real-world exposures and the consistency of test results. Accelerated corrosion tests are performed under controlled conditions with a limited number of variables, which generally do not duplicate the vast variety of variables that occur in any one location in a real- world environment. Comparison standards can be used to compensate for this. Comparison standards are properly prepared, representative test pieces from a product with a known "track record" of exhibiting acceptable performance from exposure in applicable real-world environments and/or also acceptable corrosion resistance after being exposed to the specified accelerated corrosion test(s). They then can be used as standards against which other tested pieces are compared. This process helps especially product developers and also quality professionals predict how a new product or production run of an existing product will perform when used. It is usually not possible, unless additional "long-term, real-time", comparative outdoor or "in-service" exposure data is available, to directly compare any given number of hours in an accelerated corrosion test with a given number of years exposure in real-world environments. The development of additional variations on basic accelerated corrosion tests have allowed engineers, technicians, and quality professionals to better evaluate durability of products to be used in a wider variety of environments, under multiple corrosive influences, and under constantly changing service conditions.

The issues are: consistency in the accuracy of test results from subsequent runs of the same test in a single test chamber; and consistency for comparison of test results obtained from the same test run in other chambers. These issues have been addressed with the development of ASTM methods for evaluating this necessary consistency. This verification is called repeatability of results from subsequent runs of the same test in a single test chamber and reproducibility of results from subsequent runs of the same test in other test chambers (regardless of how many other corrosion test chambers are involved). These important verification procedures are covered in Section X3 of the Appendix of the ASTM B117 test standard and incorporate "Mass Loss" Corrosion Coupons described in that section. A sim-

ilar variation of this Mass Loss Corrosion Coupon procedure is described in Paragraph 8.7 of ASTM B368, using nickel coupons for the "CASS" test.

CRITERIA FOR CYCLIC TESTS

The American Iron and Steel Institute, in cooperation with the Automotive Corrosion and Prevention Committee of the SAE, conducted a study of existing cyclic corrosion tests (completed in 2003, revised in 2007) in order to develop tests that could be used to rank performance of materials used in automotive "cosmetic" applications. Approximately 20 existing corrosion tests were selected for study. These included "static" exposure condition tests (tests where the exposure conditions do not vary over the duration of the test), such as ASTM B117, and "cyclic" exposure condition tests such as ASTM G85 Annex 5 and GMW14872 (formerly GM9540P), (tests which subject test pieces to a variety of different exposure atmospheres and conditions over the duration of the test). Ten different test materials were exposed in each test. The results of the tests were compared to real-world exposure results from 10 sites around the globe utilizing duplicates of the same materials. It was concluded from results that an acceptable corrosion test must: (1) simulate the rank order of performance of coatings in actual service; (2) produce the same type (character) of failure as found in real-world experience (example: blistering); (3) be reproducible; (4) be of relatively short duration; and (5) be feasible and cost effective.

The test established as a result of this effort is the SAE J2334 Laboratory Cyclic Corrosion Test. The SAE J2334, GMW14872 (formerly GM9540P), and ASTM G85, Annex 5 meet the above criteria and are some of the more commonly used cyclic corrosion tests in the U.S. and around the world. The SAE J2334 and the GMW14872 were originally developed for testing cosmetic finishes on automotive components. Fortuitously, they have been shown to produce more "realistic" corrosion results and, therefore, are used to test a much wider variety of materials, finishes, and applications. ASTM G85, Annex 5, is known to be particularly useful for testing both: architectural coatings and industrial maintenance paints as well as other applications.

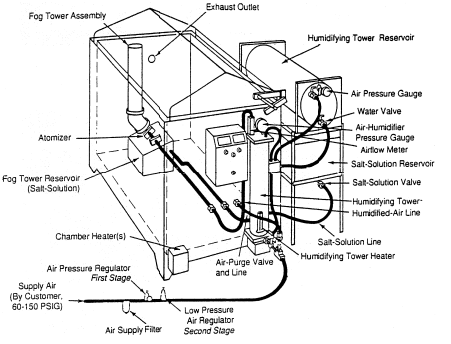


Fig. 1. Schematic drawing of a typical salt fog test chamber.

TYPES OF TESTS

For the purposes of this discussion ASTM B117 is described first. The other ASTM Corrosion Test Standards discussed are described in terms of how they vary from the basic B117 Standard. Only those aspects of these standards, which are different from the B117 standard, will be discussed.

Table II. Equipment Requirements for Various Test Standards

Standard	*Chamber Requirements*
B 117	Insulated cabinet made with inert materials or inert coating on the interior Salt solution reservoir ASTM D 1193, Type IV (DI) water supply Humidifying tower One or more fogging towers with atomizer and baffles Compressed air supply Bottom drain Exhaust Heating apparatus for humidifying tower and chamber exposure zone Temperature displays for wet and dry bulb temperatures and humidifying tower Appropriate gauges and safety apparatus Test piece supports
D 1735	B 117 chamber without any traces of salt B 117 salt solution reservoir is used for ASTM D 1193, Type III (DI) water
D 2247	B 117 chamber Humidity only, no fogging tower Able to accommodate 6 to 8 in. of ASTM D 1193, Type IV water on bottom or large internal water tanks in chamber exposure zone Heating apparatus for water and bottom 12 in. of chamber exposure zone Method A, no humidifying tower Method B, equipped to bubble humidified air through air manifold submerged in bottom of exposure zone water Humidifying tower, only if using bubble method
B 368	B 117 chamber Add bypass on humidifying tower

	Annex 1	B 117 Chamber
G 85	Annex 2 and Annex 3	Modified or purpose built B 117 type test chamber with appropriate cyclic timing controls and automatic mechanical apparatus to execute required exposure zone temperature and atmosphere changes.
	Annex 4	Modified or purpose built B 117 type test chamber with appropriate cyclic timing controls and automatic mechanical apparatus to execute required exposure zone temperature and atmosphere changes. So_2 supply and dispersion method. Flow meter
	Annex 5	Modified or purpose built B 117 type test chamber with appropriate cyclic timing controls and automatic mechanical apparatus to execute required exposure zone temperature and atmosphere changes.

G 87	Modified or purpose built B 117 type test chamber with appropriate cyclic timing controls and automatic mechanical apparatus to execute required exposure zone temperature and atmosphere changes. No fogging apparatus or humidifying tower Internal capacity of 300 L Supply of sulfur dioxide and inlet tube no less than 50 mm from floor of chamber Means to relieve excess pressure Heat externally on floor and lower walls External heater for water Metering apparatus Located away from pollution, direct sunlight, and draft



Fig. 2. Typical water-jacketed-type corrosion test chamber mostly used for static condition tests.

ASTM B117 — Standard Practice for Operating Salt Spray (Fog) Apparatus

The ASTM B117 Standard is primarily used to test the corrosion resistance of organic and inorganic coatings on metals. Examples are paint or plated finishes on metal items and exposure of products to "marine" or "nearshore" environments. This standard will also be the base against which this article will describe other corrosion tests. The B117 Standard is a "static" (constant) condition, continuous test, preferably run in multiples of 24-hour periods. The test pieces are exposed to a salt fog atmosphere from atomized solution made up of 5% sodium chloride and 95% ASTM D1193 Type IV water by mass and held to purity standards specifying that it contain: not more than 0.3% by mass total impurities. Halides (Bromide, Fluoride, and Iodide) other than Chloride, shall constitute less than 0.1% by mass of the salt content. Copper content shall be less than 0.3ppm by mass. Sodium Chloride that has had anti-caking agents added shall not be used because such agents may act as corrosion inhibitors. This solution is then atomized into the chamber exposure zone, which is maintained at a temperature of 35 +/- 2°C (95 +/ - 3°F) and a relative humidity of at least 95%, creating a fog that has a condensate collection rate of 1.0 to2.0 ml/hr per 80 m^2 of horizontal collection area. To maintain these conditions, the chamber is heated and best maintained with a wet bottom condition in the exposure zone. The equipment needed to maintain these test conditions will meet the requirements described in Table II and be made such that all component parts that come in contact with the exposure zone, water, or solutions are made of, or coated with, inert materials. Typical test chamber components and operational connections are illustrated in Fig.1.

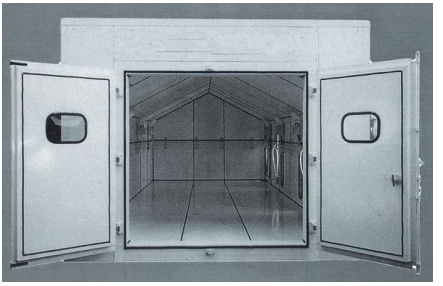


Fig. 3. Typical large-size drive-in-type corrosion test chamber.

ASTM D1735 — Standard Practice for Testing Water Resistance of Coatings Using Water Fog Apparatus

The ASTM D1735 Standard uses a standard fog-generating chamber as used for the ASTM B117 Standard. The primary variations are the chamber temperature, which is held at 38°C (100°F) and the elimination of the corrosive salt (elec-

trolyte). The fog is created by atomizing ASTM D1193 Type IV water without any salt whatsoever. This test method is used to gauge the life expectancy of coating systems by measuring their resistance to water penetration.

ASTM D2247 — Standard Practice for Testing Water Resistance of Coatings in 100% Relative Humidity

The ASTM D2247 Standard is used to investigate how a coating resists water, which can help predict its useful life. This is generally a pass/fail test; however, the time to failure and degree of failure can be measured. A coating system typically passes if there is either no sign of water-related failure after the specified test period or less than an established specified amount of failure.

For the ASTM B2247 Standard the ASTM D1193 Type IV water is placed in the bottom of the exposure zone to a depth of 6 to 8 in. and then heated. The area of the exposure zone above the water is not heated directly in order to cause condensation on the test pieces. The water is introduced into the chamber before the test pieces and maintained at a temperature approximately 5 to 10°C (10–20°F) higher than the temperature of the vapor above it. The major variation in the chamber is the elimination of the fogging tower. The 100% humidity results from the vaporization of the heated water in the bottom of the chamber and/or having heated humidified air pumped through the water. The humidifying tower is used when the option of having air pumped through the heated water is chosen. The exposure zone is maintained at 38° ± 2°C (100° ±4°F) and 100% relative humidity. This test method is performed in water-jacketed chambers (see Fig.2) with the 6 to 8 in. of water mentioned above in the bottom of the exposure zone and the water jacket filled to 12 in. above the bottom to ensure that the immersion heaters are submerged. It can also be run in larger chambers, such as walk-in or drive-in size units (see Fig. 3), equipped with heated water tanks in the exposure zone to generate the required humidity. A primary concern when conducting the ASTM D2247 test is that the chamber be sufficiently insulated. Figure 4 is a schematic of a typical ASTM D2247 humidity test chamber configuration. To ensure that the ASTM D2247 test is being performed consistently, it is recommended that a control test piece with known durability be included in each test run.

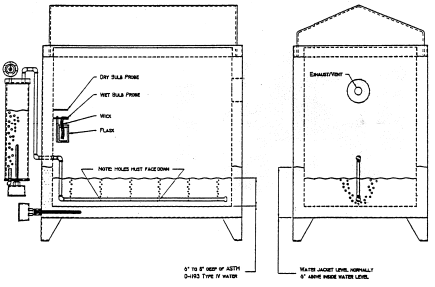


Fig. 4. Humidity test chamber schematic drawing.

ASTM B368 — Standard Test Method for Copper Accelerated Acetic Acid-Salt Spray (Fog) Test (or CASS Test)

The ASTM B368 Standard, originally developed by the National Association for Surface Finishing (NASF), is used primarily in the development of coated metal products, including decorative coatings, which will be exposed to severe service and more corrosive environments and also to evaluate the performance and protective properties of more durable coatings which would not be affected by

the typical ASTM B117 type salt fog test. This test method is particularly applicable to the evaluation of the performance of decorative copper/nickel/chromium or nickel/chromium coatings on steel, zinc alloys, aluminum alloys, anodized aluminum and plastics designed for severe service. This test meets the challenges of providing a simulated service evaluation to test product specifications in research and development and provide manufacturing controls for environmental changes caused by human intervention. The B368 Standard is a variation on the basic ASTM B117 Salt Spray (Fog) Test. For this variation, adjust the pH of the 5% salt solution into the range 6.0 to 7.0, and then add 0.25 grams of reagent-grade copper chloride per liter of salt solution. The test is not considered to start until the temperature within the exposure zone has reached 49°C +/- 1°C (120° +/- 2-°F) and is then run continuously for 6 to 170 hours as agreed upon between purchaser and seller prior to the start of the test. It is required that the temperature within the exposure zone be checked twice a day only on regular business days when the chamber may be periodically opened for "short" durations (preferably less than 5 min) to work with test pieces and/or replenish solution.

Another variation from the standard salt spray (fog) test is in the mandatory verification for consistency of test exposure conditions. In ASTM B using "Nickel Mass Loss Coupons" rather than steel (as used in the B117 Practice, Section X3 [nonmandatory]). The B368 Standard uses corrosion test chamber apparatus that meets the requirements for the ASTM B117 Standard and will withstand the increased temperature and stronger electrolyte solution used for this test.



Fig. 5. Typical cyclic-type corrosion test chamber with PLC control for automatic operation of changeable atmospheres, temperatures, and durations of various steps in cycle.

ASTM G85— Standard Practice for Modified Salt Spray (Fog) Testing

Five variations of this standard have been developed to accommodate its use to different purposes. The variation that is used by interested parties in any situation must be agreed upon prior to the start of testing. Following are brief explanations of each of the five individual test variations:

Annex 1—Acetic-Salt Spray (Fog) Testing

The Acetic Acid-Salt Spray (Fog) Test is used to test ferrous and nonferrous metals and inorganic and organic coatings for resistance to additional and more corrosive environments than the ASTM B117 Standard. This test is designed as a continuous exposure test without interruptions. It uses a 5 ±1 part by mass solution of sodium chloride in 95 parts of ASTM D1193 Type IV water. The pH of the solution is adjusted with the addition of glacial acetic acid to be within the range of 3.1 to 3.3. This solution is then atomized into the exposure zone to

create a fog that has a condensate collection rate of 1.0 to2.0 ml/hr per 80 m^2 of horizontal collection area while the temperature of the exposure zone is being held at a constant 35° +/- 2°C (95° +/- 3°F). This variation is particularly useful in research when evaluating the effect of altering the parameters of an electroplating process or evaluating the quality of the process on decorative chromium plating. It is used primarily for steel and zinc die-casting substrates. It should be noted by users that even though this test is utilized as a more severe alternative to the ASTM B117 Salt Spray (Fog) test, the type of actual corrosion produced is not necessarily of a "like-kind" to that resulting from the B117 test on the same test specimen material.

Annex 2—Cyclic Acidified Salt Fog Test

For this variation the pH of the test solution is adjusted to a range of 2.8 to 3.0, the exposure zone temperature is raised to 49°C (120°F), and the humidifying tower temperature is raised to 57°C (135°F); however, the most significant change is the wet and dry cyclic nature of the test. This change in the test requires that the test chamber be equipped with apparatus to produce differing atmospheres for the various steps in the test cycle and timing apparatus that will cause the atmosphere within the chamber to vary as follows. Every 6 hours, the test pieces will be exposed to 3/4 of an hour spray of atomized salt solution, then a 2-hr dry period, during which the chamber is purged of humidity. The final cycle is 1 ¾ hours of high humidity as described by the temperature and collection rates specified. Adding the cycles to this test increases its effectiveness if evaluating how products perform in a continuously changing environment.

Annex 3—Acidified Synthetic Sea Water (Fog) Test

The addition of 42 g of synthetic sea salt and 10 ml of glacial acetic acid per liter of solution, in this variation, is to increase its usefulness for production control of exfoliation-resistant heat treatments used in producing 2000, 5000, and 7000 series aluminum alloys. The pH is adjusted into the range 2.8 to 3.0 and the test is performed at a temperature of 49°C (120°F). When using this variation to test organic coatings on metallic substrates the test is performed at a pre-selected temperature in the range 24 to 35°C (75–95°F). The collection rate specification for fog cycles of this test is unchanged from the B117 Standard at 1 to 2 ml/hr of operation; however, 2-hr cycles are used throughout the test period. Because of the cyclic nature of this test, prior to starting the test a separate 16-hour salt fog test is necessary to establish and verify proper condensate collection rates. The test chamber must be equipped with apparatus and controls that will cycle the exposure zone repeatedly through a ½ -hr spray step then 1 ½ hours of soak time at 98% relative humidity (see Fig. 5).

Annex 4—Salt/SO_2 Spray (Fog) Test

In this test either a sodium chloride or synthetic sea salt solution can be used. The determination of which will be used is dependent on the product being tested and the requirements of the interested parties. A primary difference in this test procedure is the addition of sulfur dioxide (SO_2) to the exposure zone using a predetermined cycle. The requirement of the ASTM G85, Annex 4 standard is that all the cycles during the test period be equal in length. Introducing SO_2 into the exposure zone on a periodic basis requires additional apparatus. The chamber can

be equipped with a device that will disburse the SO_2 evenly throughout the chamber without directly impinging on any test pieces. The SO_2 supply source attached to the chamber must have a regulator, flow meter, and timer to allow for accurate introduction of SO_2 in accordance with any set cycle. It is imperative to address all safety issues: equipment, personnel, apparatus, and procedures prior to testing with SO_2, since it is a very hazardous highly toxic gas. Note that the primary changes to the chamber are to allow for the correct introduction of the SO_2. All parts of the chamber that come into contact with the SO_2 must be made of materials that are inert to SO_2 gas.

Annex 5—Dilute Electrolyte Cyclic Fog/Dry Test

For this test the electrolyte solution contains 0.05% sodium chloride and 0.35% ammonium sulfate in 0.60% by mass of ASTM D1193 Type IV water. This solution is much more dilute than the standard salt spray (fog) test and is run using 2-hr cycle times comprised of 1-hr fog at ambient 24°C ±3°C and relative humidity below 75%, followed by 1-hr dry off at 35°C. That is, the test pieces are exposed to 1 hour of spray fog at controlled "room" temperature, then 1 hour dry-off time at 35°C (95°F). The collected condensate shall have a pH within the range of 5.0 to 5.4. Because of the cyclic nature of this test, a separate 16-hr salt fog test is necessary to establish and verify proper condensate collection rates prior to starting the cyclic test. Because of the differences in humidity in this test method and the cyclic nature of the test, the chamber will need to have a separate air line and valve to allow the atomizing air to bypass the humidifying tower and timing apparatus to control the cycle times, temperature changes, spray, and airflow. This test is a modification of the British Rail "Prohesion" test developed in the 1960s for the industrial maintenance coatings industry. This test is best suited for the testing of paints on steel.



Fig. 6. Custom-sized, computer-controlled corrosion test chamber for cyclic testing.

ASTM G87—Conducting Moist SO_2 Tests

The ASTM G87 standard is an adaptation of the sulfur dioxide tests used in Europe and is particularly effective in producing easily visible corrosion on metals as would be observed in an industrial or marine environment. This test requires 2 ±0.2 L (122 in3 ±12 in3) Type IV water in the bottom of the test chamber and does not use a fogging apparatus. The apparatus used to generate the necessary humidity is the same used in the ASTM D2247 test. The gas introduction apparatus is the same as used in the ASTM G85 Annex 4 test. Once the test pieces are placed in the chamber 0.2, 1, or 2 L (12, 61, or 122 in3 ±12 in3) of sulfur dioxide (SO_2) with a purity of 99.9% (liquid phase) is introduced. Then the temperature of the chamber is raised to 40 ±°C (104 ±5.4°F) in 1 ½ hours and remains at this level for the duration of the test cycle. One test cycle is 24 hours. A test can

Table III. Typical Uses and Products Tested Under Various Test Standards

Use	*Product*	*ASTM Standard*
Research and Development, Quality Assurance, Marine Exposure Environments	Inorganic and organic coatings, aluminum, and other metals	B 117 Operating Salt Spray (Fog) Apparatus
Research Studies, Quality Assurance	Decorative chromium plate and materials resistant to long-term B 17 exposure as well as exfoliation of aluminum alloys	G 85—Annex 1 Acetic Acid Salt Spray
Research and Development, Quality Assurance	Electroplating and cadmium plating on steel or zinc die castings as well as exfoliation of aluminum alloys	G 85—Annex 2 Cyclic Acidified Salt Spray
Quality Assurance, Development of heat treatment perimeters, and simulation of marine or near-shore environments or applications	Exfoliation-resistant heat treatments on 2000, 5000, and 7000 series aluminum alloys and materials, coatings, or equipment utilized in marine-type environments	G 85—Annex 3 Acidified Synthetic Sea Water
Research and Development, Quality Assurance, and simulation of industrial, marine, or near-shore environments or applications	Decorative electroplating and materials, coatings, or equipment utilized in industrial, aerospace, and marine-type environments where corrosive pollutants, exhaust gases, or acid rain effects may be present	G 85—Annex 4 Salt Spray/SO_2
Research and Development, Quality Assurance	Paints on steel	G 85—Annex 5 Dilute Electrolyte Cyclic Fog/Dry
Specification Acceptance, Service Evaluation, and Quality Assurance for severe service conditions	Anodized aluminum, decorative electroplating, design for severe service	B 368 Copper Accelerated Acetic Acid
Evaluating Service Life for water-resistance coatings	Coatings, substrate treatments, and coating systems	D 1735 Water Fog Humidity
Evaluating contamination of substrate, inadequate surface preparation, and deficiencies in coatings	Coating systems	D 2247 100% Condensing Humidity
Research and Development, Quality Assurance	Metals, coatings, and equipment used in industrial and marine-type environments where corrosive pollutants, exhaust gases, or acid rain effects may be present	G 87 Moist SO_2

be run for as many cycles as are agreed upon between the purchaser and seller; however, the SO_2 and water must be changed for each 24-hr cycle. The 24-hr test cycles are executed in one of the following ways: 1. Continuous – change of water and SO_2 with as little disturbance as possible 2. Alternating Exposure – 8-hr exposure; drying in ambient for 16 hours with 20–30°C (68–86°F) and 75% relative humidity The variations differing from the B117 practice are that for this test method all test pieces be placed on the same horizontal plane and all test pieces in a given test run be of similar reactivity. **NOTE:** While adding corrosive gases may expedite degradation of the protective properties of the coating on the steel

substrate, the purpose of the test must be kept in mind. This gas introduction may be acceptable when testing materials used in an environment that may include similar acids, such as roofing materials, that could be exposed to acid rain.

EQUIPMENT

With continued developments in accelerated corrosion testing, basic changes and improvements have been made to the equipment. The basic requirements for accelerated corrosion testing equipment are listed on Table II under the ASTM B117 Standard. The adjustments required for each variation on the accelerated corrosion-testing model are then listed next to the appropriate ASTM standard. Typical applications are listed in Table III. Along with the basic operating requirements, improvements have been made in the materials used in the construction of the chambers, the hardware and software controls, and data recording capabilities. Programmable logic controller (PLC) systems provide for increasingly sophisticated data acquisition, manipulation, and display (see Fig. 6). As a result, both test chambers with manually entered settings for automatic operation, and test chambers with increasingly sophisticated programmable controls for automatic temperature changes; varying levels of controlled humidity; automatic changes for different environmental atmosphere cycles; and automatic data logging/accumulation, record keeping, and output with graphic data display, are available through a variety of suppliers. These comprehensive capabilities allow each laboratory to find accelerated corrosion testing equipment that meets their specific needs.

TEST PIECE PREPARATION/CLEANING

In order for any of the above accelerated corrosion tests to obtain comparable results, all test pieces must start the test in a similar condition without contaminants present on the surface of interest. The ASTM test standards discussed above indicate reference standards to be used for the preparation and cleaning of test pieces. Particular attention must be paid to the wide variety of materials being cleaned and recognition of differing specialized material and coating operations. ASTM test standards state that the cleaning method is to be dependent on the product being cleaned and then refer to ASTM D609 Standard Practice for Preparation of Cold-Rolled Steel Panels for Testing Paint, Varnish, Conversion Coatings and Related Coating Products where required. This standard describes five cleaning and preparation methods. The preparation methods described are: Procedure A—Conversion Coating; Procedure B—Vapor Degreasing; Procedure C—Solvent Brushing; Procedure D—Solvent Wiping; and Procedure E—Alkaline Cleaning. Procedure A (Conversion Coating) addresses the issue of ensuring that the test piece be protected from rusting between the manufacturing process and the corrosion test. Procedure B (Vapor Degreasing) exposes the test pieces to solvent vapors within controlled conditions to remove contaminants. This procedure is currently discouraged for environmental reasons. Procedures C (Solvent Brushing) and D (Solvent Wiping) both use Mineral Spirits as the cleaning agent. Procedure E (Alkaline Cleaning) describes methods for cleaning with an alkaline cleaning agent that is appropriate for the product. The cleaning method and cleaning agent chosen for any test run should be as agreed upon between the purchaser and seller. ASTM D609 refers to the water break test as a method of checking test pieces for contaminants. The procedure is simply to

run a small amount of water over the surface of the test piece. If it is free of oils and contaminants the water will run over it in a sheet and off in one fall with no breaks. Finally, ASTM D609 discusses the handling of cleaned test pieces and storage in paper impregnated with volatile corrosion inhibitor (VCI) if the test pieces are not to be run immediately after cleaning.

EVALUATION OF RESULTS

Some primary ASTM Standards that have been developed to assist in the evaluation of corrosion test results are: ASTM D1654—Standard Test Method for Evaluation of Painted or Coated Specimen Subjected to Corrosive Environments; ASTM D610—Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surfaces; ASTM D714—Standard Test Method for Evaluating Degree of Blistering of Paints; and ASTM B537—Standard Practice for Rating of Electroplated Panels Subjected to Atmospheric Exposure. Irrespective of the title wording, the text of ASTM B537 states that it is also used to evaluate panels subjected to laboratory accelerated corrosion tests. Other standards are also available for evaluation of specific materials and finishes.

ASTM D1654 is used for the evaluation of substrates, pretreatments, coating systems, or a combination thereof. This standard is also used when the coating has been scribed prior to exposure to the corrosive environment. ASTM D1654 recommends a straight-shank tungsten carbide tip or equivalent scribing tool to produce a cut through the coating to the substrate of the test piece. The scribe serves as a deliberate failure of the coating system prior to corrosion testing. Once the test piece has been through the selected accelerated corrosion test it is then cleaned by rinsing with a gentle stream of water at 45°C (110°F). Loose coating is then removed using compressed air to blow it off or a scraper to scrape it off. The "creepback" (perpendicular distance of failure from the scribe line) of the coating is measured at uniform intervals and the rating system described in the standard applied. ASTM D610 provides a series of photographic reference standards that demonstrate degrees of rust on the surface of a test piece. The test pieces are first gently cleaned then the amount of rust observed is reported from comparison to the photographic standards and the additional use of established standardized terminology from the test standard. It is important to compare only rust and not surfaces stained by rust. ASTM D714 is used to evaluate coating adhesion by observing the amount of blistering that has occurred. The test pieces are first gently cleaned then compared to the series of included photographic references and the additional use of the appropriate "standardized" terminology indicated in the test standard. They are graded first by the size of the blisters that appear on the surface and then the number of blisters that appear per unit area.

CONCLUSION

The corrosion tests discussed in this article are some of the most utilized tests of this type. They also demonstrate the diversity of the tests and some of the advancements in accelerated corrosion testing and complexity of the subject. They also provide a solid basis for evaluating the performance of a wide variety of products and materials. These standards have been developed, evolved and refined through cooperative efforts of experts and interested parties from: ASTM International, industry, government, and other trade organizations worldwide.

COATING THICKNESS MEASUREMENT

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A variety of recognized methods can be used to determine the thickness of organic coatings. The method employed in a specific situation is most often determined by the type of coating and substrate, the thickness range of the coating, the size and shape of the part, and economics. Commonly used measuring techniques are (1) nondestructive dry-film methods such as magnetic, eddy current,ultrasonic, or micrometer measurement; (2) destructive dry-film methods such as cross sectioning or gravimetric (mass) measurement; and (3) wet-film measurement.

MAGNETIC

The magnetic technique is used to nondestructively measure the thickness of nonmagnetic coatings on ferrous substrates. Most coatings on steel and iron are measured this way. Gauges use one of two principles of operation: magnetic pull-off or magnetic/electromagnetic induction.

Magnetic Pull-Off

These gauges consist of a permanent magnet, a calibrated spring, and a graduated scale. The attractive force between the magnet and the magnetized steel pulls the two together. As the coating thickness separating the two increases, it becomes easier to pull the magnet away. Coating thickness is determined by measuring this pull-off force. The weaker the force, the thicker the coating. Testing is sensitive to surface roughness, curvature, substrate thickness, and alloy content.

Magnetic pull-off gauges are rugged, simple, inexpensive, portable, and usually do not require any calibration adjustment. They are the instruments of choice when a low number of readings per day is required. Pull-off gauges are typically classified as either pencil-type or roll-back dial models.

Pencil-type models mount a magnet to a helical spring (see Fig. 1). The spring acts perpendicularly to the surface to pull the magnet off. Most have large magnets and are designed to work in only one or two positions, which partially compensate for gravity. A more accurate version is available, which has a tiny, precise magnet to measure on small, hot, or hard-to-reach surfaces. A triple indicator ensures accurate measurements when the gauge is pointed

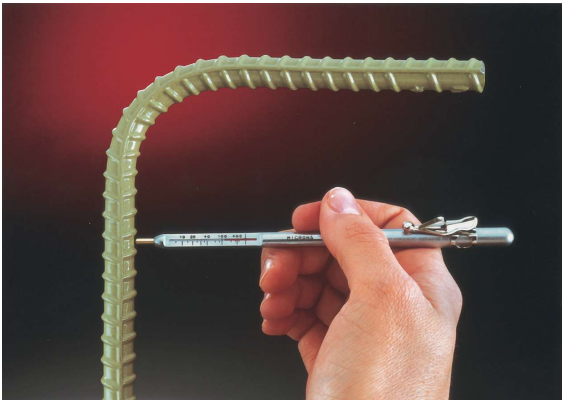


Fig.1 Pencil-type magnetic pull-off thickness gauge.

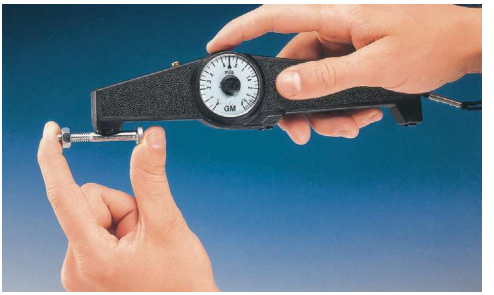


Fig. 2 Roll-back dial magnetic pull-off thickness gauge

down, up, or horizontally with a tolerance of ±10%.

Roll-back dial models are the most common form of magnetic pull-off gauge (see Fig. 2). A magnet is attached to one end of a pivoting balanced arm. This assembly is connected to a calibrated hairspring. By rotating the dial with a finger, the spring increases the force on the magnet and pulls it from the surface. These gauges are easy to use and have a balanced arm, which allows them to work in any position, independent of gravity. They are safe inexplosive environments and are commonly used by painting contractors and small powder coating operations. Typical tolerance is ±5%.

Magnetic and Electromagnetic Induction

These electronic instruments measure the change in magnetic flux density at the surface of a magnetic probe as it is brought near steel. The magnitude of the flux density at the probe surface is directly related to the distance from the steel substrate. By measuring flux density the coating thickness can be determined.

Magnetic induction instruments use a permanent magnet as the source of the magnetic field. A Hall-effect generator or magneto resistor is used to sense the magnetic flux density at a pole of the magnet. Electromagnetic induction instruments use an alternating magnetic field. A soft, ferro magnetic rod wound with a coil of fine wire is used to produce a magnetic field. A second coil of wire is used to detect changes in magnetic flux.

Electronic magnetic gauges come in all shapes and sizes (see Fig.3). They commonly use a constant pressure probe to remove operator influence and quickly display results on a liquid crystal display (LCD). Optionally, they can store measurement results, perform instant analysis of readings on their displays, and output results to a printer or computer for further examination. Typical tolerance is ±1%.

The manufacturer's instructions should be carefully followed for most accurate results. Standard methods for the application and performance of this test are available in ASTM D 1400, ISO 2360, and ISO 2808.

EDDY CURRENT

This technique is used to nondestructively measure the thickness of nonconductive coatings on nonferrous metal substrates. Paint on aluminum and acrylic on copper are typical examples. Eddy current inspection is based on the principles of electromagnetic induction and, therefore, has many similarities to the electromagnetic induction test method. A coil of fine wire conducting a high-frequency alternating current (above 1 MHz) is used to set up an alternating magnetic field at the surface of the instrument's probe. When the probe is brought near a conductive surface, the alternating magnetic field will set up eddy currents on the surface. The magnitude of the eddy currents is related to substrate characteristics and the distance,or coating thickness,



Fig. 3 Electronic magnetic induction thickness gauges.

from the probe. The eddy currents create their own opposing electromagnetic field that can be sensed by the exciting coil or by a second, adjacent coil.

Eddy current coating thickness gauges look and operate like electronic magnetic gauges. They are used to measure coating thickness over all metals but steel and iron. They commonly use a constant pressure probe and display results on an LCD. Optionally, they can store measurement results or perform instant analysis of readings and output to a printer or computer for further examination. The typical tolerance is ±1%.Testing is sensitive to surface roughness, curvature, substrate thickness, type of metal substrate, and distance from an edge.

The gauge manufacturer\'s instructions should be carefully followed for the most accurate results. Standard methods for the application and performance of this test are available in ASTM B 244 and ASTM D 1400.It is now common for gauges to incorporate both magnetic and eddy current principles into one unit. Some simplify the task of measuring most coatings over any metal by switching automatically from one principle of operation to the other, depending upon the substrate. These combination units are popular with painters and powder coaters.

ULTRASONIC

The ultrasonic pulse-echo technique is used to nondestructively measure the thickness of various coatings on nonmetal substrates. Applications include paint on plastic, lacquer on wood, and epoxy on concrete.

The probe of the instrument contains an ultrasonic transducer that sends a pulse through the coating (see Fig. 4). The pulse reflects back from the substrate to the transducer and is converted into a high-frequency electrical signal. The echo wave form is then digitized and analyzed to determine coating thickness. In some circumstances, individual layers in a multilayer system can be measured.

Couplant is typically used between the probe and the surface to be measured. Typical tolerance is ±3%. The manufacturer's instructions should be carefully followed for most accurate results. Standard methods for the application and performance of this test are available in ASTM D 6132.

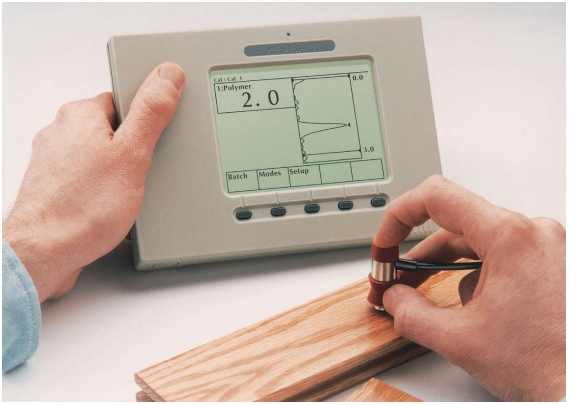


Fig. 4. Ultrasonic gauge can measure the thickness of coatings on nonmetallic substrates.

MICROMETER

Micrometers are sometimes used to check coating thickness. They have the advantage of measuring any coating/substrate combination but the disadvantage of requiring access to the bare substrate. The requirement to touch both the surface of the coating and the under side of the substrate can be limiting, and they are often not sensitive enough to measure thin coatings. Two measurements must be taken: one with the coating in place and the other without. The difference between the two readings, the height variation, is taken to be the coating thickness. On rough surfaces, micrometers measure coating thickness above the highest peak.

CROSS SECTIONING

Coating thickness can be measured by cutting the coated part and viewing the cut microscopically. It can also be determined by making a geometrically designed incision through the dry-film coating and viewing it cross sectionally with a scaled microscope. A special cutting tool is used to make a small, precise V-groove through the coating and into the substrate. Gauges are available that come complete with cutting tips and illuminated scaled magnifier.

While the principles of this destructive method are easy to understand, there are opportunities for measuring error. It takes skill to prepare the sample and interpret the results. Adjusting the measurement reticule to a jagged or indistinct interface is a source of inaccuracy, particularly between different operators; however, direct observation of these conditions is sometimes informative. This method is used when inexpensive, nondestructive methods are not possible, or as a way of confirming nondestructive results. ASTM D 4138 outlines a standard method for this measurement system.

GRAVIMETRIC

By measuring the mass and area of the coating, thickness can be determined. The simplest method is to weigh the part before and after coating. Once the mass and area have been determined, the thickness is calculated using the following equation:

$$T = (m \times 10)/(A \times d)$$

where T is the thickness in micrometers, m is the mass of the coating in milligrams, A is the area tested in square centimeters, and d is the density in grams per cu-



Fig. 5. Typical coating thickness calibration standards.

bic centimeter.

It is difficult to relate the mass of the coating to thickness when the substrate is rough or the coating uneven. Laboratories are best equipped to handle this time-consuming and often destructive method.

WET-FILM MEASUREMENT

Wet-film thickness gauges help determine how much material to apply wet to achieve a specified dry-film thickness provided that the percent of solids by volume is known. They measure all types of wet organic coatings, such as paint, varnish, and lacquer, on flat or curved smooth surfaces.

Measuring wet-film thickness during application identifies the need for immediate correction and adjustment by the applicator. Correction of the film after it has dried or chemically cured requires costly extra labor time, may lead to contamination of the film, and may introduce problems of adhesion and integrity of the coating system.

The equations for determining the correct wet-film thickness (WFT), both with and without thinner, are as follows.
Without thinner:

WFT = desired dry film thickness % solids volume

With thinner:

WFT = desired dry-film thickness of solids by volume/[100%] + % of thinner added]

There are four types of gauges: notch, lens, eccentric roller, and needle micrometer. Each has its own unique operating procedure. Notch gauges, also called step or comb gauges, are most common. They are inexpensive field gauges, which can either be thoroughly cleaned after each reading and reused or disposed of. The notch-type, wet-film thickness gauge is a flat aluminum, plastic, or stainless steel plate with calibrated notches on the edge of each face. The gauge is placed squarely and firmly onto the surface to be measured immediately after the coating application and then removed. The wet-film thickness lies between the highest coated notch and the next uncoated notch. Notched gauge measurements are neither accurate nor sensitive, but they are useful in determining approximate wet-film thickness of coatings on articles where size and shape prohibit the use of more precise methods, such as the lens and eccentric roller gauges (refer to ASTM D 1212).

The gauge should be used on smooth surfaces, free from irregularities, and

should be used along the length, not the width, of curved surfaces. Using a wet-film gauge on quick-drying coatings (inorganic zinc, vinyls, etc.) will yield in accurate measurements. ASTM D 4414 outlines a standard method for measurement of wet-film thickness by notch gauges.

THICKNESS STANDARDS

Coating thickness gauges are calibrated to known thickness standards. There are many sources of thickness standards but care must be taken to ensure they are traceable to a national measurement institute such as NIST. It is also important to verify that the standards are at least four times as accurate as the gauge they will be used to calibrate. A regular check against these standards verifies the gauge is operating properly. When readings do not meet the accuracy specification of the gauge, the gauge must be adjusted or repaired and then calibrated again.

TROUBLESHOOTING COMMON (AND SOME NOT-SO-COMMON) PROBLEMS RELATED TO PAINT, POWDER COATINGS, AND SURFACE PREPARATION

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(Editor's note: This section is dedicated to the memory of Ron Joseph, Metal Finishing's long-time organic coatings editor, who passed away in 2011.)

MATCHING HVLP NOZZLE SIZE TO YOUR APPLICATION

Q: *What is the best spray gun and tip to use while spraying Imron 5000 & 6000? I am using an Iwata HVLP with a 1.3 tip, and I'm still having trouble with heavy metallics.*

A: First, you didn't mention the Iwata HVLP model number. The vendor recommends nozzle sizes for each spray gun model. For instance, I went online and reviewed the nozzle sizes for the LPH 2003 HVLP spray gun. If you scroll down their Web page you will find recommended fluid nozzle sizes, given in millimeters and inches. For your particular spray gun you should review the nozzle sizes Iwata has recommended.

The HVLP spray gun might be perfectly adequate, but you might need to play with the fluid flow rate and air atomizing pressure. Invariably, painters use too high a fluid flow rate and the atomizing air can't adequately break up the paint stream. I suggest that you set up your spray gun from scratch. Take a piece of aluminum foil and attach it onto the spray booth wall. Turn the fluid needle, fan control knobs, and the air atomizing control valve all the way closed. Now open the air atomizing control value a quarter turn and do the same with the fluid knob. If no paint emerges from the gun, open the air a little more. Perhaps also open the fluid control knob another quarter turn. Continue opening the air atomizing valve until some paint emerges from the gun orifice. Eventually, a wet round circle of paint will deposit on the foil. At this point, start to open the fan control knob to widen the fan pattern. By opening the air valve, fan control, and fluid control knobs in small increments, you should be able to get a setting that will produce a good-looking paint finish.

This will take time and patience, but the process usually works. If these steps fail, perhaps you need to change to a smaller or larger tip size.

PAINT ODORS AND SPRAY BOOTHS

Q: *I own an upholstery company, and every so often my neighbor spray paints outside. The smell is quite horrible. When I leave my warehouse door open, the odor enters and I must close the door to keep out the obnoxious smell. Are there regulations preventing him from painting outdoors?*

A: Depending on how much paint is used, the painters might need to install a ded-

icated spray booth. While this will not stop the odors, it will force the solvents through an exhaust stack, approximately 30 ft above ground level. This will considerably minimize the odor.

If the painters use very small quantities, such as one quart per day, they might not be required by regulation to install a paint spray booth. Please bear in mind that every state has its own regulations regarding when one is required to install a spray booth. However, you can report the nuisance odors to your local air quality control district. If the inspectors agree that this is a nuisance condition, they can require the painters to desist from painting, or they can ask the painters to do their work after hours when you and others have gone home for the day.

FEDERAL STANDARD COLOR VS. PRODUCT NUMBER

Q: *I often receive blueprints that request the supplier to powder coat per Fed. Std. 595, Color #26231. Can you please explain to me the difference between a Fed. Std. 595 color and a powder coat color number?*

A: Federal standard colors are ones by which the U.S. government specifies its colors. It is a long-standing color standard used by architects, engineers, and others. Colors can be purchased in low-, medium-, and high-gloss ranges. The standard can be applied to any type of paint, alkyd, acrylic, epoxy, polyurethane, or any other resin type. The paint can be liquid or powder. You might like to read more about Fed. Std. 595 at wikipedia.org.

Powder and liquid coatings can be purchased to the Fed. Std. 595b standard, to a manufacturer's unique color range, or to a company's own custom color. For instance, most large corporations, such as Deere & Co., Caterpillar, Coca-Cola, Pepsi, Federal Express, UPS, United Airlines, etc., design their own unique colors. Therefore, the color numbers given by paint manufacturers [suppliers] are unique to that manufacturer. If two or more paint manufacturers make a color for the same corporate customer, the color number might be assigned by the customer. On the other hand, it is equally possible that each paint manufacturer will assign its own number to that color. Generally, custom colors do not carry the same nomenclature as Fed. Std. 595 colors.

ACHIEVING A GOOD-LOOKING AUTOMOTIVE FINISH

Q: *I am trying to paint my car with Rust-Oleum semi-gloss black paint. The label on the can says to mix the paint with mineral spirits. How much should I use to get a good finish?*

A: You should add as little mineral spirits as possible. I suggest that you try spraying some of the paint without adding mineral spirits. If you get too much orange peel then add a small amount and try again. On the one hand you want to avoid getting unacceptable orange peel, but on the other you don't want the paint to be so thin that it runs down the doors and vertical surfaces. The label on the can should tell you the maximum amount that you can add. Bear in mind that your local environmental agency might have VOC regulations that prohibit you from adding any thinners to your paint.

ALTERNATIVES TO CHROMATE-CONTAINING PRETREATMENTS

Q: *I am writing to ask if you have any information about specific plumbing fixture companies that use alternatives to hexavalent chromium in their finishing processes. We are a "green"*

design and consulting firm, and we currently have a client who is interested in using products that have such alternative finishing treatments.

A: I don't have any dealings with plumbing fixture companies, but there are several non-chromate pretreatments that can be used in finishing processes. Chemical companies, including Henkel Surface Technologies and Chemetall, sell non-chromate products. You can find both companies and many others on the Internet. (Be sure to listen to Chemetall's recent webinar on www.metalfinishing.com.)

CORROSION-RESISTANT PRIMER FOR AUTOMOTIVE REFINISHING

Q: *I live in England and I am about to rust proof my 36- year-old Mark 2 Ford (Mercury) Capri. What would be the best primer to use after I have taken it back to bear metal? I can get my hands on red oxide fairly cheaply, but I was wondering what would be the most effective primer? After experiencing a few days under my car with a grinder, I never again wish to repeat this tiresome task.*

A: An inexpensive red oxide primer is not what you want. In my opinion, I would apply an epoxy primer that contains an effective rust-inhibitive pigment, such as zinc chromate. Bear in mind, however, that the use of zinc chromate is being limited in some areas due to its potential toxicity (it is a known carcinogen). Alternatives are strontium chromate, zinc phosphate, and other inhibitors. I suggest you check with your local automotive paint store.

VISCOSITY OF AUTO REFINISHING PAINT

Q: *What is the typical Zahn cup viscosity of paints used in the auto refinishing industry? Would it be possible to coat a sphere evenly on the circumference with paint? Also, what kind of air guns would you use for this process?*

A: The approximate viscosity of solvent-borne automotive paints is in the range of 22–30 seconds on a Zahn No. 2 cup. It should be possible to coat a sphere evenly at this viscosity. If you are located in the U.S., you would probably want to use an HVLP spray gun. Alternatively, if you live outside the U.S. and are not required to meet environmental regulations, you can use a conventional air spray gun; either pressure fed or siphon will work.

SELECTING BETWEEN AIRLESS AND HVLP SPRAY GUNS

Q: *As part of a low-cost basement-refinishing project, I would like to leave the ceiling unfinished but paint it black. I own a 30-gal compressor and will be using a 2 ½ -gallon pressure tank. Which type of spray gun would you suggest for a quick application where coverage is more important than finish: traditional airless or HVLP? Since it is an enclosed area, I am concerned about overspray; ventilation is limited.*

A: You would be better off using a commercially available airless spray gun rather than a high-volume low-pressure (HVLP) spray gun. HOWEVER, I must warn you to please read the instructions and thoroughly familiarize yourself with its operation. Since such guns operate at pressures usually in excess of 1,000 psig, they can be dangerous, and it is critical you understand how to operate it safely. For your situation, the advantage of airless over HVLP is you can get the job done quickly without generating much overspray. HVLP will generate signifi-

cant overspray, and you have already said you do not have good ventilation in the basement.

WHICH PAINT SPRAY APPLICATION METHOD PRODUCES A DRIER COATING?

Q: *I was pondering over two issues: First, if all variables are held constant, and you apply an automotive waterborne paint, which application would produce a drier film (using an ESTA bell) one at 35,000 RPM or one at 55,000 RPM? Second, which application is drier: electrostatic or conventional?*

A: If all variables are held constant, I would imagine that the faster rotational speed of the electrostatic bell would break up the paint into finer particles, leading to a drier finish. As I have never performed this experiment, this is only a guess. I would imagine that the same applies to your second question: whichever method produces smaller particles would produce a drier finish. In this case, I presume the electrostatic spray gun may produce smaller particles, as it can be expected to accelerate evaporation of the solvent compared to a conventional process.

CALCULATING AIR FLOW IN SPRAY BOOTHS

Q: *I have a product that I will be coating with Waterborne Camouflage Aliphatic Polyurethane Chemical Agent Resistant Coating (CARC). I will apply the coating with an HVLP sprayer at approximately 65 psi with a 0.070" tip. I calculated the sprayer volume flow rate to be about 4 SCFM.*

I am trying to calculate air flow needed for my spray booth and the corresponding energy consumption. If my makeup air is coming from outside, I have to condition the air for humidity and temperature prior to entering the paint booth.

I estimate my booth will have a footprint of 100–150 ft2. There will be two operators in the booth: one doing prep; one painting. The product will be hanging on a conveyor at working height.

I have read about cross-draft and down-draft booths with velocity requirements of 100 ft/min and 50 ft/min, respectively. Would one flow rate be preferred over the other for waterborne CARC? What is the main difference between the two flow rates? To calculate the volume flow rate needed, do I multiply the velocity spec by the area of the filter area? How do I know how much filter area I need? Can I bring make-up air into the booth from the main building in which the spray booth is located? Do I draw the make-up air into the booth with my exhaust fan or push it in with another fan? If I do have to bring in make-up air from outside, do you know a reputable company that manufactures efficient equipment for controlling the temperature and humidity?

A: The air flow rate inside the booth is independent of the spray gun, its pressure, air throughput, etc. According to the National Fire Protection Association (NFPA) Bulletin 33, you need to move air through the booth at approximately 100 ft/min. You can calculate this by using the cross-sectional area of the booth. Therefore, if the width times the height of the spray booth equals 80 ft2 you would need an air flow rate of 8,000 ft3/min.

If you wish to lower this, you need to calculate the lower explosive limit (LEL) of the WD-CARC, but this is not a simple calculation. With this information, you then need to calculate the air velocity that will maintain the concentration of solvents at 25% LEL plus a sufficient safety factor. Suppose you were to find that for

the amount of WD-CARC you intend to use, the air velocity would only need to be 20 ft/min to achieve 25% LEL, then the velocity would be so low that all the overspray would fall onto the floor and not be carried to the filters.

The smaller the filter area, the higher the velocity of air that passes through the filters. This then increases the filter resistance, and you will need to purchase a stronger fan to pull the air through. On the other hand, the larger the filter area, the more efficiently the filters will be able to capture the overspray. Bear in mind, the spray booth is not only there to withdraw the VOCs, but almost equally important is the filters' ability to capture the sticky, messy paint particles. For a nice clean paint job, you would like the overspray to be quickly carried to the filters; otherwise, they can deposit on freshly painted surfaces and result in dry spray.

You most certainly can bring air into the booth from the main building, but you must exhaust the air to the outside. You can pull it into the booth with a single exhaust fan or push it in with an air make-up fan, whichever you prefer.

MEASURING SPRAY BOOTH AIR VELOCITY

Q: *I need to confirm that our spray booth meets OSHA requirements of 100 fpm per 29 CFR 1910.107. Where do you take the measurements in a large spray painting booth (25 ft wide x 15 ft high x 60 ft deep); at the face of the booth, midway inside the booth or at the open end?*

A: When I measure booth velocity, I stand a few feet from the filters and measure in various locations so that I can calculate an average. You will find that as you get close to the side walls the velocity will usually be close to zero. Therefore, I don't stand within 3 ft from the walls. If you have poor seals in the double doors at the entrance of the booth, you will find that there is a spike in air velocity in the center of the booth. Therefore, try to avoid measuring air flow along the centerline between the doors.

My method measures the air flow at the points where the painter stands, which is, after all, the intention of the regulation. On the other hand, you can measure the velocity directly in front of each filter and then average your readings. Multiply this by the area of all the filters to get the volumetric flow rate (CFM) passing through the booth. Since your filter plenum is probably narrower than the width of the booth, you can now divide the volumetric flow rate by the cross-sectional area of the booth (in your case 25 ft W x 15 ft H) to arrive at the average velocity across the booth. This velocity will usually be considerably higher than my measurement, because air often travels along the ceiling of the booth and not where the painter stands.

As you probably know, 29 CFR 1910.107 provides Table G10 that lists the air velocities for different situations. However, for a typical USCG side-draft spray booth, 100 ft/min is a good number to work with.

AIRFLOW RATES FOR DOWN-DRAFT SPRAY BOOTHS

Q: *I have a project where an existing down-draft spray booth 54ft (L) x 19.3ft (W) x 16ft (H) (with exhaust pit) is used to spray helicopters. It has an airflow rate of 33,000 CFM and provides a down-draft velocity of approx 32 fpm. I have been told that the velocity should be 100 fpm. In reviewing NFPA and industrial ventilation standards, I have found little information about reduced flow in down-draft booths. It appears that the airflow meets the LEL.*

A: My friend and colleague Rich Thelen of Global Finishing Systems has kindly agreed to answer this question..."Spray booth velocities are not cited in NFPA-33. They are vestigial requirements from US 29 CFR 1910.107 (OSHA) that list velocities in certain circumstances, such as electrostatic painting or other painting. Some of these standards have worked their way into other codes in various fashions. The U.S. Military Guides (UFC-3-410) list different velocities for different spray techniques, including HVLP, electrostatic and airless.

OSHA has deferred to NFPA-33 in the design of spray booths and has published its interpretation online at http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=INTERPRETATIONS&p_id=21875

OSHA considers the use of velocities other than those listed in 1910.107 as "de minimis" violations. "De minimis" violations of standards that have no direct or immediate relationship to safety and health are not included in citations, but the velocities must conform to NFPA-33.

The focus for air velocity is on NFPA-33, which simply states that the airflow shall be sufficient to keep the concentrations of solvents below 25% of the Lower Flammable Limit (LFL). NFPA is concerned with fire protection, whereas OSHA is concerned with human health and safety. Jointly, they cover health, safety and fire issues, and both agree that NFPA-33 is an acceptable rule. So much for legal issues!

"A spray booth must also remove overspray in a manner that gives a good paint finish, while at the same time providing high transfer efficiency. These are production issues that must be addressed by the owner. Regulations will not guarantee a good finish! As spray booth manufacturers, we recommend airflows of 75-125 fpm in cross-draft paint booths and 40-50 fpm in down-draft booths. These velocities consider cross-sections that are normal to the booth airflow. We have found that these airflow velocities are well above the 25% LFL requirement and they yield good paint jobs.

"Velocities below these numbers may also yield good paint jobs, but generally lower velocities are more likely to cause the airflow in the spray booth to stratify and lead to painting (and heating) problems. This happens particularly in large spray rooms. Stratification in downdraft booths occurs at lower velocities than in cross-draft booths. Because the direction of overspray particles is downward, and gravity contributes to particulate removal, down-draft booths are more efficient at removing overspray at low velocities than cross-draft booths. It can be costly to remedy stratification, because changing the exhaust and supply fans is a major project."

REDUCING PAINT DEFECTS—AIRLESS SPRAY GUNS

Q: *Please give me advice about reducing paint overspray while using a fast-dry paint and an airless spray gun.*

A: The only method of which I am aware for reducing paint overspray while using an airless spray gun is to lower the hydraulic pressure. However, if you lower the pressure too much you will not get "tails" and you will not be happy with the finish. If your painter stands closer to the surface he is painting, then he might be able to lower the pressure sufficiently to make a difference.

CAN I ELIMINATE THE EPOXY PRIMER WHEN APPLYING CARC?

Q: *I am curious to know if it is always necessary to utilize an epoxy primer prior to applying [chemical agent resistant coatings] CARC? Would a substrate, such as fiberglass, be able to skip the primer and still meet the military specifications?*

A: I do believe it is possible to apply the CARC topcoat directly over fiberglass, especially if you apply sufficient film thickness > 1.8 mils to provide the necessary IR camouflage properties. However, I am not able to give you permission to omit the epoxy primer. For that you will need to get approval or a waiver from the weapons manager of the product you paint. You might even need to first obtain a letter from the Army Research Lab (ARL) advising that the omission of the epoxy is acceptable or necessary for adhesion of the polyurethane CARC to the fiberglass. Address your e-mail to Mr. John Escarsega, jescarse@arl.mil

GROUNDING OPERATOR WHEN USING AN ELECTROSTATIC SPRAY GUN

Q: *What options are available for grounding the operator in a hand-held electrostatic spray gun system?*

A: The handle of all electrostatic hand-held spray guns should be grounded. Therefore, if your painter is experiencing electrostatic shocks, your first approach should be to test that the gun handle is grounded. The best option for a painter is to hold the handle firmly in the palm of his bare, sweaty hand and make good contact with the handle. By wearing gloves the painter isolates himself from the ground and will tend to build up an electrostatic charge. If he does wear a glove, he should cut a hole in the palm, so that he can have physical contact with the handle. Alternatively, one can purchase conductive gloves that are suitable for electrostatic paint application. Additionally, leather-soled shoes are better than rubber soles. I have also heard of painters wearing a grounded waist band, where the band or belt is in direct contact with the painter's skin.

MEASURING DRY FILM THICKNESS ON VEHICLES

Q: *I am wondering if you can help me find the paint thickness specifications for a 2006 Pontiac G6. My car measures between 12–15 mils per panel. I measured two other panels, which ranged from 4–6 mils per panel. I think that, for some reason, the vehicle was painted twice in the factory.*

A: From the film thickness measurement you mentioned, I would agree with your assumption. A film thickness range of 4–6 mils is more realistic. I have never seen published data on the film thickness ranges for individual vehicles. Automotive assembly plants develop their own internal specifications for film thickness and might make this data available to their vendors, but I don't think the film thickness values are generally available to the public.

If you are really diligent (and lucky), you might be able to find similar vehicles in public parking lots or at dealerships. If you get permission from the owner to measure film thickness, you're in luck. After measuring the film thickness on several identical vehicles, you will know for sure if your vehicle's panels were repainted.

VISCOSITY MEASUREMENTS OF THIN COATINGS

Q: *We currently measure the viscosity of our coatings using an S90 #2 Zahn Cup. Typical efflux times for various products range from 13–17 seconds. I understand this is lower than the range typically measured with a #2 Zahn cup. Should we be using a Zahn #1 cup instead? Note: The product is a solvent-borne coating.*

A: A viscosity of 13–17 seconds is so short that a small error in stopping the stop watch has a significant effect on the measurement. If you were to use a smaller diameter orifice, such as the #1 Zahn cup that you suggested, you would lessen the potential error. When you go to a smaller orifice, ensure that toward the end of the measurement the flow of the effluxing paint should not start, stop, start, stop, etc. When almost all the paint has drained from the cup, you should get a clean cut-off of the paint stream.

POLYURETHANE VS. URETHANE

Q: *I am hoping that you will be able to help me with this problem. I am a guitar maker and use polyurethane/standard automotive lacquer for the finish. However, I find this a little soft, plus it is hard to build. Can you suggest an alternative that I can use, but not nitro-cellulose?*

Also, what is the difference between polyurethane and urethane?

A: Polyurethane is probably the best coating I can suggest. I don't know why you find it soft, because it should be extremely mar resistant. Are you sure you are mixing it properly? Also, I don't understand what you mean by "hard to build." You can apply approximately 1 mil (0.001 inches) per application. It occurs to me that perhaps you are applying too many coats too soon, and not allowing the solvents to evaporate. You could consider a hard furniture coating, such as a catalyzed wood lacquer, but I don't know if that is any harder than the polyurethane.
There is no difference between urethane and polyurethane.

SETTING POWDER COATING CONTROLS

Q: *I am having trouble getting our process of powder coating dialed in. Specifically, on perforated panels for our products. These panels are typically made of sheet steel 16–18 gauge thickness. Regardless of the experience of our painters, we seem to continually get a drip that collects at the bottom of the panel. They are typically small but are considered as rejects by our customers.*

Our oven is running at 415°F on a typical day. I have asked our painters to isolate the panels in question to one rack. Parts with differing metal thickness are powder coated on other racks. We are using Tiger Drylac as our powder supplier. Any ideas would be greatly appreciated.

A: I asked my colleague, Mike Cravens, to tackle this one, and here is his reply: "The dripping (or heavy edge coverage on the bottom surfaces) is likely caused by the powder material's gel time characteristics. Powder materials are heat activated. The powder material, once applied, must melt, flow, gel, and polymerize or cure. The typical gel time of a normal powder with a normal cure cycle is 20 seconds. Some materials are formulated with extended gel time to reduce orange peel and eliminate minor outgassing. I must also note that if you are applying the powder on a hot substrate (above the melt temperature of the powder) you may be forcing the powder through two flow stages."

If your panel hangs vertically inside the oven, then as its surface temperature

increases the powder will melt and start to flow. Its viscosity will have dropped considerably. If this were liquid paint we would expect it to sag. After a few more seconds, depending on the powder, the viscosity increases dramatically and flow essentially stops while the powder starts to cure hard. The time it takes until you reach the high viscosity is called the gel time. It is possible that you are using powder with a long gel time and, hence, there is sufficient time for the powder to form drips. Of course, you can consider looking for a powder of the same color and texture that has a shorter gel time, or you can better control the coating film thickness that your painter applies. The thicker the film, the more prevalent the drips.

DETERMINING VOC CONTENT FOR SEMI-VOLATILE COMPOUNDS

Q: *I just ran some paint solids test on our epoxy/amine catalyzed product according to ASTM D2369 "Standard Test Method for Volatile Content of Coatings". The product is a benzyl alcohol containing amine, but essentially no volatile from benzyl alcohol was detected. What do we report to EPA for this compound?*

A: The ASTM test is conducted at 230°F (110°C) for one hour and at that temperature most volatiles evaporate. However, benzyl alcohol has a boiling point of approximately 337°F (205°C) and very little might evaporate from the coating at the 230°F test temperature. The vapor pressure for this compound is approximately 0.11 mm Hg at 25°C.

Many years ago, probably in the late 1970s or early 1980s, the EPA established 0.1 mm Hg as the vapor pressure above which all volatile organic compounds would be considered as "VOCs". The EPA was referring to those volatile organics that participated in smog (ozone) formation. Compounds with a vapor pressure < 0.1 mm Hg were considered to have negligible potential to form smog and were not counted in VOC regulations. On the other hand, some volatile organic compounds, such as acetone, methyl acetate and a few others with vapor pressures > 0.1 mm Hg were considered to be exempt from regulations because they do not participate in the photochemical reactions that lead to smog formation.

EPA no longer implements the 0.1 mm Hg guideline and ASTM D2369 (which forms part of EPA Method 24A) is now the defining test. However, it is worth noting that benzyl alcohol, with a vapor pressure of approximately 0.11 mm Hg, is on the borderline of VOC status. Since its boiling point is considerably higher than the 230°F temperature at which the ASTM test is conducted, very little will evaporate during the one hour test period. Therefore, it is understandable that the lab that conducted the test on your behalf did not detect any significant amount of benzyl alcohol. Bottom line: even though this compound is volatile at higher temperatures, you need only report the portion that evaporates during the ASTM test.

WASH PRIMERS FOR MILITARY SPECS

Q: *I'm not clear on the difference between MIL-C-8514 and DOD-P-15328 wash primers. What are the benefits/drawbacks of each?*

A: The two wash primers look very similar to each other, and I cannot discern a difference unless I spend more time comparing the ingredients and their respective percentages. MIL-C-8514C is intended for aircraft metal, predominantly aluminum alloys, whereas DOD-P-15328 is predominantly used on steels. It is possible that MIL-C-8514C contains less acid to ensure that when it is applied to aluminum one does not have excess un-reacted acid remaining on the surface.

When working for a military contractor, I always recommended that when DOD-P-15328 was applied to aluminum, painters were to dilute the wash primer with alcohol to reduce the acid concentration.

Therefore, my recommendation is as follows: for aluminum surfaces apply MIL-P-8514C; for steel surfaces apply DOD-P-15328. I urge you to call the paint suppliers from whom you purchase the coatings and ask the chemist in the laboratory to provide a recommendation.

CLARIFICATIONS ON SUITABILITY FOR POWDER COATINGS FOR MILITARY APPLICATIONS

Q: *We build communications equipment for the military. Most of this equipment is used in sheltered applications and, thus, is not exposed to the weather. We paint to meet MIL-DTL-14072 Finishes for Ground Based Electronic Equipment. We currently use one part alkyd enamel paints, and two parts epoxy paints. We are interested in adding powder coat paints, but this MIL Spec doesn't reference its use. I have found one MIL Spec on powder coat paint, MIL-PRF-24712. However, I'm unable to find a paper trail that will allow us to use this paint on our products.*

I've read that the military is interested in the use of powder coat paints, and that companies are using powder coat paint for military applications. However, it sounds like you have to get special permission to use it. Can you point me in the right direction?

A: This is a very good and somewhat timely question. Powder coatings are one of (if not the best) coating technologies to protect a vast array of military products. They are tough, extremely durable, can be formulated in all colors and glosses, and are the most regulatory compliant of all industrial coating technologies. The specification you cite, MIL-PRF-24712 was originated in 1989 and revised in 1995. Surprisingly, there are no qualified products recognized by the military agency responsible for this specification.

The specification covers a cornucopia of powder coating chemistries ranging from epoxy, to polyester, acrylic, and polyurethane. It also describes three different classes related to service environment (dry, immersion and immersion with weather exposure) and performance requirements. The military has recognized that MIL-PRF-24712A has become obsolete, and it is diligently working on a major revision. Part of this revision involves separating the immersion service classes from MIL-PRF-24712 and embodying it in MIL-PRF-23236. NAVSEA initiated this change to cover powder coatings used primarily as corrosion-control materials. The new version of MIL-PRF-24712 is expected to be published before the end of the year (2009).

As for whether powder coating technology exists to meet MIL-PRF-24712 and MIL-PRF-23236, the answer is "yes." It is just a matter of an interested powder coating manufacturer submitting appropriate products to the governing military agency for qualification. I can provide contact information of individuals who may be willing to work with you in qualifying powder coating for these specifications.

POWDER COATING MAGNESIUM ALLOYS

Q: *I have a cleaner/phosphate that is supposed to treat magnesium, but how should it be handled as far as dry-off and cure temps? I tried a couple of parts this morning, with a low-gloss clear coat and they came out looking like Desert Storm camouflage. This was cured for 12 minutes, at 360°.*

A: Magnesium alloys are a tricky substrate to powder coat unless you know how to do it. Most magnesium-fabricated products are cast, resulting in a certain degree of porosity on its surface. Cleaning the substrate is a great idea; however, the cleaners/pretreatment can remain harbored in the pores. Indeed, even without cleaning, air resides in the pores. As the powder melts and flows, the cleaners and air escape from the pores. Most powders are curing at this point and can't recover or reseal the holes caused by the volatiles. The result is pinholes, low gloss, and unsightly surface disruptions.

My advice is to continue cleaning as you are doing at present, but run the parts through a relatively high-temperature dry-off before you apply the powder coating. It's preferable to coat the parts very soon after the dry-off, even while they are still warm, so they don't re-absorb ambient moisture. As for dry-off temperature, 400°F for 10 minutes is a good place to start.

You should also be aware that many powder suppliers offer product lines that are better suited for porous substrates such as magnesium. It may be best to use one of these with a well-controlled dry-off process.

MEASURING POWDER COATING DENSITY

Q: *Is there any method, equation, or software program to calculate powder density?*

A: I am aware of two methods used to determine powder density. Both are covered in detail in ASTM D5965–02(2007) Standard Test Methods for Specific Gravity of Coating Powders.

One uses the volume displacement of the powder into a fluid (kerosene or hexane) with a known density. The weight of the powder is known, so the relationship between weight and volume can then be calculated.

This method involves introducing the fluid into a graduated cylinder. The volume and weight of the fluid is recorded. Next, a given weight of powder is mixed into the fluid and the displaced volume is determined. It is essential that you eliminate all air pockets in the mixture to obtain a reasonably accurate measurement. Please be aware that this method doesn't easily account for the surface porosity common with most powder coatings and typically results in a lower-than-true specific gravity. Nonetheless, it can be used as a decent tool to compare powders.

A much more accurate method, based on the Ideal Gas Law, utilizes a gas pyncometer instrument that measures volume of a known weight of powder by gas displacement. These are relatively expensive instruments and are available from a number of commercial instrument suppliers. Each instrument is slightly different—some measure volume; others can measure volume and density. You would have to consult the specific procedure provided by the instrument manufacturer to successfully measure specific gravity of powders.

$$\text{Powder-Specific Gravity} = \frac{\text{Weight of Powder (g)}}{\text{Final Volume} - \text{Original Volume (ml)}}$$

I recommend you use the simpler fluid method, but always run a control sample of know specific gravity along with your samples to be evaluated.

PROBLEMS COATING OVER CERTAIN SUBSTRATES

Q: *We have a problem when we apply metallic silver powder coating over black E-coated automobile truck wheels. During tire assembly an iron rod is used to [seat] the tire. After fixing the tire when the rod is withdrawn from the parts, we could see a heavy scratch mark at the edge of the part. Is it due to compatibility over e-coat.? How can we avoid this? Lastly, is there any need to improve the powder system? Note: My scratch resistance is 3,000 gms and impact resistance is 250 kg-cm.*

A: This sounds like a tough one. First of all, the surface properties of the powder topcoat do not appear to be a function of the compatibility with the e-coat primer. Incompatibility with the e-coat might cause intercoat adhesion issues, but not surface slip problems.

The scratch resistance and surface slip of the powder coating can be improved. Your powder supplier can increase the crosslink density and, thus, the hardness of the powder by using a more functional (containing more chemically reactive groups) resin. They can also increase the surface slip of the coating by incorporating a polytetrafluoroethylene/wax blend into the formula.

Both measures will help. However, I do not think that this will completely eliminate scratching caused by an iron bar. You may not have the ability to influence the manner in which the tires are installed, but using a more forgiving tool may be the best answer. If the tire installer can use a bar that has a softer surface (nylon or PTFE rich) the scratching could be eliminated.

TROUBLESHOOTING PROBLEMS PERTAINING TO OUT-GASSING ON ALUMINUM

Q: *We have been painting these parts for another company. Lately we have had trouble with out-gassing. I think the quality of the aluminum has decreased. We are using Rohm & Haas Midnight Black Wrinkle. Our pretreatment chemicals are from DuBois. We have a five-stage wash. I really think it is the aluminum, since the steel parts painted at the same time are perfect. What are your thoughts?*

A: Indeed, it sounds like your aluminum may be declining in quality. Before you conclude this, you should also take a close look at your own process. Has the pretreatment system changed? Is it in control (i.e., pH, solids, temperatures, etc.)? Are you running your production line at the same speed as before? Are you running the same amount of parts through the finishing system? Is your oven steady and in control?

Out-gassing is most common with cast alloys (aluminum and magnesium) and galvanized substrates. A high level of porosity can spell trouble. If you suspect the aluminum is getting worse, I suggest you take a few parts and preheat them, allow them to cool to just above ambient temperature, then powder coat them. The preheating should expel any entrained volatiles, and the finished part should not exhibit any blisters from out-gassing. If this is the case, then you should get in touch with your part supplier to investigate a change in the quality of their parts.

Alternately, you can also investigate the use of an "out-gassing-forgiving" powder coating, which many powder suppliers offer. These minimize the effect of inconsistent porosity in substrates.

CRITICAL FACTORS AFFECTING WET SCRUBBER PERFORMANCE

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Wet scrubbers are used for the abatement of chemical emissions from process equipment. Many wet scrubbers in operation are achieving less-than-expected emission results and require frequent shutdown due to problems that can be eliminated or reduced with proper design and operation. The goal of this paper is to familiarize the owner/engineer/operator of common design and process errors that lead to undesirable conditions, frequent maintenance, and safety hazards. Design, process and operation suggestions will be provided in order to maximize wet scrubber performance.

The following three topics will be addressed: Causes of poor scrubber operation; design considerations for ease of maintenance and optimum efficiency; and techniques for reduction or elimination of biological growth.

Causes of poor scrubber operation. It is implausible to assume that a scrubber is functioning properly if the pump is on and fan is drawing air. Various items within the scrubber unit and supporting equipment must be checked and maintained after installation and start-up. Even with proper operation and a good checklist, poor design can lead to less-than-desirable operating conditions and downtime. The following items are common causes of reduced efficiency:



Inadequate sump fluid replacement. For scrubbers using overflow or blowdown to maintain fresh solution, the fresh water make-up rate must be adequate to maintain the concentration gradient between the liquid and gas phase. The concentration gradient for a given unit is dependent upon a number of variables—and, if not maintained, the efficiency of a system can drop quickly and significantly. In some cases, if the gradient is lost, contaminants can be stripped from solution. In these cases, the inlet loading of a particular contaminant can be lower than the tested outlet concentration.

As mentioned earlier, two techniques for sump replenishment are overflow and blowdown (the overflow

method being more common and simple to operate with no instrumentation other than a flow meter). Fresh water is added through an adjustable flow meter at a continuous rate, while the sump liquid overflows into the scrubber drain at a predetermined location. In the blowdown method, liquid is forced to drain by the recirculation pump. If blowdown is inadequate, the rate of scaling and algae growth will increase, as will sedimentation. Sump level controls and solenoid valves or flow control valves have to be provided in the recirculation piping to allow fluid to be discharged at a measured rate.

In either method, the make-up water rate must be high enough to compensate for evaporation losses, which can range drastically depending system size and atmospheric conditions. This is the key point for keeping the concentration gradient in check.

Improper pump size. To determine pump size and selection for a given unit, it is necessary to perform hydraulic calculations for the recirculation system. Three parameters affect the required design head of a pump: friction losses through piping and fittings, pumping height, and pressure loss of nozzles. If add-in items, such as basket strainers, are not accounted for in the design of a system, the pump flow rate will suffer, thereby affecting efficiency.

Improper addition of scrubbing liquid. Inadequate addition of scrubbing liquid can significantly reduce performance of scrubbers. If ammonia is being scrubbed and sulfuric acid is the neutralizing agent, outlet readings can be higher than inlet readings if pH is not maintained.

Location of the pH probe. A common error with pH control systems is location of the pH probe versus the location of the chemical supply injection. Locating a pH probe within 12 inches from the chemical injection pipe will not give true indication of the pH of the scrubber liquid. The pH controller and on/off switch for chemical injection will continually chase each other.

Excessive velocity profile considerations. Unfortunately, scrubbers have velocity constraints that play a key role with performance. Once a scrubber is in operation, the cross-sectional area has forever been established. If a unit is designed for 10,000 CFM, and the fan is exhausting 14,000 CFM, the performance and efficiency decreases while the pressure loss increases. Exceeding the design velocity profile of a unit affects mist eliminator performance, absorption, and evaporation losses.

Channeling caused by plugged spray nozzles. Spray nozzles can be an operator's nightmare and the cause of frequent and expensive unplanned shutdowns. Plugging should be expected when using scrubbers that incorporate spray nozzles. When a nozzle plugs, the area of packing directly below is not receiving liquid. This will create an area where no absorption is taking place and, therefore, decreases the efficiency of the scrubber.

Channeling Caused by Poor Air Distribution and Rectangular Housings. In vertical scrubbers, inlets are located 90 degrees from the air direction through the packed tower. The incoming air stream must make an abrupt 90-degree turn into the packing. Very few scrubbers are designed to account for this abrupt turn. (Air

follows the path of least resistance.) Air will continue straight through the inlet to the back wall of the vessel where it is disturbed and will spiral and vortex up through the packed bed section. This channeling creates dead spots within the packed bed. The now channeled air streams will pass through the packed bed at higher velocities below the designed retention time.

Air will also follow the same general undisrupted path through rectangular scrubber housings. Dead spaces are common in rectangular vertical and horizontal scrubber housings. Design for these units must also account for air distribution inefficiencies. Theoretical analyses suggest decreases in performance for units without proper design.

Biological growth. Build-ups of biological growth in packed bed sections and mist eliminators will adversely affect performance of scrubbers. In acid scrubbers, where pH is typically maintained in the 8–9 range, biological growth is a commonality. Without treatment, the growth can create areas of channeling and increase the pressure drop through the scrubber.

DESIGN CONSIDERATIONS FOR EASE OF MAINTENANCE AND OPTIMUM EFFICIENCY

Pumps. Scrubbers should include redundant pumps and ensure the control system is capable of automated switchover in case of loss of pump or low flow. Utilize pressure gauges and flow meters on discharge piping. Oversize pumps by 125% to ensure adequate capacity and operation.

Controlling pH. It is best to monitor pH away from the chemical injection area. To measure pH as it exits the packed bed section, utilize a catch cup just below the packing to capture liquids falling from above. The catch shall be plumbed to the exterior portion of the unit where liquid will gravity flow through the pH probe and down back into the sump area. Chemical injection should be as close to the pump suction as possible. Utilize a pipe with small perforations to act as a distribution device as chemical is brought into the unit. Chemical should exit the pipe near the pump suction area. The holes in the pipe will allow sump water to mix with the neutralizing chemical prior to entering the recirculation piping. The pump impellers will provide an excellent means of turbulence and mixing to prevent the channeling of liquid through the piping and packed bed.

Instrumentation. Monitor and Alarm the following:

- **pH**
- **Fresh water make-up**
- **Pump flow rate**
- **Pump pressure**
- **Pressure drop (scrubber and mist eliminator)**
- **Sump Levels**
- **Blowdown**
- **Sump temperature**
- **Air flow should also be monitored in the duct system at a suitable location before the scrubber.**

Access considerations. Design mist eliminators for ease of removal for inspection, cleaning and replacement. Mist eliminators should be encapsulated to prevent potential bypass. Access doors should be provided for an operator to inspect the packed bed section, sump area, pump area, and liquid distribution section. The access for the sump area should be above water level to prevent leak points. View ports should be provided for easy inspection of internals. (Borosilicate glass works best as a window; it resists fading, unlike clear PVC or Plexiglas, and withstands the heat of the high-intensity lights.) Locate widows between the water line and packing bottom, at the packed bed section, and at the liquid distribution section. Utilize slide shades to keep light from entering the scrubber where possible.

TECHNIQUES FOR REDUCTION OF BIOLOGICAL GROWTH

Following are some guidelines to reduce bacterial growth, which could impede scrubber function:

- **Acid wash the unit periodically or shock it with sodium hypochlorite (5% solution) to destroy algae and other biological organisms.**
- **Use a chlorinating or brominating system to destroy algae and other biological organisms.**
- **Use UV light devices for disinfecting supply and recirculation liquid.**
- **Segregate VOC exhaust from scrubbed exhaust. Field experience indicates less evidence of growth with non-VOC exhaust.**
- **Segregate all sources of phosphoric acid or other phosphates that feed algae and scrub them with a strong caustic solution at a pH of 10 to 11.**
- **Field experiences suggest reduced growth in polypropylene constructed units versus FRP construction. Porosity and pin holes tend to be breeding areas, which are common in FRP units.**
- **Utilize sliding shades over all clear view doors to prevent light from entering the unit.**

CONCLUSION

This article touches on just a few common causes of reduced efficiencies in scrubber systems. Proper design of a high-efficiency scrubber system requires much more than just a pump, vessel and spray header. Routine preventative maintenance schedules are important to avoid compounding problems and costly downtime. Reputable scrubber manufacturers can provide periodic preventative maintenance inspections and follow-up reports that allow for trending of system parameters and early recognition of arising problems. For more information on wet packed bed fume scrubbers, please visit www.kchservices.com.

WASTEWATER TREATMENT

BY THOMAS J. WEBER
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Today, some 15,000 companies in the United States perform electroplating and metal finishing operations. These firms discharge their spent process wastewaters either directly to rivers and streams, or indirectly to Publicly Owned Treatment Works (POTWs). Metal finishing, by far, comprises more individual wastewater discharges than any other industrial category. Typically, pollutants contained in metal finishing process waters are potentially hazardous, therefore, to comply with Clean Water Act requirements, the wastewaters must be treated, or contamination otherwise removed, before being discharged to waterways or POTWs. Regulations, in general, require oxidation of cyanides, reduction of hexavalent chromium, removal of heavy metals, and pH control.

Understandably, for companies discharging wastewater directly to waterways (direct discharges), regulations promulgated through the years require attainment of the more stringent concentration-based limitations for toxic wastewater constituents necessary for protection of aquatic life. These stream standards were developed from Federal Water Quality Criteria and limit in-stream pollutant concentrations to levels that will not adversely affect drinking water quality and aquatic life. Since the mid 70s, state agencies have continued to drive direct discharge limitations downward to levels well below water-quality-based stream standards, using antidegration, antibacksliding, and existing effluent quality (EEQ) policies, and the number of direct dischargers has dropped precipitously. Implementation of biological-based criteria through biomonitoring and bioassay testing will continue to force direct discharging facility closures and relocation to POTWs.

As the overwhelming majority of metal finishing companies are discharging to POTWs, wastewater treatment systems for these firms are installed for compliance with federal pretreatment standards, or local pretreatment limitations if more stringent than the federal regulations. Federal standards are technology-based, i.e., developed through historical sampling and testing of conventional wastewater treatment system discharges collected at select, best-operated facilities. The base level technology was called Best Practicable Control Technology Currently Available (BPCTCA), or simply BPT. The more stringent level was termed the Best Available Technology Economically Achievable (BATEA), and is usually referred to as BAT. The treatment technology of BAT differs mainly from the conventional physical-chemical treatment of BPT in that it includes subsequent polishing filtration, and normally addresses improved methods of plating bath recovery.

The purpose and intent of federal and local pretreatment regulations are to prevent the introduction of pollutants into POTWs that will interfere with their operations; to prevent the introduction of pollutants, which will pass through the POTW and contaminate receiving waterways; to prevent pollutant concentrations that are incompatible with biological processes or otherwise inhibit the process; and to reduce the pollutant concentrations of POTW sludges.

Since the pretreatment regulations became effective in 1984, the metal finishing



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Table I. Electroplating Job Shop Effluent Guidelines—Pretreatment Standards for Existing Sources Greater than 10,000 gal/day

Pollutant	*Maximum for any 1 day*	Average of daily *values for 4 consecutive monitoring days shall not exceed*
Cadmium	1.2	0.7
Chrome	7.0	4.0
Copper	4.5	2.7
Lead	0.6	0.4
Nickel	4.1	2.6
Zinc	4.2	2.6
Cyanide, total	1.9	1.0
Total metals[a]	10.5	6.8
Total toxic organics	2.13	—

All values in mg/L; total metals is the sum of chromium, copper, nickel, and zinc.

industry has taken major strides in pollution control through wastewater treatment system installation and operation, admirably fulfilling the regulatory intent. Substantial historical reductions for all metals have been demonstrated at many POTWs nationwide.

STATUS OF WASTEWATER REGULATIONS

The federal regulations listed in Tables I and II have now been in existence in excess of 10 years since the 1984 compliance dates. For those metal finishing companies still fortunate to be limited by these regulations, each limit and the applicability of the regulations are of intimate familiarity and compliance is being achieved on a day-to-day basis. Increasingly, POTWs are imposing, or are being forced to impose, local pretreatment limitations that are much more stringent than the federal regulations. Often, these local limits are 10-25% of the Table I and II concentrations.

Properly selecting wastewater treatment technology, modifying production

Table II. Metal Finishing Pretreatment Standards for Dischargers to POTWs

	Existing Source		New Source	
Parameter	1-day maximum	30-day average	1-day maximum	30-day average
Cadmium	0.69	0.26	0.11	0.07
Chrome	2.77	1.71	2.77	1.71
Copper	3.38	2.07	3.38	2.07
Lead	0.69	0.43	0.69	0.43
Nickel	3.98	2.38	3.98	2.38
Silver	0.43	0.24	0.43	0.24
Zinc	2.61	1.48	2.61	1.48
Cyanide, total	1.20	0.65	1.20	0.65
Cyanide, amenable	0.86	0.32	0.86	0.32
Total toxic organics	2.13	—	2.13	—

POTW, publicly owned treatment works.
All values in mg/L.

operations and processes, and improving waste minimization and resource recovery techniques have become prerequisite to achieving compliance. Implementation of the basic BPT and BAT technologies is often inadequate to meet frequently unreasonable, and usually unnecessary, local limits set far below the technology-based standards. Increasingly, local limitations are being based on mathematical models using faulty software programs and arbitrary POTW effluent standards, rather than good science and environmental ncessity.

Although federal regulations have remained unchanged since their 1984 effective date, the U.S. EPA proposes to get back into the act of tightening pretreatment standards for metal finishers. In late 1994, the U.S. EPA proposed drafting Metal Products and Machinery (MP&M) Effluent Guidelines, which would impose specific concentration limitations on many metal fabricating and machine shops presently not covered under any federal industrial pretreatment category. U.S. EPA estimates the regulation would bring another 20,000 companies nationwide under the pretreatment requirement umbrella. The proposal, however, includes the prospect of shifting all metal finishers and electroplaters to the MP&M Guidelines, thus eliminating the current regulations. The MP&M limits are expected to be developed from reassessing technology-based pollutant concentrations. This could effectively reduce federal pretreatment limitations by 50-90%, depending on the pollutant, as current effluent quality among metal finishers is much lower, for many reasons, than in the 1970s when the original BPTs/BATs were established.

Although metal finishing and POTW effluent quality have continued to improve annually, the incidence of enforcement actions and amounts of the resultant penalties have increased. Many municipalities have adopted "automatic" penalties for any discharge violation, and have modified pretreatment ordinances to make it easier to collect penalties.

The U.S. EPA was required to draft the MP&M Guidelines in March, 1995. As of the date of this writing, the regulation has not been published. If the regulation is drafted per the original proposal, future regulatory enforcement will be more likely to increase. Improved treatment system operation and performance will become an even greater economic necessity of the metal finisher.

Furthermore, the treatment focus will further shift from conventional physical-chemical treatment to the more advanced, more expensive treatment methods of microfiltration and ion exchange polishing, and closed-loop, zero-discharge

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SYSTEM SELECTION CRITERIA

Four major factors contribute to the size, complexity, and cost of conventional wastewater treatment systems.

Pollutant Type

The complexity of the treatment system needed to effectively remove pollutants from a wastewater is determined by the type and nature of the pollutants encountered. A basic system will only require simple neutralization and chemical precipitation prior to solids separation for certain, although few, metal finishers. The process use of complexing or chelating agents in production baths would increase system complexity, often requiring two-stage treatment or neutralization and the need to apply chemical coagulants or specialty metal precipitants to reduce metal solubility.

Other pretreatment processes, including hexavalent chromium reduction and cyanide oxidation, are only required when the plating operation utilizes these common chemicals. Oil separation on a segregative basis may be necessary in facilities where oil and grease concentrations in the combined raw wastewater exceed 200 mg/L.

Increasingly, today's metal finishers are modifying processes and getting rid of certain finishes to eliminate problem pollutants and the resultant system complexity, or simply to reduce discharge violations. Over the years, there has been a major industry shift to noncyanide bath finishes. Curbing or modifying the use of complexing chemicals and conversion to trivalent chromium finishes has further reduced system complexity through changes in pollutant type.

Pollutant Loading

Treatment chemical costs and solids handling equipment sizes/costs increase proportionally to pollutant loading to the wastewater treatment system. Clarification, sludge storage, filter presses, and sludge dryers are sized in accordance to projected loads and solids generation. Increased size requirements result in higher capital equipment costs and higher disposal costs for waste residuals.

Proper selection of plating baths with reduced metal maintenance levels and precise control of bath concentrations will reduce loadings. Other common loading minimization practices include implementing a rigorous housekeeping program to locate and repair leaks around process baths, replacing faulty insulation on plating racks to prevent excessive solution drag-out, installing drip trays where needed, etc.; using spray rinses or air knives to minimize solution drag-out from plating baths; recycling rinsewater to plating baths to compensate for surface evaporation losses; using spent process solutions as wastewater treatment reagents (acid and alkaline cleaning baths are obvious examples); using minimum process bath chemical concentrations; installing recovery processes to reclaim plating chemicals from rinsewaters for recycle to the plating bath; and using process bath purification to control the level of impurities and prolong the bath's service life.

Hydraulic Flow Rates

The size and capital costs for wastewater treatment are largely dependent on the instantaneous flow rate of wastewater requiring treatment. The major contrib-

utor to the volume of wastewater requiring treatment is rinsewater used in the production processes coming in direct contact with the workpiece. The conversion to air-cooled rectifiers from water-cooled rectifiers, and installation of chillers and cooling towers for reuse of bath and rectifier cooling water, have largely eliminated noncontact hydraulic loadings.

Other common practices used to reduce wastewater volume include implementing rigorous housekeeping practices to locate and repair water leaks quickly; employing multiple counterflow rinse tanks to reduce rinsewater use substantially; employing spray rinses to minimize rinsewater use; using conductivity cells to avoid excess dilution in the rinse tanks; installing flow regulators to minimize water use; and reusing contaminated rinsewater and treated wastewater where feasible.

Negative results impacting treatment system operation, however, have resulted from zealous water-reduction programs. Rinsewater reductions invariably result in increased contaminant concentrations undergoing treatment, and occasionally to problem levels. Increases in alkaline cleaner and chelating chemical concentrations, in particular, commonly impede conventional treatment, resulting in poor coagulation and floccuation.

Environmental Regulations

The stringency of the concentration-based discharge limitations affecting a metal finisher is often the leading criterion in selecting treatment processes and systems. Generally, conventional chemical precipitation systems, perhaps with polishing filtration, are suitable to attain compliance with federal regulations or reasonable local standards.

For those firms residing in communities that have adopted local standards with metals limitations ranging from 0.1 to 1.0 mg/L, cost and complexity of the system can be substantial. Multiple conventional treatment trains in series operations are relatively simple, but effective. Advanced microfiltration, cation exchange polishing, reverse osmosis, and complete evaporation may be necessary to meet stringent standards or totally eliminate the discharge.

CONVENTIONAL METHOD OF WASTEWATER TREATMENT

To this day, the majority of metal finishers are meeting, or attempting to meet, effluent limitations by treating wastewater by conventional physical-chemical treatment. The process basically involves the use of chemicals to react with soluble pollutants to produce insoluble byproduct precipitants, which are removed by physical separation via clarification and/or filtration.

Conventional treatment systems often include hexavalent chromium reduction, cyanide oxidation, and chemical precipitation in a neutralization tank. Typically, these steps are followed by clarification. As clarification is not a 100% solids separation device, additional polishing is often required using one of many filtration devices. Increasingly, it is becoming common to eliminate the clarification stage totally, and its polymer flocculation step, in favor of direct microfiltration. The sludge from either separation stage is stored/thickened in a sludge tank, then dewatered via a filter press.

Chromium Reduction

Chromium in metal finishing is normally used in the hexavalent ion form (Cr^{6+}) in plating or chromating. As it soluble at all pH values, the chemical reduction step

to its trivalent (Cr^{3+}) form is necessary to ensure removal by precipitation. Commonly, trivalent chromium replacement processes are being employed for safety considerations and the elimination of the reduction wastewater step. Exercise care in selecting trichromium replacements that may contain ammonia and other chemicals, which can cause complexing of other metals in waste treatment.

The reduction of hexavalent chromium is achieved by reaction with sulfur dioxide gas (SO_2), or more commonly sodium metabisulfite (MBS). The speed of the reaction is pH dependent. At pH 2.5-3, the reaction is virtually instantaneous. Above pH 4, the reaction slows to a point where it becomes impractical for use in continuous flow systems.

The use of pH and oxidation-reduction potential (ORP) controllers is common. Without automatic pH controllers, care must be exercised to ensure complete reaction, particularly in batch reactors where the pH is manually adjusted to pH 2.5 prior to MBS addition. MBS addition raises the pH of the solution, often to ranges where reduction times are lengthy. As batch processes are usually controlled visually by color change, a significant MBS overfeed often results.

Although MBS and SO_2 are the most common chemical reducers used in hexavalent chromium reduction, any strong reducing agent will suffice. Ferrous iron in many forms, including ferrous sulfate, ferrous chloride, ferrous hydrosulfide, or electrochemical ferrous production from iron electrodes, is used.

The primary benefit of ferrous reduction is that Fe^{2+} will reduce hexavalent chromium at near neutral pH values. For low concentration applications (moderate chromating use processes), ferrous addition can eliminate the complete chromium reduction stage. The ferric ion formed in the process becomes an excellent coagulant in the precipitation stage.

The only drawback to ferrous reduction is the additional sludge generated by its use, as three parts Fe^{2+} is required to reduce one part Cr^{6+}.

Chromium Reduction Process Precautions

1. SO_2 and MBS form noxious acidic vapors. Avoid excess formation and inhalation of the vapors.
2. pH control is very important. Allowing pH to drift below 2 increases SO_2 gassing vapors. Allowing pH drift upward to 4 increases reaction times to impractical levels.
3. Underfeed of SO_2/MBS causes chrome carryover. Overfeed of MBS/SO_2 causes increased metal solubilities in neutralization, and reverses the particle charge and, consequently, results in poor flocculation.

Cyanide Oxidation

Treatment of cyanide (CN) in metal finishing wastewaters is most commonly performed by oxidation in an alkaline chlorination process using sodium hypochlorite (NaOCl) or chlorine gas (Cl_2). Because of the toxic danger of Cl_2 gas, NaOCl processes are considerably more common.

The alkaline chlorination process either involves only first-stage CN oxidation, whereby simple cyanides are converted to cyanates (OCN), or the addition of a second-stage reactor to convert cyanates to carbon dioxide (CO_2) and nitrogen (N_2).

First-stage CN oxidation is carried out at a pH of 10.5 or higher. The reaction slows greatly at pH values below 10 and virtually ceases at pH values below 9. The process only oxidizes simple cyanides, such as NaCN, KCN,

$Zn(CN)_2$, CdCN, CuCN, etc. Complexed cyanides, commonly found in metal finishing wastewater as iron complexes, are not destroyed in alkaline chlorination processes. In fact, complexed cyanides are not destroyed efficiently by any common cyanide oxidation process, including ozone. The use of high-pressure/high-temperature thermal processes will, however, destroy complexes. Also, lengthy exposure to sunlight will convert complexed cyanides to simple cyanides, to a small extent.

As federal and local regulations are generally written for total cyanide monitoring and limiting, complex cyanides are often the species causing violations.

Complexed cyanides are most commonly formed by poor housekeeping, control, and rinsing. Drag-out or drippage of CN from baths or bath rinses into acids and chromates is very common. Steel electrode use in plating baths causes a significant amount of complexed cyanide input to the bath from constant decomposition. Clean steel parts allowed to fall and accumulate in CN baths are another major source of complexed CN formation.

Although complexed cyanide formation cannot be totally eliminated, reduced formation through housekeeping and improved rinsing can reduce the concentration to nonproblem levels.

Complexed cyanides are generated in both soluble and insoluble forms. The insoluble form is removed via mass settling in the clarifier. Conversion of soluble complexes to insoluble complexes can be achieved to some extent by the addition of MBS to the neutralization tank. The efficiency is improved in the presence of copper ion. Permanganate addition also has been reported to accomplish improved precipitation of complexed cyanides.

The second-stage CN oxidation process is carried out at a pH of 8.0-8.5. An amount of Cl_2 comparable to that required in first-stage oxidation (3.5 lb Cl_2:1 lb CN) is necessary to complete the conversion of OCN to CO_2 and N_2.

Most sewer use ordinances do not require cyanate oxidation or limit cyanate in the discharge. Consequently, many treatment systems only employ first-stage processes. A common problem associated with first-stage-only systems is the propensity to gassing in the neutralization tank, with resultant clarifier floating problems. This is caused by an uncontrollable cyanate breakdown, particularly when excess residual Cl_2 is present in the first-stage dischare.

Although reaction times for most simple cyanides and cyanates are 10-15 minutes, it is advisable to size reaction tanks at 1 hour and longer if affordable/practical. Certain simple cyanides, including cadmium and copper, only start breaking down after the sodium, potassium, and zinc cyanides are destroyed, thus requiring longer contact periods. Furthermore, the longer the reaction, the more efficient the gas venting becomes, reducing the incidence of clarifier floating.

Because precise control of pH and Cl_2 is important, pH and ORP controllers are recommended in all continuous control reaction tanks.

Summary of Cyanide Process Precautions

1. First-stage oxidation must be controlled at pH 10.5 or higher. (The higher the pH, the faster the reaction.)

2. Control the formation of complexed cyanides, as treatment processes do not destroy them. Add MBS to the neutralization tank if soluble complexes cause effluent violations.

3. Allow 1 hour or more reaction time to ensure completion of the reactions, and for problem gas venting.

4. Underfeed of chemical allows CN pass through; overfeeds cause increased gassing and reoxidation of trichrome.

Coagulation/Neutralization Process Considerations

Effluents from hexavalent chromium reduction and cyanide oxidation stages combine with other alkaline and acid wastewater streams in a neutralization tank. The express purpose of the neutralization tank is to create a suitable environment and retention time for soluble pollutants to react and form insoluble precipitates for eventual physical separation. The principal precipitation process employed in conventional wastewater treatment systems is that of hydroxide precipitation. Heavy metals, the prime targets of neutralization-precipitation, have varying solubilities depending on pH. In common mixed-metal wastewater streams, control of the neutralization tank at pH 9.2-9.5 is generally suitable to lower metal solubilities, as hydroxides, to concentration ranges where compliance is achievable.

In many cases, it is necessary to add chemical coagulants to the wastewater in order to achieve minimum solubilities and superior flocculation/solids separation in the clarifier. A proper coagulant will effectively tie up anionic surfactants, wetters, and species such as phosphates, which interfere with polymer flocculation; and also add bulk density for improved solids separation.

Where coagulants are required for good process performance, it is recommended that two-stage neutralization reaction tanks be employed, as coagulants perform better when reacted with the wastewater at pH values in the 5.5-6.5 range.

Common chemical coagulants include calcium chloride, ferrous salts, ferric salts, and alum.

For improved coagulation, certain specialty coagulants are available from chemical suppliers. These chemicals usually contain one of the above base salts, which are sometimes blended with polymers, generally of a cationic nature. Although these specialty products are expensive, with costs ranging from $400 to $1,000 per drum, their use is often necessary to achieve compliance.

Neutralization is generally achieved using caustic soda (NaOH) and sometimes potassium hydroxide (KOH). Hydrated lime and magnesium hydroxide also have wide utilization. Although these neutralization chemicals present certain handling and feeding problems associated with their solids content, lower metals solubilities are achieved at maintenance of lower neutralization tank pH (8.0-8.5).

The introduction of strong chemical complexers used in production processes commonly impedes the pollutant precipitation process. Common complexers/chelators include ethylene diamine tetra acetic acid (EDTA), nitrilotriacetic acid (NTA), quadrol, glucconates, glutamates, ammonia, and various amies.

Complexing agents are commonly used in electroless baths, electroplating bath brighteners, alkaline cleaners, parts strippers, and numerous other applications. Eliminating their use, where practicable, is the simplest means of mitigating their adverse wastewater treatment effects. Where critical to the process, special means and practices must be employed, which vary with the type and strength of the complexer, as well as the metal(s) being complexed.

Often off-line pretreatment is necessary, as in the case of high volume electroless bath use. In other cases, the use of specialty chemical precipitants, metered into the complexed waste stream or into the neutralization tank, is suitable and effective. Specialty chemical precipitants include dithiocarbamates, dithiocar-

bonates, starch and cellulose xanthates, poly quaternary amines, and ozone destruction/hydrosulfite reduction.

As complexing chemicals are primary reasons for noncompliance in conventional systems, much care and time are necessary to solve the problems created by them. Often significant trial testing in bench scale treatability tests and close work with chemical suppliers are necessary to resolve complexing problems.

In some cases involving simple complexed wastewaters, conversion from hydroxide precipitation to sulfide or carbonate precipitation in the neutralization process will achieve necessary reductions in metal solubility. Most metallic sulfides and metallic carbonates have lower solubilities than their hydroxide counterparts.

Reaction times required for effective coagulation-neutralization-precipitation vary among wastewater types and complexity. We recommend minimum retention times of 30 minutes, 15 minutes in first-stage reactors. As metal hydroxides tend to reduce in volume the longer they are mixed, the longest practical reaction times are most desirable.

Common problems associated with neutralization/reaction tanks, which impede clarifier separation of solids, include soluble complexes caused by chelating agents; charge reversal caused by anionic surfactants, phosphates, and MBS overfeed; solids buoyancy or flotation problems caused by excess oil and grease or gas formation including chemical gassing caused by peroxides, acetates, and carbonates or physical-induced gassing caused by suction leaks on transfer pumps, or significant mixer vortex action; overfeed of dump solutions, particularly alkaline cleaners; and high total dissolved solids (TDS), 7,000 ppm and higher, from overly zealous water conservation practices, or high percentage reuse of treated water.

FLOCCULATION/CLARIFICATION PROCESSES

The precipitates formed by the proper operation of the coagulation-neutralization stage are commonly removed in conventional wastewater treatment systems by clarification or sedimentation. This process involves solids removal by the efficient settling of solids. Buoyancy caused by oils or floating caused by the entrainment of gas bubbles will prevent efficient settling. Generally, floating problems are controllable in the typical metal finishing wastewater installation. For certain firms, which employ electrolytic/electrochemical pretreatment or ozone generation/air diffusing treatment techniques, dissolved air flotation (DAF) is the preferred unit for solids separation.

Solids separation is improved in clarifiers, or DAF units, by polymer (polyelectrolyte) flocculation. As the average charge of metal hydroxides is positive, a negatively charged (anionic) polymer is used in the flocculation process. It is imperative that the wastewater charge remain positive at all times. Coagulants and/or cationic polymers may be necessary in certain wastewater types where charge reversal is common, as in phosphating operations. Nominal flocculation time of 1 minute is recommended for floc tank size. Variable speed mixers are recommended to allow some measure of control of floc size.

The size of the clarifier generally varies with the type and style. Basic, open/empty sedimentation tanks commonly used in low-flow installations should be sized for a maximum surface loading rate of 500 gal/day/ft^2 of tank surface.

Most commonly employed clarifiers are of the lamella type or inclined plate variety. These units are sized based on volumetric flow rate per square foot of plate

pack area projected on the plate incline, or cosine of the degree of plate angle; typically 60°. Recommended loading rates are 0.2-0.4 gal/min/ft² of projected plate area, and a total suspended solids (TSS) concentration of 500 ppm or less.

Units are manufactured in basic hydraulic flow sizes, i.e., 30 gal/min or 75 gal/min, etc. In those cases of high TSS loads (500 ppm or higher), it is not advisable to size a unit based solely on flow. In these high solids load applications, clarifier selection should be based on 1 lb TSS per hour for each 20 ft² of projected clarifier settling area.

Manufacturers will supply design and operational information for their specific unit. As a general rule, it is important to evacuate sludge as it accumulates to prevent its buildup into the plate pack area. This creates blockages and increases the upflow velocity in the open areas and carries TSS with the high flow. Monthly draining is advisable to minimize ratholing and solids concretion.

EFFLUENT POLISHING

At times, clean water that overflows from a clarifier will require further removal of suspended solids or polishing to meet more stringent discharge requirements. This may be for water reuse or simply as insurance in case of a system malfunction. Sand filters, devices consisting of one or more layers of various sizes and types of granular media, are typically used. Gravel, sand, anthracite, garnet, and activated carbon are common media.

The size and number of filters is, as with a clarifier, dependent on the volume of wastewater to be filtered and the surface area of the filter media. Gravity-operated sand filters usually are loaded at 0.25-0.5 gpm/ft², whereas pressure sand filters can operate in the 5.0-10.0 gpm/ft² range, depending on the suspended solids of the effluent.

Most sand filters need to be periodically cleaned or "backflushed" to remove the solids that have built up. Clean water, process water, or dilute acid solutions may be used for this back flushing. Backflush waters are generally returned to the collection or equalization tank and returned to the treatment system. Pressure sand filters require less backwash water than larger gravity types.

Operationally, care must be taken to ensure that pumps feeding or backflushing the filters are operating at design capacity to ensure proper loading and adequate cleaning of the media. Sand filter media are rarely replaced, except when a severe system upset causes solids to block the water distribution headers.

SLUDGE THICKENING AND DEWATERING

Sludge (settled solids) produced from treatment of metal finishing wastes generally contains between 1.0 and 2.0% total solids. Disposal of such a watery sludge is very expensive. Most medium and large generators of wastewater choose to thicken and dewater sludge, thus reducing the volume of waste to be disposed.

A sludge thickener, although not always necessary prior to dewatering, serves several worthwhile functions. First, it creates storage volume for the sludge in the event that the dewatering equipment is not in operation. Second, it allows for a consistent sludge blanket level in the clarifier. Sludge can be intermittently removed from the clarifier by means of a timer on the sludge pump. This reduces the possibility of solids drafting over the clarifier weir(s) because of a high sludge blanket. Finally, sludge stored in a thickener may increase in solids content to as much 3-4%.

Increased solids content does two things: it decreases cycle time required by the

dewatering equipment (filter press, centrifuge, belt press) and, as a rule of thumb, regardless of the type of dewatering equipment, the thicker the feed sludge, the drier the sludge cake. The objective is to reduce the volume to be disposed of by removing as much water as possible.

The filter press is most often used in the dewatering of metal finishing sludges because generally it is made to handle smaller volumes of sludge, is simple to operate, and produces a dry, easily disposable filter cake. Sludge from the thickener, or directly from the bottom of the clarifier, is usually pumped via an air diaphragm pump to the filter press. The polypropylene filter media retains the solids while the liquid portion or filtrate flows through the media and discharges. Filtrate usually returns to the collection/equalization tank for retreatment. After a certain length of time (2-4 hours), the chambers of the press are completely full and a filter cake of 25-35% solids has formed. The hydraulic pressure that had been holding the plates together is now released and the filter cake is discharged.

Filter press operation requires little operator attention except at the beginning and end of a press cycle. Presses without an automatic plate shifter often require two people to separate the plates to discharge the cake, one on either side of the press. Cake that has had enough time to sufficiently dewater will literally fall out of the press upon opening.

The highest operational cost involved with a filter press is the replacement of the filter cloths. Cloth life is directly dependent on the number of press cycles per year. The metal hydroxide sludges produced from treatment of metal finishing wastes are generally of moderate pH and nonabrasive. Cloth life of 1-2 years is common. Replacement of cloths is labor intensive, especially the caulked, gasketed variety, but all the cloths, even in a large press (10 ft^3), can be changed in 3-4 hours. Because plates and cloths are usually of polypropylene construction, they can be routinely cleaned by immersion in an acid without damage.

SYSTEM OPERATION AND PERFORMANCE

The best system design may result in inadequate results unless operators and management devote the necessary resources. These resources include time, talent, and training. Sufficient time is required for normal operation and routine preventive maintenance. The talent of motivated operators is necessary to anticipate problems and take preventive steps to assure continuous compliance. Training is critical for operators to understand how system performance is affected by changes in production, chemicals, or regulatory limits.

The operator needs to keep a daily log listing volumes treated, chemicals consumed, sludge produced, and effluent results. Either the operator or management should review these results to evaluate trends so costs can be controlled and results improved. For instance, increases in sludge production without corresponding increases in production may indicate increased drag-out losses, failure of recovery equipment, or changes in treatment chemistry.

Regulatory authorities require timely and accurate analytical data to confirm compliance with effluent limitations. Operators need daily analytical data to control system performance and to make needed adjustments to treatment chemistry. This is often accomplished using inexpensive troubleshooting analytical tools including pH papers in lieu of a hand-held pH meter, and potassium iodide-starch papers for cyanide oxidation process control. Quick and easy tests

for CN and metals used in the process are important. A number of test kit suppliers are available to choose from. It is not always necessary to have the sophistication of a spectrophotometer or atomic absorption unit for in-house troubleshooting and quality control. It is important, however, to have this service and complete analytical services available from a competent outside laboratory. All regulatory agencies will require data submission based on approved test methods and procedures with report submittals.

It is imperative to know your regulator and communicate with him/her regarding system operations, both good and bad. Most agencies require notification of system upsets and slug loads. Although the typical metal finisher is reluctant to report problems, it is always better to report problems than for the regulator to find them. Notification always can be used as mitigation at enforcement proceedings.

COMMON MISCONCEPTIONS AMONG METAL FINISHERS ABOUT WASTEWATER TREATMENT

- Regulatory agencies only set effluent standards at reasonable levels necessary for environmental and POTW protection.
- Consultants and suppliers always know how to solve your problems.
- The use of ion exchange for complete wastewater treatment is a practical approach to eliminating discharges.
- Microfiltration is a sure method of compliance because it filters out everything.
- The cyanide oxidation system is not working well because you have total cyanide discharge violations.
- When floating in the clarifier occurs, the probable cause is oil and grease.
- A polishing filter will solve all the problems.
- Metal violations are always due to clarifier or polishing filter problems.
- All laboratories generate good data.
- pH and ORP electrodes only have to be cleaned weekly.
- If poor floc formation is observed, the polymer is bad or you're not adding enough.
- In most cases, sludge dryers will save you money.
- Clarifiers and filter press cloths do not need to be periodically cleaned.
- The pH reading on the controller is always correct.

WASTE MINIMIZATION AND RECOVERY TECHNOLOGIES

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The surface-finishing industry is a chemical-intensive industry. A special category of chemical processes, characterized primarily as electrochemical processes, are used to treat and condition, or "finish," the surfaces of a variety of manufactured goods and components to either enhance visual appeal, improve corrosion resistance, or to increase product durability or serviceability.

Some providers of finishing services, and most manufacturers with in-house finishing operations, are understandably inclined to view themselves as purveyors of finishing services for the end products that they process or as producers of the products that are manufactured, rather than as operators of chemical plant and chemical producing processes.

Surface-finishing processes certainly fall under the definition of chemical processes. As such, they are no less subject to the limitations and laws of chemistry and physics and to good process design and chemical engineering practice.

The similarity of chemical production processes and surface-finishing processes is strong. At the heart of electroplating and waste-treatment operations, one finds many of the classic chemical unit operations and process techniques common to chemical production: mass and energy transfer, fluid flow, mixing, evaporation, reaction, sorption, crystallization, concentration/dilution, solid/liquid separation, etc.

A broad variety of chemicals is used by the finishing industry; however, only a small fraction of the chemicals purchased for bath make-up and operation is ultimately incorporated in the finished goods. While chemical manufacturing processes generate more hazardous waste on a tonnage basis, surface-finishing processes lose a disproportionate quantity of purchased chemicals as byproduct hazardous waste. The value associated with this wastage, plus the added cost of treatment and disposal, constitute major pressure on operating margins and profit.

In addition, finishing operations also require equally disproportionate quantities of process water per unit of production for parts cleaning and preparation, for bath make-up and maintenance and, of course, for rinsing. In many parts of the country the availability of quality process water is becoming a major concern to the finishing industry.

The price and conditioning costs of raw water are also increasing. Many finishers are looking for practical ways to limit water usage and to recover and reuse as much process water as possible.

Some firms have achieved, or are approaching, the elusive goal of zero liquid discharge. Also, the added incentive of potentially not requiring an effluent discharge permit has strong appeal.

In addition, finishing processes cannot be operated with the same degree of control common to many chemical production processes. By definition, many

chemical processes are essentially steady-state processes and lend themselves to tight statistical control. In comparison, finishing processes are more readily categorized as unsteady-state processes that are relatively chaotic from a process standpoint and, as a consequence, are more difficult to monitor and control.

This characteristic has nourished the relatively straightforward "lime-and-settle" method of treating toxic wastes and has hindered the acceptance and application of what are now a well-documented set of chemical process techniques for reducing the high level of waste generated by surface-finishing processes.

In an ideal finishing process, there would be no bath drag-out. Chemical losses would be restricted only to those chemicals that are consumed in cleaning and preconditioning surfaces and to those portions of the plating baths, which produce the desired surface coating or condition.

In the real world, bath drag-out is, of course, unavoidable. Drag-out can be reduced to some extent by instituting such mechanisms as increasing dwell time over baths, decreasing bath surface tension, forward pumped spray rinses, air knives, etc. Despite such efforts, substantial quantities of bath can still be lost to the rinse system. The net result is that bath drag-out continues to be the primary contributor to the extraordinary quantity of chemical waste generated by the surface-finishing industry.

This article reviews a number of well-demonstrated and proven chemical recovery methods, collectively known as separation technologies, for reducing or in some cases reversing bath drag-out. When properly selected and applied, one or more of these technologies in combination can be confidently used to separate and recover dragged-out bath or specific chemical components or values of certain baths or solutions and to separate and condition rinsewaters for recycle and reuse in the plating process.

Each technology separates the constituents of a solution differently. For example, evaporation separates the solvent (water) from the rest of the bath constituents. All other techniques affect separation on either a molecular or an ionic level. The choice of technology, or combination of technologies, is determined by both bath chemistry (what the chemistry lets you do) and by the underlying operating economics.

ECONOMICS OF RECOVERY VERSUS TREATMENT

There are essentially four approaches that can be taken to evaluate point-source recovery potential in given metal-finishing operations.

Operating Savings

Plating facilities with existing and adequate waste treatment systems can readily assess operating savings for a candidate recovery technology. A given recovery technology is evaluated on the basis of savings on purchased process chemicals and associated waste treatment chemicals plus any resultant savings in sludge handling and disposal cost. If the payback on invested capital is attractive, the recovery system should be installed.

Avoidance of Waste Treatment Capital Cost

Operating cost is the primary consideration for a new plant or for existing plants with an inadequate treatment system. In this case the economic evaluation incorporates an added factor; the avoidance of additional capital investment for waste treatment capacity.

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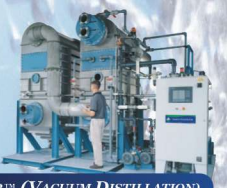
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Improvement of Manufacturing Operations

The implementation of recovery and quality maintenance methods and systems for both process water and process baths can help improve the performance of plating and surface-finishing baths and, in turn, the quality of the finish and the products that are produced. Such action will also help to reduce the amount of rejects and reworking of parts. Both aspects benefit production and quality control and will reduce operating costs and increase the value of fabricated products.

Total Avoidance of Sludge Disposal

For this scenario, justification for investment in recovery is based on the obvious desirability of eliminating generations of hazardous waste residuals. Stringent economic quantification is difficult in this case because of the uncertainty associated with determining long-term liability costs for future landfill disposal; nevertheless, there is powerful emotional appeal attached to the avoidance or minimization of long-term liability.

Evaluating Strategies

The first of these strategies is clearly the most conservative. It is easily applied and is the strategic analytical technique, which has traditionally been used by many metal finishers. The rapid escalation of sludge disposal costs makes point source recovery techniques, which were unattractive a few years ago, very enticing now.

The second strategy is legitimate but must be analyzed and applied with caution. There is a tendency to assume that recovery can be a complete substitute for treatment. Careful consideration must be given to potential downtime of recovery equipment; the generation of excess waste if the units are overloaded; the treatment of side streams such as regenerate waste or blowdown from the recovery process; accidents such as tank overflow, heat exchanger failure, spills or drips of chemicals, etc., plus unanticipated sources of regulated pollutants.

An example of the last-mentioned caution would be the presence of zinc ion contamination in the drag-out from alkaline cleaners, acid dips, and chromate dips in a zinc plating line. Too often attention is focused on recovery of the drag-out from the main plating tank, with no recognition that effluent quality may be unsatisfactory simply as a result of minor contributions from various other sources. When considering this strategy, the absolute minimum provision for unrecovered waste should be the determination of the minimum holding and treatment capacity needed to cope with the volume of unanticipated accidents or upsets.

The third strategy is the most efficient and productive way of converting waste treatment capital into waste minimization and production control efforts. Many examples today prove that the incorporation of pollution control and maintenance equipment into plating operations helps to significantly reduce batch dumps of process baths. Controlled bath maintenance limits bath impurities that cause plating quality problems and thus improve fabrication while reducing manufacturing cost. In many cases, short duration ROI objectives can be realized.

The fourth strategy is the most risky and the most difficult to support by facts. It is a rare situation where the generation of sludge can be completely eliminated, even in a theoretical sense, especially if such unanticipated occurrences as just discussed are considered.

In summary an investment in recovery technology and equipment should be

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supported by a hard, quantifiable economic analysis and supported by adequate operator and maintenance training. There is constant activity in the marketplace with new developments and promising breakthroughs in technology. Marketing claims can often make the situation bewildering, but it is appropriate to bear in mind that the laws of chemistry, physics, and economics will prevail. The fundamental law of ecology teaches that there is no free lunch.

Mother Nature is a tough task mistress. She has made it much easier and less costly to mix things together than to take them apart.

SOURCES OF WASTE

There are three categories of waste that must be considered when formulating a waste minimization program.

Bath Drag-Out to Rinses

This is the carryover of concentrated process baths on the workpieces, which is removed by stagnant and flowing water rinses.

Bath Dumps

Most of the process baths used in metal finishing are expendable and must be periodically discarded when their chemical activity is below a level acceptable for production purposes.

Floor Spills

This is a catch-all category including both accidental and purposeful incidental waste sources such as tank overflows, drips from workpieces, leaking tanks or pipes, spills of chemicals, salt encrustations, equipment and floor wash-down water, oil drips, or spills from gear boxes, etc.

Historically, most of the emphasis on recovery technologies has focused on rinsewater since it constitutes the majority of the flow leaving an operation and necessitates expensive waste treatment. Bath dumps are usually infrequent and are low in volume. Often, dumped baths can be hauled to a distant location by a waste service provider for final treatment and disposal. A subsequent section of this article will discuss the possibility of regeneration for certain of these baths to eliminate the need for periodic dumping.

Floor spills are nearly impossible to manage by the application of recovery technologies due to their unpredictable and intermittent nature and to the fact that they are so heterogeneous in composition. The primary attack on floor spills is tight operating and process control, adequate operator and safety training, programs to eliminate accidents, and, of course, good housekeeping.

The following sections will deal with the techniques applied to rinsewater. These can be divided into those that return a concentrated solution back to the originating process and those that aim to recover metals or chemicals for use elsewhere.

CONCENTRATE RECOVERY METHODS

There are a number of important factors that should be considered in regard to returning concentrate to the originating process. First, the majority of metal-finishing process baths is ultimately expendable. They have a finite life and are periodically discarded. Recycling of drag-out simply accelerates this process and will give no net gain unless some regeneration scheme is employed on the process bath itself. Thus, recovery of drag-out is most often considered only for the baths that operate in a reasonably balanced condition, primarily the process baths. A general recovery schematic for return methods is pictured in Figure 1.

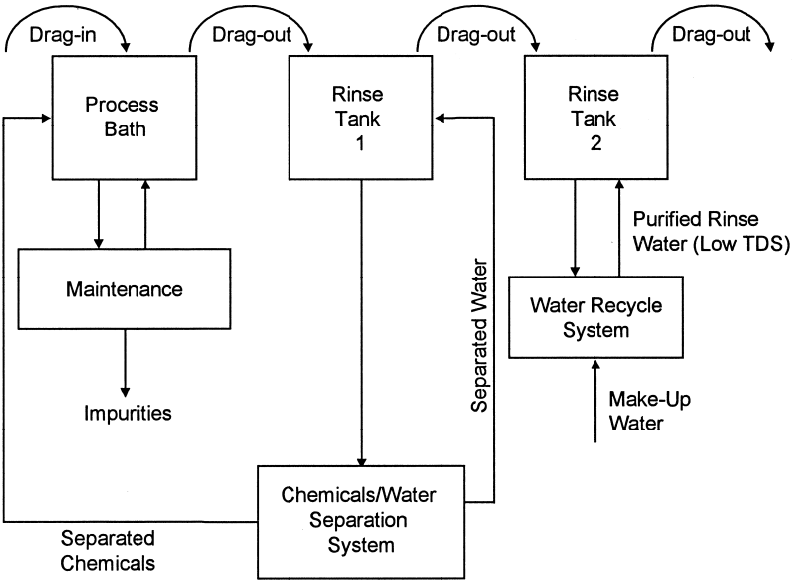


Fig. 1. General recovery schematic for return methods: evaporation, reverse osmosis, electrodialysis, ion exchange.

In the case of those electroplating baths where return of drag-out seems practical, two factors should be examined:

1. In most cases there is a tendency for harmful impurities to accumulate over time from drag-out return. These impurities can be metals or other cations or anions dragged into the bath. Or, they can be electrolytic breakdown products normally generated during bath operation. Examples of the latter would be the formation of carbonate through anodic oxidation of cyanide or the generation of undesirable organic breakdown products formed through the electrolytic breakdown of brighteners, wetting agents, grain refiners, etc.
2. In baths that use soluble anodes, the primary metal generally has a tendency to "grow" or to accumulate in the bath. This generally occurs because the electrochemical efficiency for anodic dissolution is higher than is the efficiency of cathodic deposition and/or because the bath itself has a solubilizing effect on the anodes during periods of inactivity.

In many cases both of these effects are fortunately minimized or controlled by the routine loss of bath through drag-out, filtration, purification, and by the removal of suspended solids and sludge. In some baths, however, such as bright nickel, the accumulation of impurities can be a problem in spite of the normal losses from maintenance and purification procedures.

When a high percentage of drag-out is returned by any of the technologies that will be reviewed, it may mean that the accumulation of cationic contaminants will become evident more quickly or more frequently, requiring a purposeful bleed-off of plating bath that is obviously somewhat counterproductive. In regard to

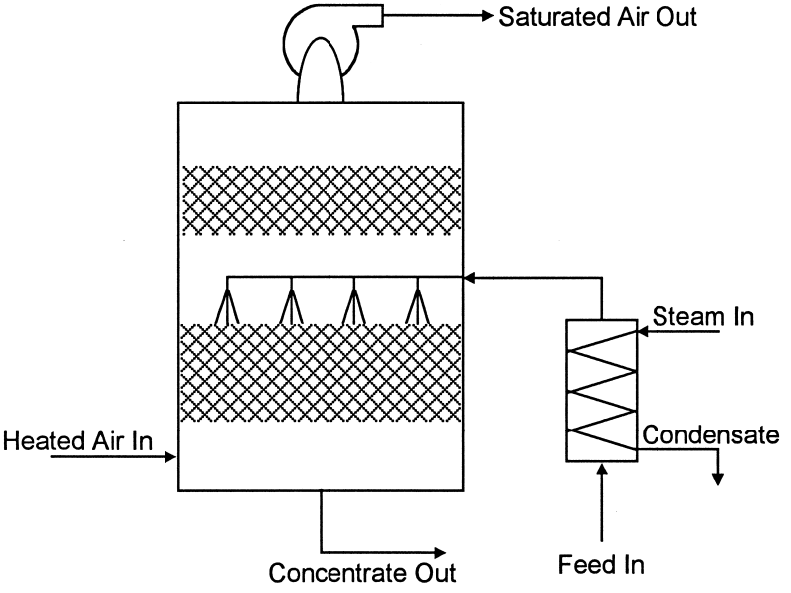


Fig. 2. Single-stage atmospheric evaporation schematic.

impurity accumulation, complete return of drag-out necessitates purification/maintenance operations or may increase the frequency of those already practiced. Since virtually every such operation creates loss of bath this is again an offsetting consideration to any recovery that is being gained.

A proper analysis of the optimum scheme should include all losses from the operation and the impact the recovery of drag-out will have on other sources of loss.

Evaporation

Evaporation is the oldest and most broadly applied of the separation technologies and has an extensive operating history. In the surface-finishing industry, evaporative recovery is classified as a concentrate and return technology and its track record and benefits are well demonstrated.

Evaporation is routinely used for point source separation and recovery of plating baths and their associated rinsewaters for recycle to the finishing system. Evaporation is also being used successfully to minimize liquid discharges from manufacturing plants by concentrating certain pretreated wastewaters, or brines, for haul-away and disposal while recovering additional process water for recycle to the process.

Compared to other separation methods, evaporation is more energy intensive; however, it is the only recovery technology that can treat plating rinsewaters to separate the solvent (water) from the dissolved chemicals and concentrate the remaining solution back to, or even beyond, bath strength. To minimize energy consumption recovery rinsewater volume can be minimized by the application of counter-current rinse hydraulics.

On the positive side, evaporation is a straightforward, rugged, reliable, broadly applicable, and widely practiced recovery technique. Materials of construction are available for virtually any process bath.

Evaporation separates volatile from nonvolatile constituents of a solution by means of heat-energy-driven phase change (converting liquid to vapor) resulting in a recovered concentrate. In the case of using a vapor condensation technique, atmospheric and vacuum evaporation generate a distillate that can be recovered in most cases as process water. Compared to other separation and recovery techniques evaporation can easily concentrate back to, and in some cases well beyond, bath concentration.

Heat energy is required to evaporate water from an aqueous solution. The amount of energy required is roughly 1,000 Btu/lb mass of water evaporated, regardless of whether the evaporation is conducted at atmospheric pressure or under vacuum. There is no exception to this rule! It can be called the rule of 1,000. To evaporate a pound of water, this quantity of heat energy must be supplied from some energy source. With the possible exception of an unlimited supply of hot, dry desert air, or of waste process heat that could be captured for use, vaporization energy is rarely "free."

Atmospheric evaporators are essentially simple scrubbing devices that use an air stream to strip water as vapor from a liquid solution. In essence, an atmospheric evaporator is an air stream humidifier. They have been widely used by industry because of their low cost and operating simplicity. Atmospheric units are generally applied singly (Fig. 2) or in multiples to dewater various plating rinse waters to recover bath concentrate.

Atmospheric evaporators operate by either pushing or pulling an air stream through a mesh bed or grid-work over which rinsewater, or in some cases, the bath itself, is circulated. Either the air stream or the bath, or both, must be heated to provide the necessary 1,000 Btu of heat energy needed to evaporate each pound of water. Heat must be supplied from somewhere or the unit won't function.

The amount of water removed with each pass is a function of the mass, temperature, and humidity of the air stream, and of the temperature of the liquid being circulated through the unit. Heat energy is usually supplied by an external heat exchanger. If a normally hot plating bath is being circulated through the evaporator, the total heat energy required may be provided entirely by the bath itself, which, of course, will have to be reheated.

The amount of water an air stream can remove from an aqueous solution is a function of a number of factors including the relative humidity of the air at the process environment; the temperature of both the air stream and the liquid solution; the relative mass velocities of both streams through the evaporator; the degree of effective contact between both streams; and the concentration of the liquid solution being evaporated. The necessary 1,000 Btu/lb of water vaporized still must be provided.

In most atmospheric evaporator designs, the vaporized rinsewater is not captured. Instead, the humid air stream is vented to atmosphere. To avoid possible carryout and discharge of hazardous substances, the air stream may require additional scrubbing through a neutralizing or water-irrigated vent scrubber before final discharge.

One recent atmospheric evaporator design has added a condenser and closed the air circuit to eliminate or minimize potential exhaust emissions. A much larger condenser is required to condense water vapor from a stream of air than would be required if air was not present. The presence of an inert gas, such as air, in the exhaust vapor stream reduces normal condensing coefficients by 90% or more.

An interesting application, which is well suited to atmospheric evaporation,

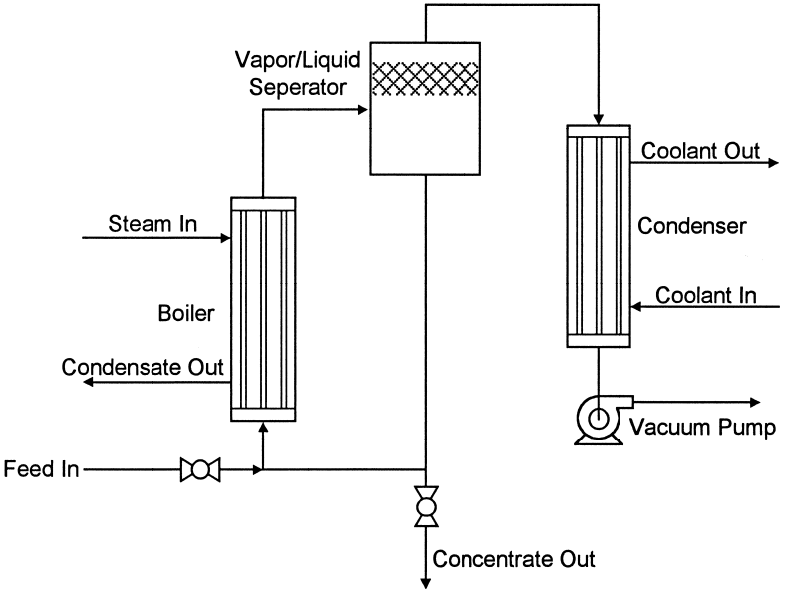


Fig. 3. Single-stage vacuum evaporation schematic.

involves the recovery and simultaneous cooling of hard chrome baths that often require external cooling to remove excess heat created by high operating amperage during plating.

In such circumstances, both rinsewater and bath may be blended for dewatering by the evaporator. In cases where the quantity of heat generated by the electric power demand of the bath is not adequate for the evaporation duty, the addition of external trim heat may be required.

Atmospheric evaporators are not considered to be energy efficient. At minimum, several pumps are required to introduce feed, to circulate the solution to be concentrated and, depending on system hydraulics, to remove concentrate. There are inherent inefficiencies in moving and heating large volumes of air. Spray temperatures must be high. Solution boiling points are higher at atmospheric pressure than under vacuum operation, which results in a lower effective temperature differential or thermal driving force.

Despite the simplicity of design and lower initial capital cost, these factors conspire toward higher energy consumption, by an estimated factor of at least 10% beyond the theoretical requirement per pound of water evaporated when compared to single-stage vacuum evaporation. Vacuum evaporators have been used successfully for more than 30 years by the surface-finishing industry for point source recovery of plating baths and rinsewaters. They are somewhat more complex and require a higher initial capital investment than single- stage, noncondensing atmospheric units.

Vacuum evaporators are instrumented for push-button, fail-safe operation and provide close and consistent control of the recovered bath concentration.

There are three main categories of vacuum evaporator used in the surface-fin-

ishing industry to recover dragged out plating bath and rinsewater: (1) single-effect (single-stage) designs, which are usually the most simple and easy to operate (Fig. 3); (2) multiple-effect (multistage) designs, which are more complex but are more energy efficient; and (3) some special designs for such applications as brine concentration. All vacuum designs are devices for distilling a liquid phase at reduced temperatures in the absence of air and for producing a concentrate. Water distillate is also recovered as a by-product.

Vacuum evaporators, as employed by the plating industry for bath and rinsewater recovery, are usually the more simple, less complex, single-stage designs consisting of a heated boiler section, a vapor/liquid separator section, a water vapor condenser, a vacuum circuit, and a control system. The boiler and condenser sections may be arranged horizontally or vertically. The most common heating source is clean, low-pressure, saturated steam, which is ideal because it is a demand energy source and requires a minimum of control. When the supply pressure is regulated, the steam temperature is automatically established and does not require further control. Units are available to accommodate hot water and electrically driven heat pumps.

Some of the benefits of operating under vacuum are that it reduces the boiling temperature of the bath being concentrated, which lessens or eliminates the potential for thermal damage to heat-sensitive constituents or additives; increases the temperature differential (the thermal driving force) between the heat source and the liquid being concentrated resulting in smaller, more efficient and less costly boiler and condenser designs; extracts resident air from the system upon startup and eliminates any possibility of carry-over of hazardous chemicals to a vent stream; excludes air from the system, which eliminates the potential for air oxidation of recovered chemicals or bath; recovers high-quality water distillate for return to the plating line; desensitizes the system to fluctuations in feed concentration when operated in a concentrate recycle mode; eliminates the potential for hazardous air emissions; lessens the tendency for scale to form on heating or other surfaces by operating at reduced temperatures; provides better management of foam; reduces the number of pumps required to one, the vacuum pump or eductor circulating pump, whichever is used; and provides tight process control by recovering bath at an adjustable and repeatable concentration.

The operating vacuum selected or recommended by the evaporator supplier is generally a function of the chemistry of the particular bath being recovered. Baths containing heat-sensitive constituents, such as expensive organic brighteners or additives, are usually concentrated under higher vacuum and lower boiling temperatures than are baths that do not require such constituents.

High vacuum operation requires physically larger evaporators to accommodate the higher specific vapor volumes encountered under those conditions and to maintain vapor velocities and system pressure drop within design ranges.

The level of vacuum, and thus the boiling point, can be varied within a specific range of vacuum for any given evaporator capacity. But, if an evaporator designed for optimum performance at 11 in. of mercury vacuum is operated below its design vacuum, say at 26 in. of mercury vacuum, vapor velocities will increase substantially and both the output capacity and product quality will deteriorate.

To satisfy the range of vacuum required by the widely differing bath chemistries used in the surface-finishing industry, suppliers of vacuum units have developed a series of standard, off-the-shelf, corrosion-resistant evaporator designs to accommodate most bath chemistries and operating requirements.

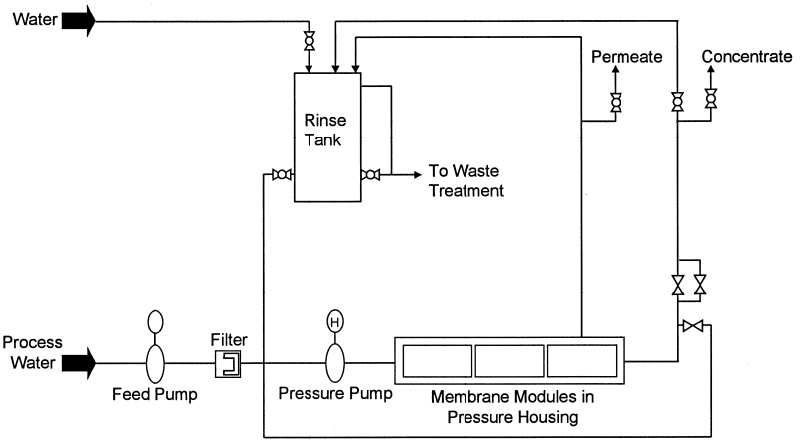


Fig. 4. Reverse osmosis flow schematic.

The energy demand of a single-stage vacuum evaporator is roughly 1,000 Btu/lb water evaporated, or roughly 9,000 Btu/gal of water evaporated (allowing for losses), the same as the theoretical energy requirement for atmospheric operation.

Because a high percentage of drag-out is usually returned with either atmospheric or vacuum evaporation, impurity removal and management may be required. Such purification techniques are well established. In the case of chrome baths, and thanks to the fact that chromium is present as an anionic complex, cation exchange or electropurification systems can be easily applied in a separate hydraulic loop around the rinse system to remove and control any cationic impurities that may accumulate. For chromium etch systems, electrolytic reoxidation of trivalent chromium or electropurification, should be considered. In this application, electropurification will produce less discharge than would a cation exchanger by its associated reagent waste stream.

Contaminant removal or purification techniques normally used with other baths, such as carbon filtration or dummying for nickel baths, membrane electrolysis for metal impurity control, or carbonate removal from cyanide baths, can continue to be applied to the process baths as required.

Vacuum evaporation has been successfully and dependably used for many years to recover a wide variety of plating baths including such difficult chemistries as encountered in chromic acid plating and chromic/sulfuric acid etch baths. Associated rinsewaters are also recovered for reuse in the plating process.

An application for vacuum evaporation of some increasing interest is brine concentration. In some localities, the discharge of pretreated metal-finishing effluent is being restricted because the effluent still has a high salt concentration. Salt is the unfortunate and unavoidable byproduct of chemical treatment of metal-bearing wastewater.

Usually, pretreated wastewater effluent is further processed by membrane systems to further separate and consolidate the mixed salt solution. The reject from this step can then be processed by any of several types of vacuum evaporator to concentrate the brine either to a level slightly below the limit of solubility of the salt mixture or slightly beyond to produce a concentrate discharge from which

the salt slurry can settle and be discharged. The supernatant liquor can be returned to the feed circuit where it will mix with the incoming feed for reprocessing through the evaporator.

Reverse Osmosis

After evaporation, reverse osmosis (RO) has the longest operating history. Most commercial recovery installations have been on nickel plating operations.

On the positive side RO is a relatively mature technology and uses considerably less energy than evaporation for the same rinsewater feed rate. A typical recovery scheme is given in Figure 4.

On the negative side, the degree of concentration of the separated bath by RO is limited. If maintaining appropriate permeate quality [10-100 ppm total dissolved solids (TDS)], the practical maximum concentration of the reject (or concentrate) is 10,000 ppm (1.4 oz/gal) TDS. If permeate quality is not an issue, then 50,000 to 80,000 ppm (6.7-10.7 oz/gal) TDS reject concentration can be achieved. In many cases, if the recovered solution is returned directly to the plating bath, there may not be sufficient natural water evaporation from the bath to accommodate the volume of recovered RO concentrate. Similar to evaporation, RO returns essentially all of the undesirable impurities.

RO has gained favor in recent years as a pretreatment for incoming process water, which has high TDS, and in some cases, for clean up of contaminated process water for recycle to the process.

RO is a pressure-driven membrane process. The driving force of this process, the hydrostatic pressure gradient, is the difference in hydrostatic pressure between two liquid phases separated by a membrane.

In reverse osmosis, particulates, macromolecules, and low molecular mass compounds, such as salts and sugars, are separated from a solvent, usually water. This is accomplished by applying a hydrostatic pressure greater than the osmotic pressure of the feed solution. The osmotic pressure of a particular feed solution varies directly with the concentration of the solution. In typical applications feed solution have a significant osmotic pressure, which must be overcome by the hydrostatic pressure applied as the driving force. This pressure requirement limits the practical application of this technology.

The transmembrane flux (permeate flow) is a function of hydrodynamic permeability and the net pressure difference—the hydrostatic pressure difference between feed and filtrate solutions minus the difference in osmotic pressure between these solutions. The osmotic pressure of a solution containing low molecular mass solutes can be rather high, even at relatively low solution concentrations.

In practice, it is practical to use RO to separate water (solvent) from all other substances of a solution in order to concentrate the solution and/or to generate or recover clean water for process reuse. The applied pressure is generally between 200 and 700 psig. In some cases, such as advanced reverse osmosis and high-pressure applications, the pressure may be as high as 1,000 to 2,000 psig.

Depending on both the characteristics of the dissolved constituents and on the practical operation of the equipment, the dissolved constituents are rejected differently. This phenomenon is called the membrane rejection rate. The fraction of nonrejected substances is called leakage. The leakage of the various salts is dependent on the following parameters: size of dissolved molecules, ion radius electrical load of the ions, and interacting forces between ions and solvents.

The rejection of organic substances is mainly dependent on the molecular weight and size of the molecules.

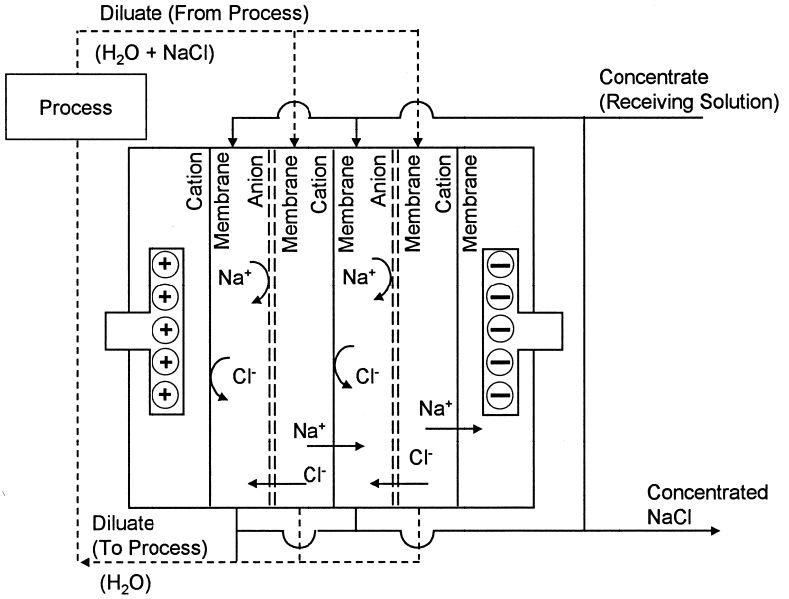


Fig. 5. Electrodialysis flow schematic.

RO has seen limited application to nickel rinsewater. RO can separate and return clean nickel bath, but usually at too low a concentration for total return to the process bath. Also, with RO, boric acid is partially transported across the membrane requiring monitoring and make-up as required.

Membrane performance decreases with operating time resulting in a decreased permeate flow rate (flux), which can be reasonably restored by periodic cleaning of the membrane. Over time, the membranes will likely require replacement due to damage from (1) hard water constituents; (2) fouling by organics; (3) general deterioration by acids or alkalis; (4) normal membrane compaction with use; and (5) destruction by oxidizing chemicals such as peroxides, hypochlorite, or chromic acid.

Electrodialysis

Electrodialysis (ED) uses a "stack" of closely spaced ion exchange membranes through which ionic components of a solution are selectively transported. The driving force is a rectifier-generated voltage imposed on electrodes at the two ends of the stack. Ionic components are pulled out of a relatively dilute rinse stream (the first flowing rinse station) and accumulated in a highly concentrated stream, which can be either returned to the process, as shown in Figure 5, or otherwise recovered.

The advantages of ED include low energy consumption, the ability to produce a highly concentrated stream for recovery, and the fact that only ionic materials are recovered, so that many undesirable impurities are retarded and rejected. On the negative side, ED is a membrane process, which requires clean feed, careful operation, and periodic maintenance to avoid damage to the stack, which is usually reconditioned by the manufacturer when required. ED units can be suc-

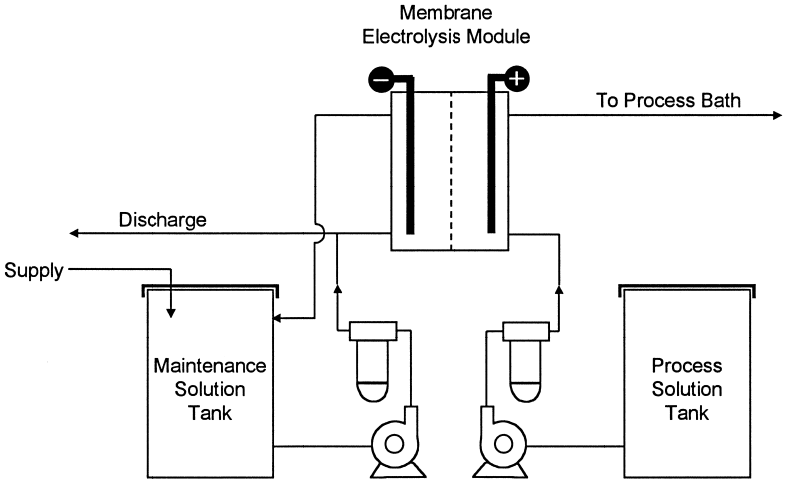


Fig. 6. Membrane electrolysis system schematic.

cessfully used to recover gold, silver, nickel, and tin electrolytes as well as selected acids and rinsewater.

An interesting feature of this technology is that a bright nickel electroplating bath can be circulated at a slow rate through the unit, thus providing a continuous removal of organic impurities, essentially eliminating the need for batch purification with its associated major losses of nickel metal.

Membrane Electrolysis

Membrane electrolysis (ME) is a membrane process driven by an electrolytic potential. It is mainly used to remove metallic impurities from plating, anodizing, etching, stripping, and other metal-finishing process solutions. This technology utilizes a diaphragm or an ion exchange membrane and an electrical potential applied across the diaphragm or membrane. Compared to electrodialysis, most membrane electrolysis systems utilize only a single membrane or diaphragm positioned between two electrodes.

The use of ion exchange membranes is advantageous because higher ion transfer rates can be achieved in comparison to inorganic- or organic-based diaphragms. Ion exchange membranes are ion permeable and selective, permitting ions of a given electrical charge to pass through. Cation exchange membranes allow only cations, such as copper or aluminum, to pass through. Similarly, anion exchange membranes allow only anions, such as sulfates or chlorides, to pass through.

The efficiency of ME depends on the migration rate of ions through the ion exchange membranes. The energy required is the sum of two terms: (1) the electrical energy required to transfer the ionic components from one solution through the membrane into another solution, and (2) the energy required to pump the solutions through the unit.

Electrochemical reactions at the electrodes are other energy-consuming processes, but the energy consumed for electrode reactions is generally less than 1.0% of the total energy used for ion transfer.

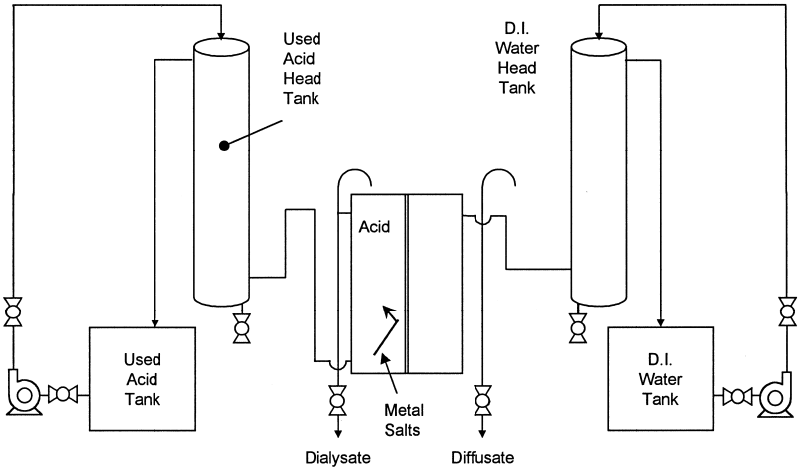


Fig. 7. Diffusion dialysis system schematic.

The total electrical potential drop across an ME cell includes the concentration polarization and the electrical potential required to overcome the electrical resistance of the cell itself. This resistance is caused by the friction between ions, membranes, and water during transfer from one solution to another, all of which results in an irreversible energy dissipation in the form of heat. Because of the heat generated, the total energy required in practice is significantly higher than the theoretical minimum energy required.

The energy necessary to remove metals from a solution is directly proportional to the total current flowing through the cell and the voltage drop between the two electrodes. The electric current required to remove metals from a solution is directly proportional to the number of ions transferred through the ion exchange membrane from the anolyte to the catholyte. The electrical energy required in ME is directly proportional to the quantity of metal (cations) that must be removed from a certain volume of anolyte to achieve the desired product quality.

Energy consumption is also a function of the electrical resistance of a cell pair. The electrical resistance of a cell pair is a function of the individual resistances of the membrane and the solution in the cell. Furthermore, because the resistance of the solution is directly proportional to its ionic concentration, the overall resistance of a cell is usually determined by the resistance of the weaker electrolyte. Figure 6 is a schematic of the ME cell.

ME can be utilized to remove metal impurities from process baths, such as etch and stripping baths, as well as conversion coating, chemical milling, and sealing solutions. An effective membrane surface area between anolyte or process solution and catholyte of 0.07 m^2 or 0.75 ft^2 allows a maximum amperage of 60 to 100 A for process solution purification. This membrane electrolysis process does not only remove metals from process solutions but also helps to maintain these solutions at certain activity levels.

When applied for the purification of a very corrosive solution that can dissolve metal electrodes, a three-compartment ME system must be used. A center com-

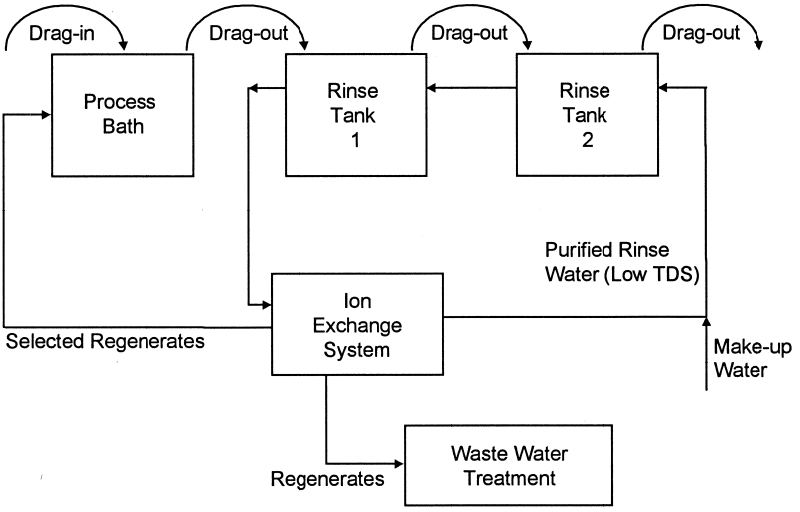


Fig. 8. Ion exchange schematic.

partment is utilized for the corrosive process solution and the adjacent compartments, which are separated by ion exchange membranes from the center compartment, operate as catholyte and anolyte compartments. During operation, anolyte/catholyte-maintenance solutions are recirculated through their corresponding cells and storage tanks. The purified process solution is pumped via a designated pump from the process tank back into the process bath.

Depending on the chemistry and the specific application, ME systems are designed either with cation or with anion exchange membranes. Typical applications for the ME technology in surface-finishing operations include regeneration of etching and stripping solutions; purification and regeneration of chromium plating baths; recycling and maintenance of chrome conversion coating solutions; and reactivation and metal removal from deoxidizing solutions.

Benefits of the ME technology are consistent performance and quality of etching agents and acids; constant production speed; accurate high-quality etching and chrome conversion coating results; reduced reject rate (no costly refinishing) reduced manpower requirement because of process automation; and reduced wastewater treatment and waste disposal result in lower operating cost.

Diffusion Dialysis

Diffusion Dialysis (DD) is also a membrane technology for separating and recovering clean acid from used or spent acid solutions. Compared to electrodialysis or ME, DD does not require an electrical potential across the membrane to effect separation. A flow schematic of a typical DD system is illustrated in Figure 7.

The separation mechanism utilizes the concentration gradient between two liquids—deionized (DI) water and the used process acid—separated by a specific anion exchange membrane, which allows natural diffusion of highly dissociated acid (anions) through the polymeric membrane structure while cations (metals) are

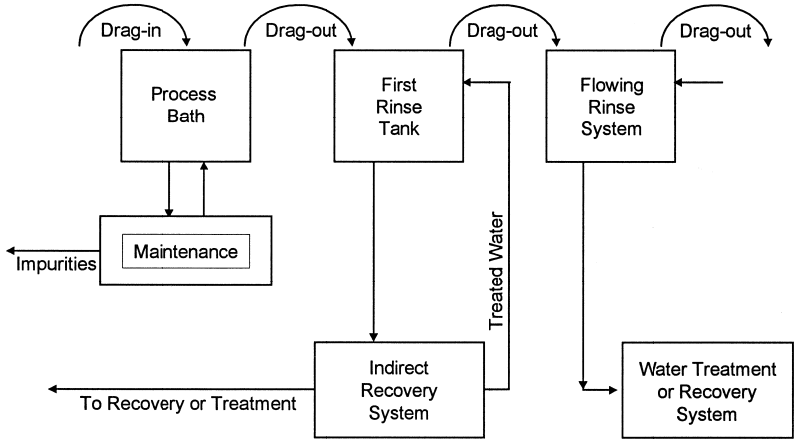


Fig. 9. General schematic for nonrecovery or indirect recovery methods.

rejected because of their positive electrical charge. The mechanism of free acid diffusion through the membrane, due to the concentration difference between the free acid and DI water, is known as Donnan diffusion.

Multiple layers of membrane are arranged in a filter-press-like stack through which both DI water and spent acid flow by gravity. Clean acid is separated from the feed stream by the concentration-driven transport mechanism across the membrane stack to effect a partition and recovery of an acid stream (diffusate) in conjunction with the generation and discharge of a waste stream (dialysate).

DD is being utilized for the following applications: recycle of hydrofluoric/nitric acids for etching stainless steel; recovery of sulfuric/nitric and sulfuric/hydrochloric acids for etching nonferrous metal; reclamation of sulfuric and hydrochloric acids for etching of steel-based materials; recuperation of sulfuric acid from anodizing processes; and regeneration of battery acids.

On the positive side DD is a low-energy, low-pressure, continuous process that requires no additional reagent or regeneration chemicals, resulting in less TDS in the plant discharges.

On the negative side, for every volume of acid recovered (diffusate), an equal volume of acidic waste (dialysate) is generated for further processing for recovery or for waste treatment. While the recovered, clean acid is generally reusable, the operating principle imposes a limit to the achievable concentration for the recovered acid, which can be fortified with concentrated acid as required.

Typical maintenance procedures for DD systems include: filtration of the feed stream to remove total suspended solids and to avoid deposition of suspended solids on the membranes; temperature regulation of the feed liquor and DI water supply within a prescribed temperature range to maintain recovery efficiency; and protection of the membranes against exposure to oxidizing agents such as chromic and nitric acids and to organic solvents, lubricants, inhibitors and surfactants.

With efficient feed filtration, membrane cleaning is generally required approximately twice per year. With observance of the above operating and maintenance practices, experience indicates membrane life can be about 5 years.

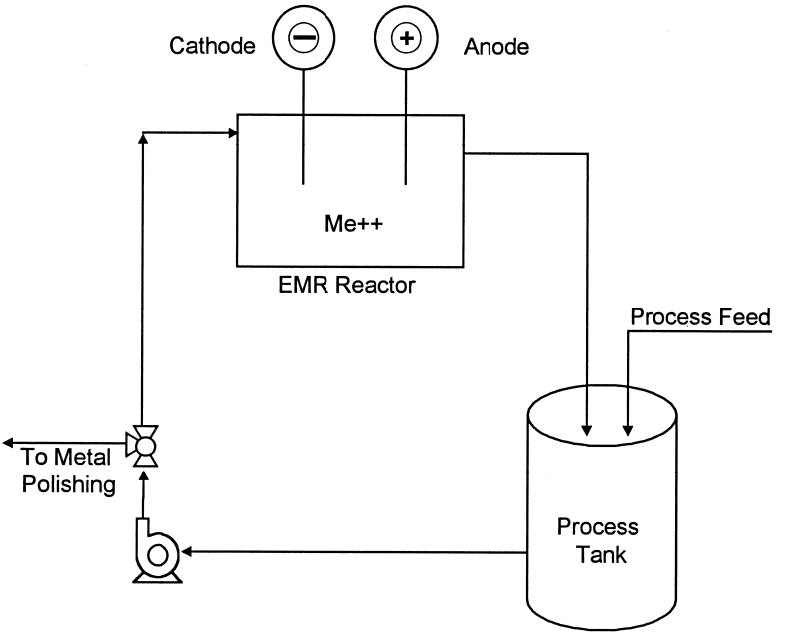


Fig. 10. Electrolytic metal recovery schematic.

Ion Exchange

Ion exchange is a chemically driven separation process. It is an ideal and useful separation method for collecting low concentrations of ionic materials, such as metal salts, from dilute rinsewater. This characteristic differentiates it from all of the previously discussed methods where relatively low flow rates and high concentrations of recoverable materials must be maintained.

From a recovery standpoint, ion exchange is not capable of producing a "highly" concentrated stream for recycle (20-25 g/L is a practical limit). It is also difficult to optimize the split between recovered metal salts and excess regenerant acid, which is intolerable in the plating bath. Also noteworthy is the fact that a waste stream containing excess regenerant must be dealt with, as shown in Figure 8.

NONRECOVERY METHODS

Nonrecovery or indirect recovery methods do not return concentrate to the originating process; thus, they obviate any concern over accumulation of impurities or the primary metal in the bath. The result is a "decoupling" of the recovery process from the basic manufacturing operation, which may be a considerable benefit if downtime or process upsets cannot be tolerated. A general schematic is given in Figure 9.

In certain instances, these nonreturn processes may also allow recovery from process bath losses other than drag-out (i.e., purification losses or plating bath desludging waste). This is in sharp contrast to the previous category of recovery methods, which can actually increase losses to purification or sludge removal oper-

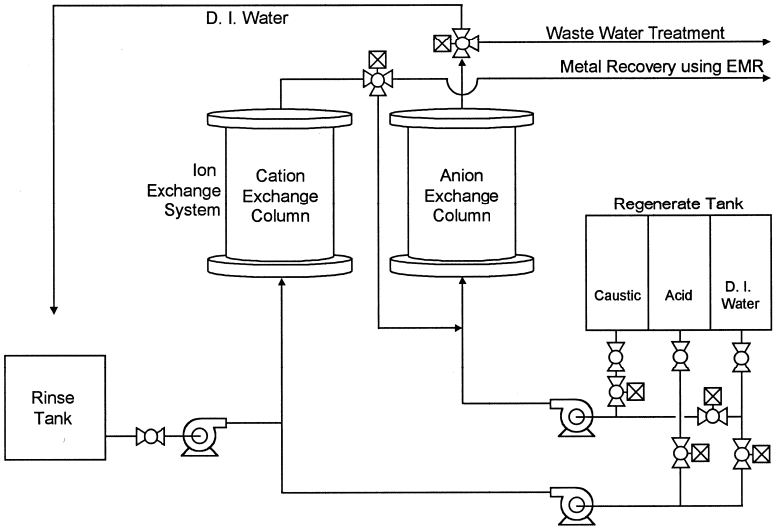


Fig. 11. Combined ion exchange and electrolytic metal recovery system schematic.

ations by increasing the frequency with which they must be performed.

Electrolytic Metal Recovery

In the metal-finishing industry electrolytic metal recovery (EMR) is both a useful and a familiar electrochemical process technique that applies special electroplating equipment to reduce the concentration of dissolved metals in many types of process solutions such as plating rinse water and dumped baths. Removing metal in solid form avoids the need to treat and convert the metal content of such process solutions to sludge. In the mining industry, EMR is referred to as electrowinning.

Recent advances in EMR cell design now make it possible to reduce the metal concentration of spent electroless baths and rinsewater prior to waste treatment and to recover metal from chloride or ammoniacal etch solutions while concurrently regenerating the etch baths.

There are three common embodiments of EMR in commercial use in the plating industry:

1. "Extractive" methods, which aim primarily to remove the metal from the recovery rinse but with little regard to byproduct value, are depicted in Figure 10. One of these deposits the metal on a sacrificial plastic starter cathode. The cost of the starter cathode and the undesirability of introducing plastic to a smelter or secondary recovery operation are a significant offset to any resale value of the metal.

   Another type of extractive cell produces a spongy or powdery deposit, which is removed as a sludgelike material (usually from the bottom of the recovery cell) and is usually of little or no value. The high surface area of the powder exposes a significant portion of the metal to oxidation. The

powder also entrains mother liquor, which is virtually impossible to rinse out completely. This results in an acidic, wet powder, often contaminated with halite ions, which in turn render the recovered metal powder difficult or impossible to reuse or sell.

2. High-surface-area recovery cells deposit the metal on some type of fibrous or filamentous substrate. In some cases, the plated metal is discarded or sold as a low- volume residue, while in others, the deposited metal is stripped chemically or electrochemically so that the end result is a concentrated solution of the metal that was recovered.
3. True EMR or electrowinning approaches recover a solid slab or sheet of relatively high-purity metal, that can be easily handled, weighed, assayed, or transported and sold for the best available price in the secondary metal markets. In certain recovery applications or circumstances, the electrodeposited metal is pure enough to be reused as anode material in the originating plating process. This type of cell usually applies some type of moving or rotating cathode, or alternatively, a high solution velocity over fixed cathodes.

To reduce the effect of electrode polarization common to low metal ion concentrations and to increase ion diffusion rates at the electrodes, it is recommended the solution be heated. Otherwise, plate-out of metal from these low concentration solutions will be hindered. Strong air agitation is another method for providing adequate mechanical mixing, but it removes heat from the system, thus reducing operating rates. Air agitation may also add to the load on air pollution control equipment.

Ion Exchange

In addition to the use discussed earlier under concentrate recovery methods, ion exchange can be used for several other applications, which include recuperation of noble metals, recovery of metals from rinsewater in combination with electrolytic metal recovery, and the purification of some process solutions such as chromate baths.

In gold recovery, ion exchange is effective in collecting essentially at traces from a dilute rinse stream. Historically, such gold-laden ion exchange resins were burned by a gold refiner who recovered the ash. Currently some companies are offering a tolling service to regenerate the ion exchange resin chemically and return it to the user.

In either case the primary disadvantages are the difficulty in assaying a heterogeneous mass of metal-laden ion exchange beads and the high tolling charges from the refiner or processor. Both of these factors preclude recovery of maximum gold value.

A second emerging application involves linking two recovery techniques; ion exchange and EMR. In this scheme, as shown in Figure 11, the ion exchange bed is used to collect metal ions from dilute rinsewater and the acid formed in the electrowinning operation serves to regenerate the ion exchange resin.

SLUDGES AS BYPRODUCTS

There has been a steady increase in the number of companies interested in using metal- bearing waste treatment sludge as a feedstock in their manufacturing processes; nevertheless, most mixed sludge has no value. In fact, the generator often

has to pay freight costs plus a fee to the processor for removal and treatment. A typical example would be a sludge containing 5 to 10% copper or nickel, which can be used as a feedstock for a pyrometallurgical operation (a smelter). Such metal-finishing sludge is a richer source of feedstock than the typical ore mined from the ground.

On the other hand metal-finishing sludge is typically highly variable in composition and can contain a significant amount of inorganic salt in the entrained water. Halides can be particularly troublesome in a smelting operation. From the standpoint of long-term liability, the metal finisher needs to consider that 90 to 95% of such sludge will not be turned into product at the smelter but will wind up in the smelter's residues. Although such recycling may appear advantageous under today's regulations, the long-term environmental significance of smelter residue needs to be factored into the decision.

A more promising situation exists if a metal finisher generates a segregated sludge that consists essentially of a single metal. Single metal sludges containing only tin, nickel, cadmium, copper, or zinc have excellent potential for being used as feedstock for reclaiming operations, which can operate in an environmentally "clean" manner, producing little or no residue. Furthermore, the metal content of such segregated sludge may be a candidate for in-house recovery by the metal finisher by redissolving the sludge and applying EMR. Segregated sludge is the natural by-product of the closed-loop or integrated rinse treatment method, which has been successfully practiced for decades in both the U.S. and Europe.

REGENERATION OF BATHS

Historically, most of the effort on recovery was focused on drag-out; however, most of the chemical load from a metal-finishing operation will usually be found in the dumps of expendable process baths and the losses from purification of plating solutions or sludge removal of the process tank. Operations, such as cleaning, pickling, bright dipping, etching, and chemical milling, are worth being investigated for recovery potential. Some of these applications are discussed in the following.

Copper and Its Alloys

EMR as described earlier is highly effective on many copper pickling and milling solutions including sulfuric acid, cupric chloride, and ammonium chloride solutions. Solutions based on hydrogen peroxide are generally best regenerated by crystallization and removal of copper sulfate with the crystals being sold as a byproduct or redissolved for EMR.

Bright dipping in highly concentrated nitric/sulfuric acid is a difficult challenge for regeneration because the solution volumes involved are usually quite small (5-25 gal) and the drag-out losses are very high. Regeneration is theoretically possible by distillation of the nitric acid and removal of copper sulfate but the economics are not likely to be attractive for most metal finishers. This approach does have potential for larger plating plants or for large-scale, centralized recovery facilities, which serve a number of plants.

Aluminum and Its Alloys

The caustic etch used in many aluminum finishing lines and the chemical milling solution used for aircraft components can be regenerated by crystallization and removal of aluminum trihydrate; however, the process must be carefully con-

trolled and maintained. The economics currently favor only relatively large installations but development of lower cost approaches is likely.

Sulfuric acid anodize solution and phosphoric acid bright dip bath can both be regenerated using DD or acid retardation, which is a sorption process using ion exchange resins. The cost and complexity of such recovery operations require economic evaluation on a case by case basis.

Chromic acid anodizing solutions can be regenerated by the use of cation exchange or ME. Both technologies can be used to remove the accumulating aluminum together with other metal impurities such as copper and zinc. The life expectancy of the resin is shorter than on normal waste treatment applications, but the method is still practical and economical. The use of ME has shown effective purification and maintenance capabilities of these baths.

Iron and Steel

Pickling is commonly used in steel mills for the surface finishing of steel products or as a pretreatment operation for a galvanizing process. Large volumes of spent acid containing metal contaminants are generated. Among the various methods available for acid purification and recovery, DD is very useful for the recovery of free acid from spent pickling baths.

Both sulfuric and hydrochloric acids are commonly used for cleaning steel. Sulfuric acid can be regenerated by crystallization of ferrous sulfate. Hydrochloric acid can be recovered by distilling off the acid and leaving behind the iron oxide. These technologies have been used for many years in large installations and by tolling reclaimers but are not likely to ever be economical for small metal-finishing or galvanizing plants where the production cannot justify the capital investment.

Plastic Etching

Concentrated chromic acid solutions are used to etch plastic surfaces prior to plating. These operations consume very high quantities of chemicals and generate large quantities of sludge. Standard practice today is to reclaim essentially all of the chromium from such an operation through a combination of evaporation and electrochemical oxidation of the trivalent chromium.

Today, a combination of evaporation and ME can be used to extend the operating time of a chromic acid etch indefinitely.

Alkaline Cleaners

Alkaline cleaners are probably the most widely used process baths in all of metal finishing. Treatment significance will increase as water recycling becomes a more prevalent practice. Most cleaner formulations are antagonistic to good treatment of a metal-finishing effluent because they are chemically formulated to keep dirt and oil in suspension. If their concentration is high enough in an effluent this same effect prevents efficient removal of the precipitated metals.

Dumps of alkaline cleaners, passing through a treatment system, are a notorious source of upsets and a high contributor to the TDS in a metal-finishing effluent. In addition there are certain cases where large finishing operations on small sewer systems, or small receiving streams, may have a problem meeting requirements for the organic content due to wetting agents and detergents.

The cleaning of parts in surface-finishing operations generates a lot of impurities in the cleaner bath. These impurities, such as oils, dirt, and soil, wear out the cleaner baths and have to be removed to extend the life of the cleaner. Free or tramp oil is usually removed with a skimmer. Emulsified oil will usually build up in the bath, with some of it splitting into a floating layer where

it will be removed by the skimmer. Most of the aqueous and semiaqueous bath formulations contain an inhibitor to provide rust protection for steel parts. Surfactants displace oil from the parts to be cleaned and form a stable emulsion. The life of the bath is dependent upon how much soil is brought in with the parts and how much drag-out occurs as the parts are moved from the cleaning bath into the rinse tank.

For many installations in surface-finishing operations continuous micro- and ultrafiltration systems using inorganic or organic membranes are successfully used to remove oils, grease, lubricants, soils, and solids from alkaline cleaners and can give the bath essentially indefinite life. An additional benefit is the steady-state condition of the cleaner, which will improve control over the process and the quality of the product being manufactured. The selection of the membranes is not only important regarding the operating temperature of the bath but also for the pore size or macromolecular structure. Elevated temperature can deteriorate organic-based membranes and too small a pore size can cause the rejection of valuable chemicals such as surfactants or inhibitors.

Phosphating Baths

Precipitates are formed continuously in phosphating operations presenting maintenance headaches and often resulting in the solution being discarded. Usually, the precipitates accumulate in the process tank, primarily on the heating coils.

When the solution is removed from the tank this accumulation of sludge can be manually removed. The solution should be decanted back into the tank to minimize wastage but this consumes space and time so the solution is often discarded and replaced.

It is far more efficient to install a continuous recirculation system through a clarifier with gentle agitation in the sludge blanket zone. This allows the solution to be used indefinitely, reduces the labor for manual clean-out of sludge, and allows a dewatered sludge to be easily removed from the bottom of the clarifier.

Chromating Solutions

Both ion exchange and electrochemical methods have been demonstrated to be effective for regeneration of spent chromates; however, in almost all cases, the metal finisher relies upon the proprietary chemical supplier to be responsible for the appropriate balance in the chromating bath. Either of these regenerating technologies makes the metal finisher responsible for the overall chemical maintenance of all constituents in the bath. It is possible that proprietary suppliers will provide a service to assist the finisher in maintaining a proper balance when one of the applicable techniques is applied. Economics are not likely to be attractive except in the case of high production operations using the more concentrated chromates, which give high salt spray resistance against "white rust."

RECOVERY AND RECYCLING OF PRETREATED WASTEWATER

Conventional techniques for water conservation (countercurrent rinsing, conductivity controls, etc.) are used extensively in the industry; however, the unavoidable end product of all waste treatment methodologies is a "salt" containing effluent, or brine. Effluent TDS from such a system can be sufficiently high to limit potential for recycle and reuse as process water without desalination.

Clearly, achieving the minimum consumption and discharge of water necessitates segregated handling of concentrated solution dumps since

they will carry more TDS over a given period of time than bath drag-out. In a similar fashion the use of segregated closed-loop treatment rinses allows the first station of the rinse system (drag-out tank) to be as high as 10 to 15% of the TDS of the process bath, greatly extending the opportunity to recycle subsequent higher quality rinses.

There is increasing interest in this country to further close the loop by desalinating a treated effluent for maximum recycle and reuse. A number of large plants have been constructed with all of the TDS being concentrated into a small volume of brine, which is hauled from the plant.

While this may be necessary and economical in some cases it is not logical for most cases. Unless the plant is located near a seacoast, disposal of the brine is likely to be problematic. It is highly corrosive to concrete and steel structures and more difficult to assimilate in the environment than a high volume effluent at 1,000 mg/L TDS. The real answer lies in reducing the consumption of chemicals in the metal-finishing operation and thus the quantity of TDS requiring discharge.

For situations where desalination and recycling of a treated effluent is desirable or necessary the following treatment technologies can be considered.

Ion Exchange

Recycling of metal-finishing wastewater through ion exchange equipment has been practiced for decades in Germany and for many years in Japan. Practical experience shows the need for segregated collection and treatment of not only batch dumps but also the first rinse after each process that flows at a rate to take away approximately 90% of the chemical load.

Secondary and/or tertiary rinses can then be recirculated through ion exchange equipment after very thorough particulate filtration and carbon filtration. Cyanide and hexavalent chromium are problematic because they are poorly released from the anion exchange resins and tend to exist as perpetual low-level contaminants throughout the plant's rinsewater system.

Aside from high cost, the major drawback of this approach is that it actually increases the TDS discharge from the plant. In theory, if regeneration of ion exchange resins could be perfectly efficient, the process would multiply the TDS removed from the recirculated water by a factor of two. In practice, however, a 100 to 300% excess of regenerant chemical is typically required. This can be reduced to the range of 50 to 100% excess by holding and reusing certain fractions of the regenerant waste stream at the cost of additional capital investment and operating complexity. As a result of this need for excess regenerant, the TDS removed from the recirculating rinsewater is multiplied by a factor of three to six.

Since it is the TDS that presents the problem for the environment and not the water, this approach does not hold long-term promise for the metal-finishing industry. In Germany, the population density has exacerbated the problem with TDS accumulating in the rivers. Practicing water chemists now recognize the counterproductive nature of this treatment process.

Evaporation/Distillation

Where either waste heat or reliable solar energy are available, vacuum evaporation or multistage vacuum distillation can be an attractive alternative for producing clean water. Capital costs are high but the ability to concentrate the brine is virtually unlimited and the equipment is rugged and reliable.

Reverse Osmosis

RO technology has been refined and extensively applied to the desalination of sea

water and brackish waters. Metal-finishing wastewater requires a relatively high degree of pretreatment and filtration to protect RO membranes from fouling. Pretreatment processes can be designed so that soluble compounds, such as metal silicates and oxides, can be removed as precipitates by a filtration stage to such a high degree that membrane fouling can be significantly avoided; however, because of the wide variety of chemicals used in metal finishing, the water chemistry can be complex, highly variable over time, and difficult to accurately predict.

The large commercial scale installations have had mixed results. Success on one plant effluent is not assurance that the next will be workable. In addition the concentration of brine that can be produced is relatively low so that large quantities of low-concentration brine require disposal.

Electrodialysis

ED has also found extensive commercial applications for desalination of brackish water; however, the efficiency of the process falls off unacceptably if the product water is not in the range of 500 to 600 mg/L TDS or higher. The process can produce a rather high concentration of brine and the water quality limitation can be overcome by using RO or ion exchange for high purity applications within the plant.

Since ED is also a membrane process, similar concerns apply as mentioned for RO; however, ED is likely to prove somewhat more tolerant of varying water chemistry. This is due to the ability to frequently reverse the electrical potential across the membrane stack, which helps offset the fouling tendency, albeit at a sacrifice in capacity.

Zero Liquid Discharge Systems

Some firms, because of their location in small towns with small municipal treatment plants or because of discharge restrictions or other circumstances, have implemented treatment and recovery programs geared to recover all possible process water for recycle and reuse within the plant. Only solid sludge or brine slurry is produced for haul-away and disposal. These firms come as close as practical to having a zero discharge operation.

While any of the foregoing methods can be applied individually to condition raw water, the recovery and conditioning of pretreated effluent requires a multistep process. It is not uncommon for a pretreated effluent to still have high TDS, mostly as sodium sulfate or sodium chloride. Some firms have successfully applied all or some of the following process steps to further process pretreated, high-TDS effluent to recover clean, reusable process water and to achieve zero liquid discharge: sand filtration, carbon filtration, single- or two-stage RO followed by mixed bed ion exchange (if necessary).

The reject from the RO system, which may still represent a considerable volume of dilute brine, can be further processed by vacuum evaporation to achieve a concentration close to the limit of solubility of the brine mixture, which is discharged from the evaporator at an elevated temperature. Upon cooling, salt crystals will separate and settle. The supernatant liquor can be mixed with the RO reject feed stream and circulated back through the evaporator. Meanwhile, the resulting salt slurry can be removed from the settling tank for further dewatering, which is not usually necessary, and readied for haul-away.

A process of this nature is probably not economically viable unless the total daily volume of process water used in the plant is in the order of 50,000 gpd or more.

REDUCING OPERATIONAL COSTS, ENVIRONMENTAL IMPACT VIA RIGOROUS PLATING/FINISHING ANALYSIS

BY DAVE FISTER, SENIOR STAFF ENGINEER, THE NEW YORK STATE POLLUTION PREVENTION INSTITUTE AT ROCHESTER INSTITUTE OF TECHNOLOGY, ROCHESTER, N.Y.

In good economic times, there is not as much motivation for a business to take a hard look at the cost of their plating or finishing processes. With fierce competition from overseas, and a weak economy, the need to look at these processes becomes much more important.

Surprisingly enough, once the real costs associated with plating and finishing lines are known, there are many options available to reduce some or all of those costs, and the economic paybacks can be very short.

We will present the methodology used by the New York State Pollution Prevention Institute at Rochester Institute of Technology to determine the baseline costs of the finishing operation. Potential improvement methods or technologies will be presented for each area typically found in any finishing line.

There are four areas common to almost every plating line and metal finishing line:

- **Rinse tanks**
- **Ventilation systems**
- **Acid cleaners, acid etches**
- **Alkaline cleaners**

It is important to collect good baseline information on each of these areas. Once that information is collected, it is easy to rank each area by cost and to look for the best options to reduce those costs. It is also very helpful to create a line layout—if one does not already exist—to help clarify the process steps and material flow. As much detail as possible should be contained in the line layout. Decisions will be much easier later in the evaluation if the layout information is complete. A spreadsheet is also helpful to aid in calculating chemical costs, water costs, etc., and can be readily updated as more information is collected.

The following question lists will provide sufficient information to develop baseline cost information.

Baseline questions for rinse tanks:

Number of rinse tanks after each process tank?

What is the rinse tank type (single rinse, reactive rinse, counterflow rinse, stagnant rinse, spray rinse)?

What is the flow rate on each rinse tank?

What water type is required for each rinse tank (reverse osmosis, deionized water, city water)?

Does the rinse water contain either high toxicity or high value material (chromic

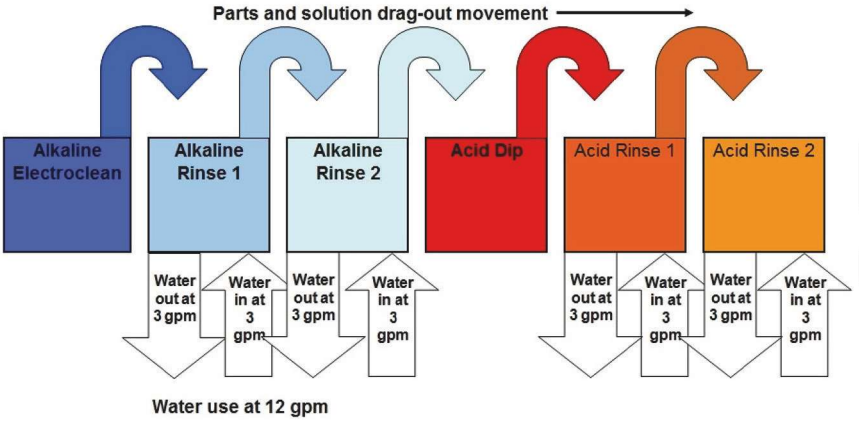


Figure 1. Rinse system with four independent rinse tanks.

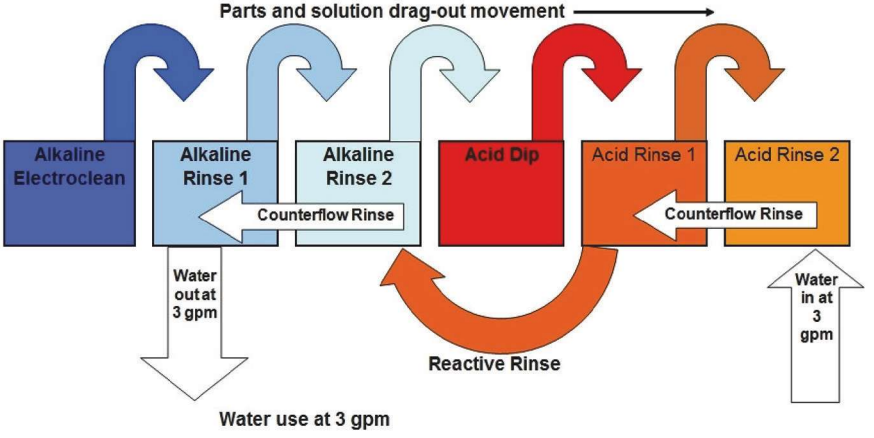


Figure 2. Maximized use of counterflow and reactive rinses.

acid, gold, etc.)?
What are the water purchase and sewer costs per 1,000 gallons of water? Note that these water costs can be either combined on one bill or separate. Rochester, N.Y., has monthly water billing and an annual sewer tax based on annual water use.

Baseline questions for tank ventilation:
How many plating line ventilation systems are there (scrubber, straight exhaust, etc.)?
What are the rated CFMs for each exhaust fan?
What is the horsepower rating or volt, amp, phase rating for each exhaust motor?

What is the total exhaust time per day?
What are the heating degree days for your location?
What is the building heating (and possibly cooling) cost by month?
Are the plating line ventilation systems tied into automatic tank covers?

Baseline questions for the acid and alkaline tanks:
What are the tank volumes?
What is the tank chemistry
concentration?
Cost of the chemistry per tank refill?
Tank dumps per year, and reason for tank dumps?
Cost to treat the chemistry after the tank dump (labor, neutralization chemicals, sludge disposal, etc.)?

Once armed with the baseline information, it is relatively easy to determine the real cost for each area. Then it is possible to prioritize the costs and target cost reduction changes. The following baseline example is from a medium-sized job shop plating company that was part of a direct assistance program through the New York State Pollution Prevention Institute. The baseline list has been ranked by cost.

1. Water use = 6,310,000 gpy (gallons per year) = $32,900/yr. ($5.22/1000 gallons)
2. Acid purchases (HCl) = $19,700 ($1.25 /gallon, 15,760 gallons)
3. Waste treatment sludge disposal = $15,600/year
4. Exhaust blower = 10,000 cfm = $7,899/yr. for 40 hours per week ($.09/kwh)
5. Caustic purchases (NaOH) = $6,400 ($2.10/lb, 3,048 lbs.)
6. Heating of make-up air = 431 decatherms = $2,154 /yr. ($5/decatherm for natural gas)

Total cost per year = $66,923/year

In this example, the water cost was by far the highest single cost to the company for their plating lines. A close second and third were the acid purchases (included line acid and waste treatment acid), and waste treatment sludge disposal.

RINSE WATER OPTIONS

It might not be typical for all metal finishing operations but it is fairly common to have water costs at or near the top of the cost of operations. Rinsing is critical in the metal finishing process, but more water use does not necessarily mean better rinsing.

Best practices for producing effective rinsing are:

- **Multiple counterflowing immersion rinse tanks between process tanks**
- **Reactive rinsing for the appropriate process chemistry combinations**
- **Spray rinsing**
- **Combination rinses such as immersion rinsing, followed by spray rinsing or reactive rinsing combined with counterflow rinsing**

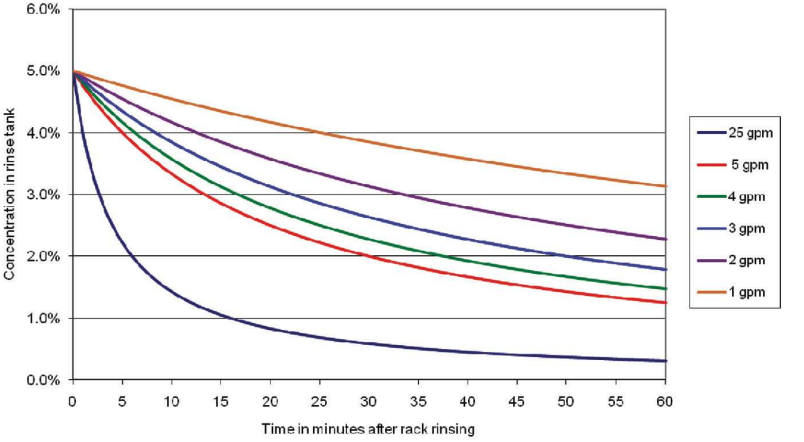


Figure 3. Rinse water flow dilution rates.

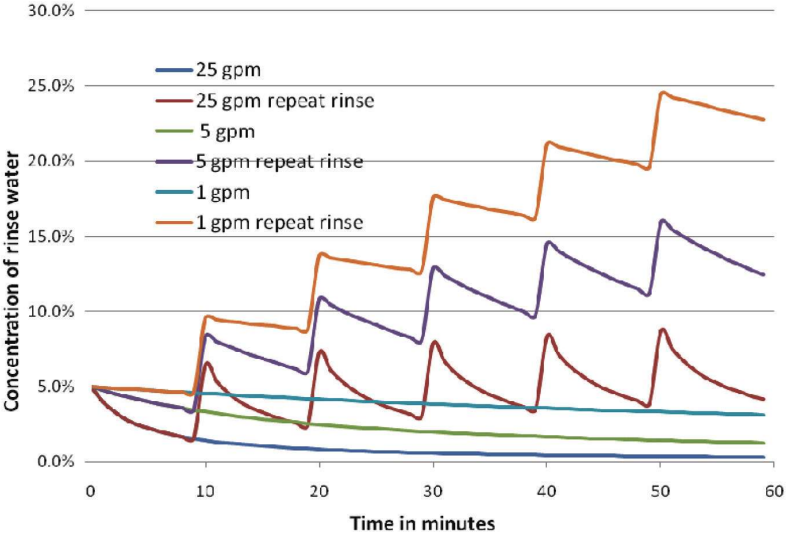


Figure 4. Parts rinsed in tank every 10 minutes vs. single rinse.

Figure 1 shows a rinse tank system with multiple rinses but with no counterflow rinsing on any of the neighboring rinse tanks. In this example, if each rinse tank is a flowing rinse, the total water use is 12 gallons per minute (gpm).

There are two means of reducing the water use in rinsing without reducing the flow rate in each tank. The first is called counterflow or countercurrent rinsing, where the relatively clean rinse water from the second rinse in a rinse tank pair is flowed to the more contaminated primary rinse tank. Therefore, cleaner water is always moving to less clean rinse tanks. The cleanest water is still used for the

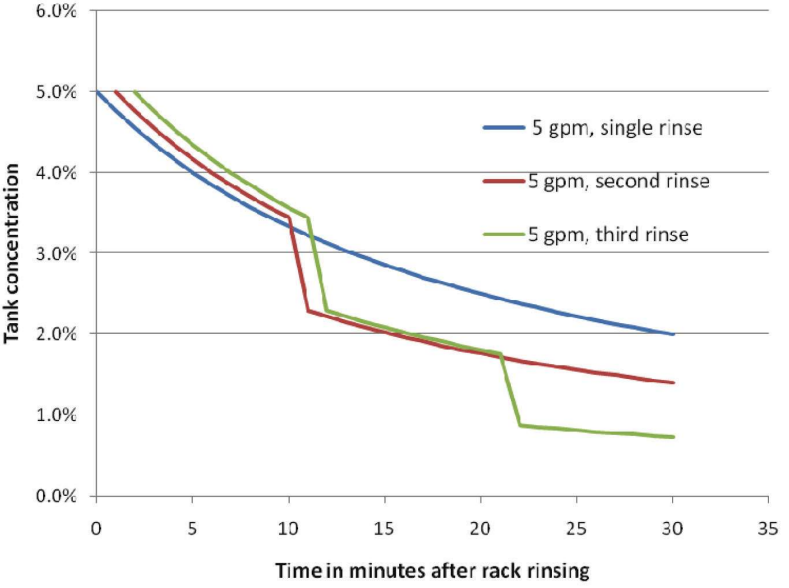


Figure 5. Contaminant concentration in two-tank and three-tank counterflow rinses.

critical final rinse, but the same rinse water is reused for the initial and least critical rinse. In Figure 2, if counterflow rinsing was the only additional water-saving method used, there would be a 50% reduction in water use (6 gpm) compared to Figure 1 (12 gpm).

The second, less commonly used method of reducing water use is called reactive rinsing. It is a method of taking rinse water around a process tank to a previous rinse tank. The example in Figure 2 shows acid rinse water (acid rinse 1) flowing to the last alkaline rinse tank (alkaline rinse 2). The acid contained in this rinse water would normally be sent to waste treatment. With reactive rinsing, the acid from acid rinse 1 now goes to alkaline rinse 2 and neutralizes the residual alkalinity in that water. Any rinse water from alkaline rinse 2 being dragged out by parts and racks to the acid tank will now contain acid which previously would have been wasted. Therefore, no acid is being neutralized by alkaline dragout to the acid tank, and acid previously lost in acid rinse 1 now has some recovery by the reactive rinse flow. Figure 2 has a total water use of 3 gpm compared to the original flow rate of 12 gpm. The cost savings is $5,400 per year at $5/1,000 gallons for an 8-hour-per-day, 50- week operation, if 9 gpm is saved.

Oftentimes, when the rinse appears to be inadequate, companies assume that the best method of improving an immersion rinse is to increase the flow rate. However, rinse flow rates can be deceptive in that high flow rates might not be as helpful as expected. Figure 3 displays rinse tank concentration over time at various flow rates. The initial conditions are: 100 gallon rinse tank, incoming (dragout) solution concentration of 100 grams/gallon, and a dragout volume per rack of 0.05 gallons. It is apparent from Figure 3 that the rinse tank does not dilute the dragged-in chemical very rapidly. Even the 25 gpm flow rate takes

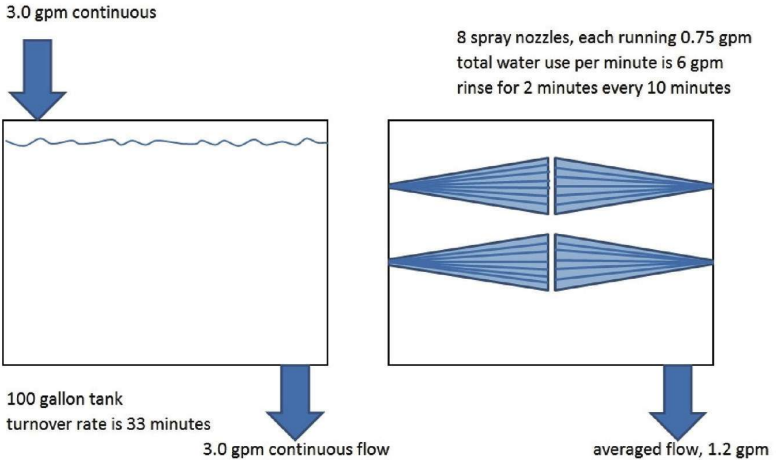


Figure 6. Spray rinsing compared to immersion rinsing.

approximately 5 minutes to drop the concentration from 5% to 2.5%. The main point is that a single rinse tank is relatively ineffective at providing critical rinsing. More importantly, increasing the flow rate in a rinse tank does not necessarily improve rinsing unless extremely high and costly flow rates are used.

By taking immersion rinse flow rates one step further, Figure 4 shows the same rinsing example as shown in Figure 3, with the exception that every 10 minutes an additional load of dragout chemical is added. Note that this causes the rinse tank concentration to rise to very high concentrations very quickly, regardless of the flow rates used. This is another reason that counterflow rinsing is so effective. The concentration of the dragout chemistry between the first rinse tank and the second rinse tank drops dramatically. Thus, the effective dilution rate due to water flow is much faster, as shown in Figure 5.

The final method of reducing rinse water volumes but still obtaining excellent rinsing is by spray rinsing. This method is somewhat limited by the geometry of the parts being rinsed in that complex geometric shapes are difficult to thoroughly rinse with an automatic spray system. In a manual line, the operator can overcome the geometry problem of a part by manually spraying the part areas that are difficult to rinse by a normal battery of spray nozzles. Figure 6 compares a spray rinse to an immersion rinse. There are two major advantages to spray rinsing over immersion rinsing. First, the water hitting the parts is always clean—unlike water in an immersion tank which always contains some residual contamination. Second, a spray rinse needs to be running water only when parts are being rinsed. The rest of the time there is no water use, which is both a cost and environmental savings. A third and lesser advantage to spray rinsing would be in the case of parts requiring a heated rinse. In-line demand heaters can be used to provide hot water as needed during the spray cycle rather than having to continuously heat an immersion rinse tank.

The spray system in Figure 6 illustrates the water savings associated with spray rinsing compared to immersion rinsing. The left illustration in Figure 6 is

Exhaust CFM	Blower hp	Annual electricity cost, $.09/kW-hr	Annual make-up air heating cost, $5/decatherm of natural gas	Total annual ventilation, heating cost
10000	50	$23,696	$6,463	$30,159
8000	40	$18,957	$5,170	$24,127
5000	20	$9,479	$3,231	$12,710
2000	10	$4,739	$1,293	$6,032

Table 1. Example of costs associated with plating line ventilation rates (operation on a 24-hour, 5-day basis).

a typical immersion rinse tank running at 3 gpm. The right illustration is a spray rinse with a battery of eight spray nozzles with a combined spray volume of 6 gpm. The spray rinse in this scenario is only turned on for two minutes while parts are in the tank. The next set of parts arrives eight minutes later. Since the spray rinse is turned on only for two minutes out of a 10 minute period, the average water use is 1.2 gpm, which is less than half of the immersion rinse tank's usage rate of 3 gpm.

One final way to reduce rinse water use in immersion rinse tanks is by controlling the rinse water valves. This method is a means of limiting flow when rinse water control consists of manually operated valves. The simplest method is to insert flow restrictors on the water valves to limit the maximum flow regardless of the valve's position.

Another method of water valve control is to insert solenoid valves into the rinse water lines which open or close based on the conductivity of the rinse water in the tanks. This requires minor up-front measurements of the water conductivity, which is often directly related to the amount of chemistry being dragged into the rinse water. The valve conductivity controls are then set to turn the water on when the conductivity (contamination) gets too high and then turn the water off when the conductivity drops to a lower set point. The advantage of this system is that the water stops running when a plating line has a break in the work flow, rather than manually turning the water on and off at both the beginning and end of the day regardless of the amount of work running through the line. These conductivity controlled valves can be purchased as systems that include the solenoid valve, conductivity probe, and conductivity control box, and typically cost between $500 and $1,000 (Myron L Company).

Water Reuse:

Most metal finishing industries have in-house wastewater treatment to economically dispose of the acids, alkali, oils, and dissolved metals in the rinse water and occasional tank disposal. However, after treatment this water is typically sent to the sewer since there are still chemicals in the water which makes it unsuitable for reuse. The main post-treatment chemicals in the water are salts such as sodium chloride from the neutralization of hydrochloric acid and sodium hydroxide. Other residual chemicals could include soaps, chelating agents, or surfactants which would be problematic in recycled rinse water.

Typical treated wastewater is:

- **Very low in dissolved metals**
- **Very high in total dissolved solids (TDS) from neutralization and treatment**
- **Consistent pH, typically slightly alkaline from metal precipitation process**
- **At room temperature**
- **Often mixed with residuals such as oils, soaps, or emulsifiers**

Both money and labor were spent to treat this wastewater and money was spent to purchase the water and send it to the sewer. Therefore, reusing the water in the process is a means of recovering a portion of that cost. A reverse osmosis (RO) system is one means of recovering at least 50% of this treated water and making it very useable as rinse water again. Reverse osmosis is a technology that filters water with a membrane and allows only water molecules and small amounts of sodium, chloride, or potassium to pass through the membrane (0.5 to 3% leakage of salts is typical). The actual process works by applying pressure to the "dirty" water, which forces the clean water through the membrane and leaves the larger molecules behind.

ADVANTAGES OF RO FILTRATION:

- **Removes everything: ions*,bacteria, viruses, solids, dissolved solids**
- **Relatively simple, low maintenance system**

DISADVANTAGES OF RO FILTRATION:

- **Low temperature water produces lower pure water yields**
- **Higher TDS water produces lower pure water yields**
- **Tends to leak small amounts of single charge ions (Na+, K+, Cl-)**
- **Membrane can foul rapidly if suspended solids are high (may require pre-filtration with an ultrafilter)**
- **The RO process is relatively slow such that the most economical RO unit will be running during both production and non-production hours (filtering stored treated wastewater and storing filtered water during off hours)**

Current technologies allow up to about 75% fresh water yields. More typical yields are 50% at optimum conditions of temperature and minimal TDS levels. Even with recovery rates of 50%, typical RO systems have a payback of one to two years with water savings. As an example from a case study, an RO unit rated for 15,000 gallons per day water recovery would cost approximately $20,000 and save approximately 3.2 million gallons per year ($17,000 savings/year).

Before purchasing an RO system, it is important to implement other water savings measures first so that the RO system is properly sized for the reduced

water volumes. Otherwise, the RO system will be underutilized as other water savings measures are implemented.

EXHAUST SYSTEMS

Exhaust systems are an essential part of the plating line designed to remove dangerous fumes from the process tanks. Typically the highest cost of an exhaust system is the electricity used to run the exhaust blowers. The secondary cost will be very location-dependent and is the cost of reconditioning the make-up air either by heating, cooling, or both. As noted in the plating company example referenced above, the cost to run the blower was roughly four times the cost to heat the make-up air in the upstate New York climate. If the total exhaust requirements can be reduced, then the exhaust blower will be smaller and the make-up air costs will be proportionally smaller. Table 1 shows the total costs associated with various size exhaust systems as the system size changes. Average heating-degree days in Rochester, N.Y., were used to determine the heating costs.

One method used to reduce the total exhaust requirements is with automatic tank covers and variable speed fan controls within the exhaust system. If only one tank requiring exhaust is open at a time, then the exhaust system size can be reduced to handle the full required CFMs for that tank and some small additional CFMs to provide fume extraction from under the closed tank covers. Unfortunately, the best time to implement this technique is on a new plating line. Retrofitting an existing line is sometimes possible depending on the type of the line, but is likely to be more expensive than incorporating this type of system into a new line. As can be seen from Table 1, the cost savings can be significant, even if the exhaust system is reduced by only 50%.

ACID CLEANERS AND ACID ETCHANT LIFE EXTENSION

The starting point for extending the life of an acid bath is having good process controls for the acid bath. Without good monitoring and acid addition methodology, an acid bath can be prematurely disposed of just because the acid strength was not kept at the proper level. If an acid tank is minimally managed, such as running a tank for a month and then disposing of it with no acid additions or titrations over that time period, then the tank effectiveness is variable and unknown. This could lead to plating or finishing defects as the tank ages. If the tank, in reality, was in good condition in that time period, then disposing of the tank is a needless waste of acid and an added cost to treat the acid waste. In another direct assistance project, the New York State Pollution Prevention Institute was able to reduce a 500-ton-per-year acid waste stream to a 250-ton-per-year waste stream at a savings of almost $200,000 per year. Rigorous acid management practices were used to produce these savings.

Good process control means that there is a routine sampling of each acid tank for chemical analysis. On a weekly basis, and in the case of high production lines, a daily titration of the acid baths may be necessary to properly control the acid strength. Then there should be equally regular acid additions to the acid tanks based on the titration results to bring the acid levels back to their original strengths. For large operations there are systems available that do the titrations and acid additions automatically, such as Scanacon titration and acid-dosing equipment.

Second, and usually less frequently, each acid tank should be measured for dis-

solved metal content. These two tests, titration and metal analysis, are the basic requirements for the proper function of the acid process.

The main reason to dispose of an acid tank and start with a fresh chemistry is due to dissolved metal concentrations being high enough to interfere with the acid-metal reaction. Therefore, a means of extending the bath life involves either removing the dissolved metal or converting the dissolved metal to a form that no longer interferes with the acid-metal reaction.

There are three commercially available methods that deal with the dissolved metal problem.1

1. Additives to precipitate and/or sequester the dissolved metal
2. Diffusion dialysis
3. Acid sorption

1. Additives

Metal precipitation/sequestering is an in-tank means of removing a portion of dissolved metal by precipitation and a portion by sequestering (possibly chelation). PRO-pHx™ (www.pro-phx.com) is one example of such a chemical method. PRO-pHx has a proprietary formulation, but it is believed that part of the chemical reaction produced by PRO-pHx™ involves metal being sequestered because dissolved metal concentrations can go much higher than what would be expected without any apparent loss of acid-metal activity. The high concentrations of dissolved metal are prevented from interfering with the normal acid-metal activity which would indicate some form of sequestering action.

In normal operating use, PRO-pHx is added to the acid tank to maintain a 1% concentration of the additive. A portion of the dissolved metal forms a precipitate that can be filtered. The remainder of the dissolved metal stays in the acid tank but in a form that is not active.

2. Diffusion dialysis

The diffusion dialysis process makes use of a membrane that allows the acid's negative ions (SO4-2, NO3-2, Cl-1, etc.) to pass through while preventing the positive metal ions from passing through. A typical system is 90% efficient, meaning that 90% of the acid is recovered and 90% of the metal is removed in each membrane pass. The results are a waste stream that is high in dissolved metal and a acid stream that can be returned to the acid tank.

3. Acid sorption

The process of acid sorption works on the same principle as ion exchange in a water deionization system. The acid anions (negative charge) are captured from the acid solution stream by an ion exchange resin while allowing the positive metal ions to pass through. Then the resin column is back-flushed with fresh water to free the acid anions. This back-flushed solution is, therefore, rich in acid and poor in dissolved metal. The acid-rich solution can then be returned to the acid tank. This method is between 80% and 90% efficient.

The acid sorption process is commonly used in large aluminum anodizing systems to maintain the amount of dissolved aluminum in the correct range.

The economics will determine which method of acid recovery makes sense for each metal finisher. Again, that is why it is critical to know the cost of acid purchases and disposal to determine the payback for acid recovery systems.

ALKALINE CLEANER CONTROL AND LIFE EXTENSION

In the typical metal finishing process, the alkaline cleaning tanks are first in line and take the bulk of the dirt load. Whether the tanks are soak, ultrasonic, or electrocleaners, their purpose is to remove oils, grease, wax, polishing compound, particulates, and light oxides from the part surfaces. Depending on the detergent additives in these tanks, the tanks could build up surface oil, oil emulsions, suspended solids, or sludge at the bottom of the tank or any combination of these contaminant types. As with acids, the cleaning chemicals are consumed in the process of removing and preventing redeposition of the contaminants.

First, there should be a procedure in place to monitor the alkaline cleaning strength of a bath. It may be as simple as measuring the pH. Typically the cleaning chemistry supplier can either do the testing or provide test kits or test methods to monitor and correct the cleaning chemistry as it ages.

Second, the surface oils can be segregated and removed by a combination of surface sparging and the use of various oil skimmers available on the market.

Third, the heavy particles that can settle on the bottom of the tank can be removed by bag filtration or some other simple filtration method.

Finally, there are the emulsified oils and suspended solids. These are more difficult to remove by normal filtration methods. Ultrafiltration is a method that can often break the oil emulsions and remove the suspended solids without removing the active cleaning chemistry. Some of the commercially available ultrafiltration systems can handle pH from 2 to 11 and temperatures up to 160°F. One unique ultrafiltration system manufactured by Arbortech Corporation has filtration capability of a 1 to 14 pH range and temperature limits of over 200°F. Therefore, this system can easily filter hot alkaline cleaners without filter damage. By whatever ultrafiltration method used, the resulting filtered cleaning solution should have minimal loss of the cleaning chemistry and maximum removal of the suspended solids and emulsified oils such that the cleaning chemistry is ready to use again.

Again, the economics of the cleaning process will drive the decision- making process. If the cleaning chemicals are inexpensive and easy to treat in wastewater treatment, and if tank life is already extended before contamination levels become excessive, then only the simplest and least expensive methods need to be used to provide acceptable cleaning chemistry maintenance.

SUMMARY

In conclusion, there is often a large opportunity for plating industries to reduce their costs, minimize their environmental footprint and remain competitive in their sector by various relatively simple and sometimes low- cost process changes. By developing a baseline for the energy use, chemical use, and water use for the process, a list of priority focus areas will be determined and the opportunities for cost savings will become evident. In regards to the finishing line, an essential first step is to develop a set of best practices for rinsing and rinse control for water use optimization, along with good process control for the acids and alkaline cleaners. By understanding the overall detailed costs of the metal finishing process, decisions can be made to determine where the major opportunities are and implement changes that financially benefit the bottom line.

FILTRATION AND PURIFICATION OF PLATING AND RELATED SOLUTIONS AND EFFLUENTS

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This introduction reflects the response needed by platers for quality control, to meet just-in-time deliveries, and to achieve zero rejects. It also addresses the need for platers to continue to reduce solid waste after neutralization and employ filtration wherever possible to recycle or lengthen the service life of cleaners, etchants, and rinses.

Filtration usually includes the use of carbon for undesirable organic impurity removal, which years ago also doubled as a filter media along with other forms of filter aids.

Today's acceptance of granular carbon in many situations has lessened the need for powdered carbon and almost eliminated the weekly or monthly batch purification treatment. There are, however, some occasions when powdered carbon may be the only answer, and for that reason a separate piece of equipment held aside for such a need should be considered.

Platers who appreciate the value of filtration must first understand that it is not as much an art as it is a science. The requirement of a science is to have an orderly body of facts, facts that can be correlated and anticipated results yielded. Although there has been some work done in this area over the last 5-10 years, platers must still rely on experience to a great extent.

In the past, it has been suggested that the plater decide the level of quality sought and, using statistical quality control, determine if this goal has been achieved. It is further recommended that the plater needs to know the parts per million of contamination (solids) so that the necessary size or dirt-holding (solids) capacity of the filter could be established. The plater must also know the nature of the solids, which would be critical to success. Slimy, stringy, or oily contaminants blind a dense filter media surface quickly, whereas coarse, grainy, sandlike particles build a thick cake and still allow solution to pass, which provides for continued solid/liquid separation.

By first assessing these factors, platers can ascertain what results can be achieved. For example, slimy solids would require more surface area, whereas gritty particles could get by with less area (i.e., less solids-holding capacity).

However, all filter media are not manufactured in the same manner, for instance, filter paper, cloth, and plastic membranes provide a single junction to stop solids. Filter aids can enhance the ability of the filter media by creating a porous cake, which improves surface flow, but to really be successful a continuous mixing of filter aid and solids must be coordinated to maintain suitable porosity.

Other types of filter media can provide the necessary junction to stop solids but are built in such a manner as to achieve results from a combination of surfaces or juncture points, which achieve the solids retention by impedance. Thus, it is possible for continuous solid/liquid separation to be maintained over a longer period of time.

Most filter media are rated according to the size of particles that they are capable of stopping. Such a rating is based on laboratory tests and expressed in micrometers. A coarse media would be 100 μm; a dense media would be 10, 5, or 1 μm. The number suggests that at an efficiency level of 85 to 99%, all such particles would be stopped, whereas if the micrometer retention level is expressed in "absolute" ratings, 100% of the stated micrometer size and larger sizes would be removed. It further stands to reason that the coarser media will offer more solids-holding capacity, and the denser media will offer less solids-holding capacity.

Next we discuss where these troublesome solids come from and how they can be most effectively removed.

DIRT LOAD

The "dirt" (impurities) in a working plating bath can come from drag-in, anodes, water, and airborne sources. For their efficient removal, the system must be designed for the amount and type of contaminants present in the plating tank; these vary for each installation. Even without prior operating experience, an estimate of the dirt load can be made by reviewing the cleaning and plating processes to select and size the equipment needed.

A filter with insufficient dirt-holding capacity will require frequent cleaning or servicing. The rapid pressure buildup in the system as solids are retained increases the stress and wear of pump seals. By minimizing the dirt load, maintenance of the filter and pump can be reduced considerably. Even after thorough cleaning and rinsing, some solids and contaminants cling to parts, racks, and barrels. Thus, they are dragged into the plating solution. The amount of drag-in contamination depends primarily on the type of parts, plating method (rack or barrel), cleaning efficiency and rinsing cycles.

In most plating plants, the type and amount of parts being processed may vary considerably. For trouble-free operation, the filtration system should be designed for the heaviest work load and most difficult-to-clean parts. Drag-in contamination with barrels is high, due to incomplete draining of cleaners and difficulty in rinsing of loads. Filtration and purification on automatic barrel lines must be continuous, and equipment must be of sufficient size to minimize servicing and work interruption.

The amount of drag-in can often be reduced by improving the pretreatment. With the conversion of many vapor degreasing processes to aqueous cleaning, proper maintenance of cleaners and electrocleaners is of greater importance, particularly with machined or buffed parts carrying oil and lubricants. Recirculation and coalescing with an overflow weir on cleaner tanks will effectively skim off oil and scum, which would quickly foul the filter medium and carbon. More effective descaling will minimize the dirt load. Several countercurrent rinse tanks and a final spray rinse with clean water will also reduce the drag-in contamination. Due to the nature of the cleaning process, contamination of the solution with organic soil (oil, wetting agents) and/or inorganic (metallic) compounds is sometimes unavoidable. These can generally be controlled by carbon treatment at the rinse tank before plating.

Filterability depends on the nature, amount, and size of suspended particles, which, in turn, are contingent upon the type and chemistry of the plating solution. Generally, alkaline solutions, such as cyanide baths, have slimy or flocculent difficult-to-filter insolubles, whereas most acid baths contain more gritty solids, which are relatively easy to filter even with a dense filter media. A

quick test of a representative sample with filter paper in a funnel will determine the nature and amount of solids present. This test will also indicate the most suitable filter medium. Bagging of soluble anodes will materially reduce the amount of sludge entering the plating bath. Airborne dirt from ceiling blowers, motor fans, hoists, or nearby polishing or buffing operations may fall into the plating tank and cause defective plating. Good housekeeping and maintenance will, of course, reduce dirt load and contamination of the plating solution.

Prevention of deposit roughness is perhaps the foremost reason for filtering plating solutions. Better covering power with less chance of burning is also achieved with a clean bath. In addition to suspended solids, the plater also has to contend with organic and inorganic (metallic) impurities, which are introduced into the solution primarily by drag-in. If this contamination is allowed to build up, it will affect deposit appearance. Continuous or periodic purification of the solution with activated carbon and/or low-current-density electrolysis (dummying) will often remove these impurities before a shutdown of the plating line becomes necessary.

The trend of Environmental Protection Agency (EPA) regulations is to severely restrict the amount of suspended solids and dissolved metal impurities in wastewater discharged to sewers and streams. To comply, plating plants have had to resort to some chemical treatment of their effluents to precipitate the metals as hydroxides. The filtration of these hydrated sludges is difficult and requires special separation equipment. Closed-loop systems, recycling, and recovery are being employed and require greater attention to filtration and purification.

Most filtration systems consist of a filter chamber containing the filter media and a motor-driven pump to transfer or circulate the solution from the plating tank through the filter. The many filters and pumps on the market today make it possible to select and justify a cost-effective filter system for each and every solution, regardless of volume.

When engineering a filter system for a plating installation, it is necessary to first establish the main objectives, such as: high quality finish—maximum smoothness and brightness; optimum physical properties—grain size, corrosion, and wear resistance; or maximum process efficiency and control—covering power, plating rate, purification, and clarification.

Then the following factors must be considered before selecting the size and materials needed for the filter media, chamber, pump, and motor:

1. Dirt load—suspended solids, size, kind, and amount; also soluble organic and inorganic impurities.
2. Flow rate—turnovers per hour for a given volume of solution necessary to maintain clarity.
3. Frequency of filtration and purification—batch, intermittent, or continuous required to remove dirt and contamination and filter servicing interval desired.

When agitating solutions with air, a low-pressure blower is usually employed. This makes it virtually impossible to achieve good filtration of the air while keeping the solution clean, because the plating solution then acts like a fume scrubber.

If effluent regulations make it necessary to remove or reduce total suspended solids (TSS) from wastewater, the amount discharged per hour or shift can be

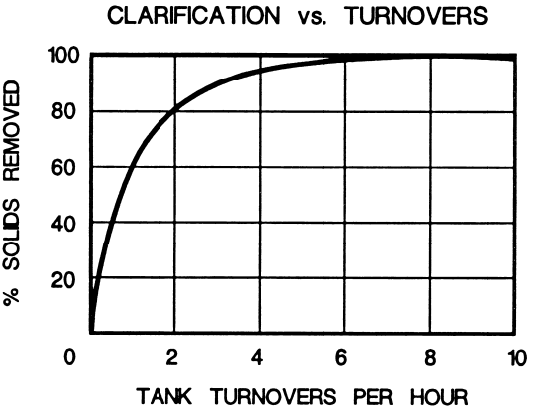


Fig. 1. Higher clarification is achieved by, increasing the number of tank turnovers per hour.

readily determined. For instance, a 100 gal/min (gpm) effluent containing 100 ppm TSS (100 mg/L) will generate 5 lb of solids per hour, as calculated below:

100 gpm 3.79 L/gal 100 mg/L 60 min/hr (1000 mg/g 454 g/lb) = 5 lb/hr (2.3 kg/hr)

Therefore, the filter must have sufficient capacity to hold approximately 40 lb of solids/8 hr of operation. A horizontal gravity filter would be the most cost efficient for this dirt load and would operate automatically; however, if dryness of the retained solids is to be achieved, then a filter press would be recommended.

Filtration and/or purification during nonproductive hours makes it possible to remove dirt at a time when no additional contaminants are being introduced into the tank, such as insolubles from anodes, chemical additions, plus that which would otherwise be dragged in from improper cleaning of the work. Again, individual tank operating characteristics and economics will determine the ultimate level of acceptable quality.

This brings up an important consideration. Contamination by organic compounds, inorganic salts, wetting agents, and oils is not removed by filtration, but by adsorption on activated carbon. Some plating solutions, such as bright nickel baths, generate organic byproducts during plating. It cannot be assumed that both types of contamination increase at the same rate. A batch treatment, therefore, may eventually become necessary, either because of insoluble or soluble impurities. A check of clarity, flow rate, and work appearance and a Hull cell test will indicate the need for transfer filtration and/or carbon treatment.

If analysis shows that the concentration of insolubles (in ppm) has increased, it would indicate that the solution is not being adequately filtered. Therefore, transfer pumping of the solution through the filter should be employed as the quickest way of getting all the solids out at once and returning the clean solution to the plating tank. Soluble impurities can be detected by inspection of the work on a Hull cell panel. Pitting, poor adhesion, or spotty appearance indicates the need for fresh carbon. Here again, it may be desirable to completely batch treat the solution to restore it to good plating quality; however, since this

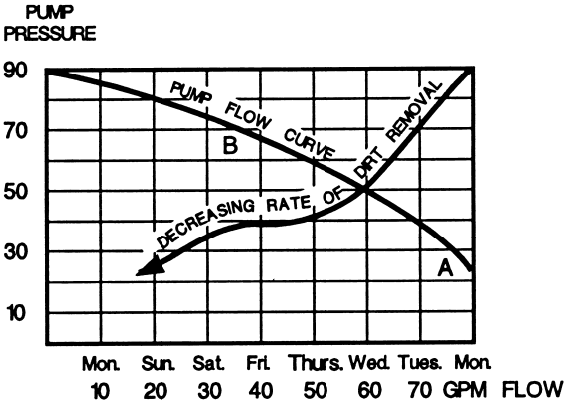


Fig. 2. Clean filter at point A will flow 4,800 gph and dirt removal is maximum. Flow rate has dropped to 2,000 gph at point B. Situation applied to a 2,000-galtank would represent a reduction in flow from almost 2.5 tank turnovers per hour to one tank turnover per hour during a time interval of one work week. If filter continued to operate without servicing, the rate of dirt removed would soon be less than the rate of dirt introduced into the system. The time interval during which the filter is performing effective filtration will be determined by job conditions.

necessitates shutting down the plating line and requires considerable labor, every effort should be made to maintain solution clarity and purity continuously, without having to resort to such batch treatment.

FREQUENCY OF FILTRATION AND PURIFICATION

Since it is desirable to plate with a solution as free of suspended solids as possible, the quickest way to achieve clarification is by transfer pumping all of the solution from one tank, through a filter, to another tank (batch treatment); however, to maintain both clarity and uniform deposit quality, continuous recirculation through a filter is most effective. Although continuous filtration is more desirable, there are some plating installations that require only intermittent filtration, because relatively small amounts of solids are present. In other cases, it is necessary to filter and purify the bath continuously, even when not plating.

A high flow rate is essential to bring the particles to the filter as quickly as possible and to prevent settling of dirt on parts being plated. Although plating in a solution completely free of solids would be best, this ideal can be approached only in the laboratory. Some contamination always exists, and must be accepted. Continuous filtration at a high flow rate can maintain a high level of product quality by keeping suspended solids to a minimum. As Figure 1 indicates, four to five complete tank turnovers effectively remove 97% of all filterable materials if no additional solids are introduced. Since, in many installations, the rate at which contamination is introduced is higher than the rate at which it is removed, the impurities and solids gradually increase with time unless filtration is continued even during nonplating periods.

The greater the turnover rate, the longer the plating bath can be operated before the reject rate becomes too high and batch (transfer) filtration is necessary. In practice, contaminants are not introduced at a steady rate; for instance,

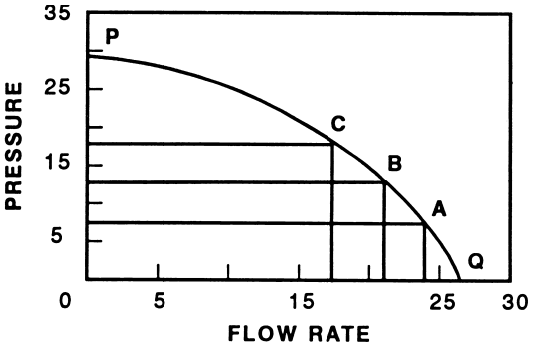


Fig. 3. Typical flow versus pressure curve. Q represents the maximum open pumping against no restriction, whereas P represents the pressure that the pump can develop at zero flow. A might indicate the pressure drop across a depth type media or a bare support membrane, whereas points B and C indicate the reduction in flow caused by the addition of filter aid and carbon, respectively.

most are introduced with the parts to be plated and, therefore, at the moment of immersion the degree of contamination is sharply increased until it is again reduced by the action of the filters. It then increases again when more parts are put into the tank for plating.

Figure 2 indicates the reduction in flow caused by the dirt buildup in the filter on a day-to-day basis, where one week's filtration would be effected before service of the filter becomes necessary. This reduction in flow rate could also have been representative of a longer time interval between filter cleanings. Graphically, it indicates why platers may experience roughness at varying intervals in the plating filtration cycle. The amount of solids increases in the tank as the flow rate decreases to a level that may cause rejects. After the filter is serviced, the increased flow rate agitates any settled solids. Therefore, it is advisable to delay plating of parts until the contaminant level is again reduced by filtration to within tolerable limits. This phenomenon generally occurs in a still tank, since the dirt has more chance to settle. For this reason, when the solution is pumped into a treatment tank, sludge may be found on the bottom of the plating tank.

Dirt in an air-agitated tank can settle any time after the air is shut off. If carbon and/or a filter aid is used in the filter during the continuous filtration cycle, it should be borne in mind that, as these solids are collected on the media, the pressure increases appreciably, reducing the initial flow rate by almost 25% and the overall volume pumped through the filter by as much as 50% before servicing is necessary (Fig. 3). Frequent laboratory checks will verify the amount of insolubles in the plating tank, which will tell whether a uniform degree of clarity is being maintained or whether it is increasing slowly toward the reject level. More frequent servicing of the existing filtration equipment will increase the total volume pumped and, in turn, maintain the lowest possible level of contamination and minimize the need for batch treatment.

It is, therefore, necessary for the plater to determine the particle size to be removed and then select the media that provides the most solids-holding capacity. Then, knowing the efficiency of the media, multiply it by flow rate

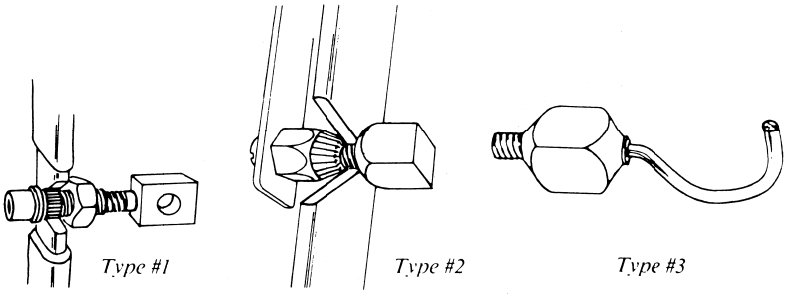


Fig. 5. Various types of replaceable tips.

so that all of the solution passes through the filter in a certain period of time, such as 1 hr or 1 min. Note the small amount of solution that is filtered in 5 min if a rate of one turnover per hour is used (Fig. 4) as compared with the amount that would pass through at a rate of ten turnovers per hour (assume a 100-gallon solution):

At one turnover per hour,

1 100 gal/60min = 1.6 gpm 5 min = 8 galfiltered

At ten turnovers per hour,

10 100 gal/60 min = 16.6 gpm 5 min = 83 filtered

The point here is that if nearly the entire solution is turned over every 5 min, then the plating bath will exhibit a high degree of clarity and purity. The net result should be fewer rejects caused by occlusion of particulate matter in the deposit.

In modern electroplating, no area that can result in improved quality should be overlooked. The plater can use the principles of high tank turnover and solution velocity to his advantage in his quest for zero rejects.

During recent years the flow rate through the filter, or tank turnover as it is referred to, has increased to two or three per hour or higher for most plating solutions (see Table I). This means that 1,000 gallons require a flow rate of at least 2,000 to 3,000 gallons per hour (7.6-11.5 m3/hr); however, platers should recognize the need and employ turnovers of 10 or even 20 times per hour when all solids must be removed (see Fig. 1).

Alkaline solutions may require even higher flow rates for more effective solids removal by recirculation. Depending on the filter medium and its retention efficiency, flow rates in the range of 0.5 to 2 gpm (2 to 8 Lpm) per square foot of filter surface area are obtainable. Although 5 gpm per 10-in. (25-cm) cartridge is permissible, flow rates under 1.5 gpm per cartridge offer better economy. In fact, at a given flow rate with a cartridge filter, servicing, cartridge cleaning, or replacement can be reduced significantly by increasing the size of the filter. For example, *if the size of the filter was multiplied by four the annual amount of filter cartridges consumed would be cut in half and the filter itself would operate unattended for at least four times as long before cartridge cleaning or replacement was necessary*. This is an important consideration to reduce media consumption.

It has also been found that the effective life of surface filters may often be tripled by doubling the surface. By increasing the dirt-holding capacity and reducing the frequency of filter servicing and replacement, the cost of filtration

Table I. Guide to Filtration and Purification of Plating Solutions

Process	pH	Temp. (°F)	Filtration	Turnovers/ hr [a]	per 100 gal.[b] Surface Area	per 100 gal.[b] No. Filt. Carts.	Media Fiber/ Core [c]	Porosity (μm) [a]	Carbon Treatment
Anodizing	1	60–90	Optional[d]	1–2	3.5	1	U/U	15	No
Nickel acetate seal	5.5	200	Desirable[d]	2–3	7	2	U/S	15	Batch/Continuous
Brass, bronze	10	100–200	As required[d]	2–3	7	2	U/U	15	No
Cadmium	12	100	As required[d]	2–3	7	2	U/U	30	No
Chromium, hexavalent	1	110–130	Optional[d]	1–2	3.5–7	1 or 2	M/U or glass[e]	15	No
Chromium, trivalent	2–3.5	75	Continuous	2–3	10.5	3	U/U	1–5	As needed
Copper acid	1	75–120	Continuous	2–3	10.5	3	U/U	15	Batch/Continuous
Copper cyanide	11–13	70–150	Continuous	2–3	10.5	3	U/U	15	Batch/Continuous
Copper, electroless	14	100–140	Continuous	1–2	7	2	U/U	3	No
Copper fluoborate	1	70–120	As required	1–2	3.5	1	U/U	15	As needed
Copper pyrophosphate	8–9	110–130	Continuous	2–3	7	2	U/U	10–20	As needed
Gold acid	3–6	80–125	Continuous	2–3	7	2	C/U	1–5	Periodic
Gold cyanide	7–12	75	Continuous	2–3	7	2	C/U	5	Periodic
Iron chloride	1	195	Continuous	2–3	7	2	U/U	15	Yes
Lead fluoroborate	1	100	Continuous	1–2	3.5	1	U/U	15	No
Nickel, bright	3–5	125–150	Continuous	2–3	7–10.5	2 or 3	C/U	15–30	Yes
Nickel, semi-bright	2–5	130	Continuous	2–3	7	2	C/U	15	Yes
Nickel chloride	2	120–150	Continuous	2–3	7	2	C/U	15	Yes
Nickel, electroless	4–11	100–200	Continuous	2–3	7	2	U/U	15	As needed
Nickel sulfamate	3–5	100–140	Continuous	2–3	7	2	C/U	15	Yes
Nickel, Watts	4	120–160	Continuous	2–3	7	2	C/U	15	As needed
Nickel–iron	3.5–4	135	Continuous	2–3	7–10.5	2 or 3	C/U	15–30	Yes
Rhodium acid	1	100–120	As required	1–2	3.5–7	1 or 2	U/U	5	Periodic
Silver cyanide	12	70–120	Continuous	2–3	7	2	C/U	5	Periodic
Tin acid	0.5	70	As needed[d]	1–2	3.5	1	U/U	15	As needed
Tin alkaline	12	140–180	As needed[d]	3–4	10.5	3	C/U	30	No
Tin–lead (solder)	0.5	100	Continuous	1–2	3.5	1	U/U	15	Periodic
Tin–nickel	2.5	150	Continuous	1–2	7	2	U/U	15	Yes
Zinc acid chloride	5–6	70–140	Continuous	2–3	14	4	U/U	15	As needed
Zinc alkaline	14	75–100	As needed[d]	2–3	10.5	3	U/U	30–50	Optional
Zinc cyanide	14	75–90	Continuous	2–3	10.5	3	C/U	30–100	No

[a] Increased turnover allows for use of coarser media to increase solids holding capacity. As many as 20 turnovers have been used on critical applications.

[b] (Surface area measured in sq. ft.) Increasing number of cartridges improves efficiency, reduces pump velocity and reduces amount of cartridges used.

[c] C - Cotton, U - Polypropylene, S - Stainless Steel. Depending on tank size and space, select appropriate in-tank or out-of-tank pump with nonmetallic solution contact. Either sealless magnetic or mechanical seal horizontal pumps are most common. For electroless plating solutions, a water flushed double mechanical seal pump, or vertical sealless pump is required.

[d] For best results, continuous filtration should always be considered.

[e] Immersion-test filter media fibers to select most cost effective.

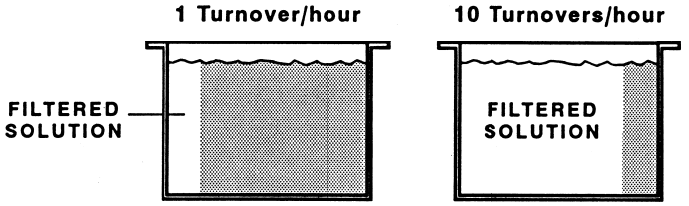


Fig. 4. Comparison of filtered volumes for 100 gal of solution after 5 min of filtration at respective turnover rates.

on a per month or per year basis is substantially reduced.

TYPES OF FILTER SYSTEMS

After estimating the dirt load and determining the flow rate and filtration frequency required, a choice of filter method and medium must now be made. The most common types of filters used in the plating industry are discussed below. These filters may be placed inside or outside the tank.

In-Tank Considerations:

Tank space
Motors located over fumes
Limited size of filter (less service life of media if used on pump suction)

Out-of-Tank Considerations:

Remote possibility for easy service
Employ sealless magnetically coupled pumps or direct-drive with single or double water-flushed seal
More suitable for use with slurry tank for chemical or filter aid/carbon addition or backwashing
Larger dirt holding and flow capacity from cartridges or surface media

Cartridge Filters

Cartridges offer both surface and depth-type filtration characteristics, providing various levels of particle retention at different efficiencies (nominal and absolute), manufactured in natural and synthetic (plastic) materials to provide a wide range of chemical resistance, flow rates, and particle retention capacities. Pleated-surface media offer initially higher flow rates, are available with a choice of porosities (usually in the denser range), and are sometimes given an absolute particle-retention rating.

Depth-type media are available in 1- to 100-μm particle retention and, because of the variety of porosities available, they are sometimes best suited to handle high-dirt-load conditions. This is a result of the manner in which the depth-type cartridge filter is manufactured. Basically, it consists of a series of layers, which are formed by winding a twisted yarn around a core to form a diamond opening. The fibers, which are stretched across the diamond opening, become the filter media. Succeeding layers lock the previously brushed fibers in place and, since there is the same number of diamond openings on each layer, the openings become larger due to the increase in circumference; other fiber-bonded types also increase density across the depth of the media.

During filtration, the larger particles are retained on the outer layers of the car-

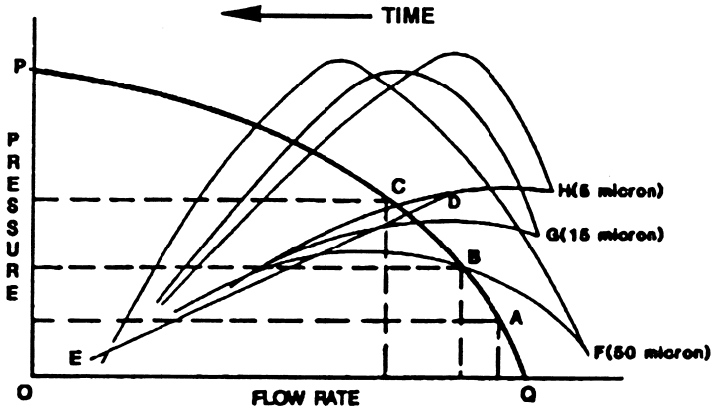


Fig. 5. In comparison with Figure 3, these curves show the effect on the rate of contaminant removal by using a coarser filter medium. Dirt pickup may increase for a while due to more effective filtration; the solids pickup increases the filter medium density after which it decreases as flow rate is also reduced. A, the highest possible flow rate; B, addition of filter aid reduces flow; C, addition of carbon; D, maximum dirt particle removal; E, no flow.

tridge where the openings are large, whereas the smaller particles are retained selectively by the smaller openings on succeeding inner layers. This, then, makes it possible for an individual cartridge to have a dirt-holding capacity equal to 3.5 ft^2 of surface filter area of the same density. Cartridges having a 15- to 30-μm retention will often hold 6 to 8 oz of dry solids before replacement is necessary, whereas cartridges of 10 μm down to 1 μm will have a dirt-holding capacity of perhaps 3 oz to less than 0.5 oz. These figures merely indicate that the coarser cartridges have greater dirt-holding capacity, are more economical to use, and can be used longer before replacement.

Also, as pointed out earlier, dirt loads vary from tank to tank, and cartridges should be selected according to the individual requirements. A dense cartridge having less dirt-holding capacity will load up more quickly, increasing the pressure differential and, therefore, reducing the flow (Fig. 5). Using coarser cartridges (greater than 30 μm on zinc, for example) that have greater dirt-holding capacity and a longer service life may make it possible to clarify the plating tank more quickly because of the high obtainable flow rate. This will be accomplished at less cost. Usually two cartridges (three on zinc, tin, and cadmium) are recommended for each 100 gal of tank capacity.

The pump should provide a pumping rate of at least 100 gph (two tank turnovers per hour) for each cartridge. Usually, a cartridge life of 6 weeks on nickel or 4 weeks on zinc can be expected, with some tanks running as long as 12 weeks; however, much depends upon dirt load, hours of plating, and so on. With cartridges, a higher dirt load can be retained in the filter chamber because of the coarseness of the filter media. Higher flow rates can usually be employed during the entire lifespan of the cartridge. This is due, in part, to the higher head pressures of pumps employed without chancing the rupture of a cartridge. Since all of the dirt is retained on and in the cartridge, the cartridge filter can be turned off and on at will, unless the cartridges are precoated. Cartridges are

changed with very little maintenance expense and no solution loss; however, simplicity of use is perhaps the most predominant single factor in their selection.

Precoat Filters

Precoated filters consist of a membrane (leaf, sleeve, or screen) such as paper, cloth, ceramic, sintered metal, wire mesh, or wound cartridges. These membranes support the diatomite or fibrous-type filter aid, which has been mixed in a slurry of water or plating solution and picked up by the membrane openings. The dirt is retained on the outer surface of the cake. When the pressure has increased and the flow rate has decreased to a point where filtration is no longer efficient, the dirt and cake are washed from the membrane. Paper membranes are discarded and replaced.

The ability to obtain long runs is dependent upon proper selection of the foundation media, coupled with a coarser-than-usual nonfibrous-type filter aid (to be used where possible). Periodic (daily, if necessary) additions of small quantities of filter aid should be made to lengthen the cycle between servicing. The dirt-holding capacity of this type of filter is usually measured in square feet of filter surface. (If the standard 2.5 x 10-in. long cartridge is used, its outer surface when precoated would be equivalent to about 0.50 to 0.67 ft^2 of area.) Flow rate and dirt-holding capacity of the various precoated membranes or cartridges would be about equal.

Before precoating, the operator should know or determine the filtration area to be covered. The amount of filter aid used depends on its type and on the solution being filtered. Generally, 0.5 to 2 oz/ft^2 of filter is sufficient. The manufacturer's recommendations for type and amount of filter aid should be followed if optimum results are to be obtained. A slurry of filter aid and plating solution or water is mixed in a separate container or in a slurry tank, which may be an integral part of the filtration system. The slurry is then caused to flow through the filter media and create a filter cake.

Usual flow rates range from 0.5 to 2 gpm/ft^2 of filter surface. A lower flow rate improves particle retention and smaller particles will be removed. It should be pointed out that, although there may be a wide range in flow rate, the range of selectivity of particles being removed is between 0.5 and 5 μm, which is the most significant difference between precoat and depth-type cartridges and offers a wider choice of porosity.

Buildup of cake should be gradual, and recirculation should continue until the solution runs clear. Cake should be dispersed uniformly across the media before the plating solution is allowed to flow across the filter. A slurry tank piped and valved into the filtration system becomes a convenient and versatile piece of equipment. The slurry may be prepared with plating solution, rather than water, to avoid diluting critical mixtures. Via valving, the solution is drawn into the slurry tank for sampling, preparation of slurry, and chemical additions. Similarly, the solution is returned to the plating tank. This method eliminates the necessity of transfer hoses between tanks, and the subsequent risk of loosening the cake or losing pump prime. The integral slurry tank is also a convenient storage for backwash water.

Precoat Backwash Filters

These filters operate the same as, and have the same functional purpose as, ordinary filters with the further advantage that they can be cleaned quickly by reversing the flow through the filter media. Backwashing the filter aid and dirt

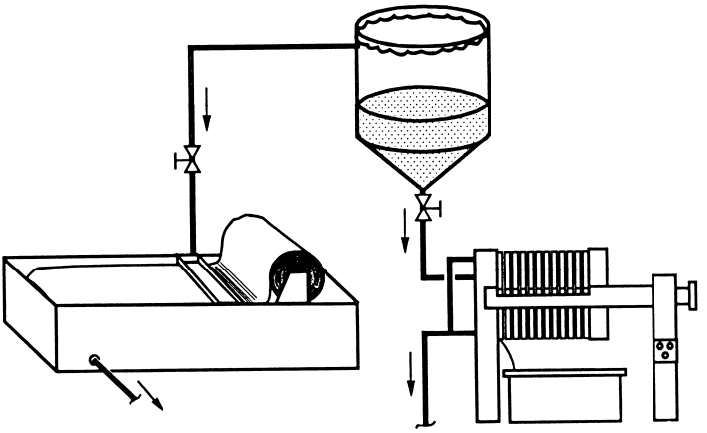


Fig. 6. Automatic disposable fabric filtration system for neutralized solid/liquid waste separation.

away makes the media available for prompt repeat precoating. The basic advantage is that the filter chamber need not be opened each time the filter requires cleaning.

Finer grades of filter aid may be precoated on top of the coarse filter aid when fine powdered carbon is to be used continuously. Here again, periodic (daily, if necessary) additions of small quantities of filter aid should be made to lengthen the cycle between backwashing. The media may be cleaned automatically with sluicing or using other devices. Iron hydroxide sludges can be dissolved by circulating dilute hydrochloric acid from the slurry tank; additional manual cleaning may also be required occasionally.

Some disadvantages of precoat and backwashing are the possible loss of solution, increased waste treatment loading, and the possibility of migration of filter aid and carbon into the plating tank. The use of rinse water for backflushing will reduce waste treatment loading; however, if evaporation is used to control drag-out, this may interfere with evaporator operation and the economies achieved by using this equipment.

Sand Filters

Using sand as the filter media, the pump and filter operate like a precoat surface filter and backwash like a precoat without the need of additional aid to achieve fine particle retention. Performance can be acceptable based on recirculation turnover rates, with the basic disadvantage coming from a smaller surface area, which increases the need for frequent backwashing and resulting solution loss to maintain the desired flow rate (turnover required).

Horizontal Fabric and Screen Filters

These filters are especially well suited for the continuous dewatering of hydrated metal sludges resulting from the neutralization of plating wastewater prior to sewer discharge. They are also effective in removing accumulated iron sludge from phosphating tanks.

In one such system (Fig. 6), the waste containing 1 to 3% solids is first allowed

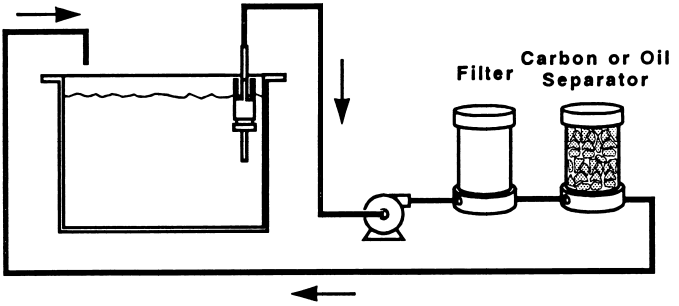


Fig. 7. Skimmer, pump, and prefilter with carbon or free oil separator.

to settle in a cone-shaped tank. The supernatant liquid drains into a head box, which directs the flow across the filter medium (paper or plastic) supported by a motor-driven conveyor belt. The liquid passes through the disposable fabric by gravity flow into a receiving tank below. When the pores of the media become clogged, the liquid level rises and a float switch activates the belt drive. Fresh media is fed over the tank and filtration is continuous. The cake on the fabric is allowed to drain before it is dumped into the sludge box. Gravity drain or an immersion pump empties the filtered water from the tank. Cycling and indexing of the filter are automatic. The occasional replacement of the filter fabric roll is the only labor required. The sediment in the bottom of the cone can also be dewatered periodically by filtration on the fabric. Other systems feature pressure or vacuum filtration. The sludge cake contains from 5 to 35% solids, depending upon the equipment and type of cake. Cakes can be further treated by air evaporation or with heat for dry disposal. The filtrate can be discharged to the sewer if it meets local effluent regulations or can be recycled through the system.

The performance of the unit can be improved greatly by the addition of coagulants and flocculating agents, such as polyelectrolytes, which increase the amount of solids, particle size, and settling rate. The flow rate is approximately 1 gpm/ft^2 with 90 to 95% solids retention; with coarse filter media, flow rates increase up to 10 gpm/ft^2. Filter aid can also be precoated to improve retention. The filter media is available in porosities of 1 to 125 μm and rolls 500 yd long. Carbon-impregnated paper is used for purification and removal of organic contaminants. The unit must be sized properly for each application to operate efficiently and with a minimum media cost. Steel, coated, stainless steel, or plastic units are available for corrosive solutions.

BATCH AND CONTINUOUS ACTIVATED-CARBON PURIFICATION

Virtually all plating solutions and some cleaners or rinses at some time will require purification via the adsorption of impurities on activated carbon. Those solutions that contain wetting agents require the most carbon; when oil is introduced into the bath, the carbon is dispersed throughout the solution and clings to the parts, causing peeling or spotty work. Solutions that do not contain wetting agents have a tendency to float oil to one corner, depending on the recirculation set up by the pump, and in this case the oil may be removed with a skimmer or coalescer (see Fig. 7).

The choice of purification method depends on the size of tank and amount of carbon required and also on other available auxiliary equipment. Generally, carbon cartridges are used on small tanks (up to a few hundred gallons), and the bulk or canister type or the precoat method is used for the very largest tanks. The canister type is also used on the larger tanks supplemental to surface or depth-type cartridges or on certain automatic filters to supplement the amount of carbon.

Batch Treatment

The quality of the carbon is important and special sulfur-free grades are available. The average dosage is 10 lb of carbon to treat 500 to 1,000 gal of warm plating solution. At least sixty minutes contact time with agitation should be allowed, followed by some settling before transfer clarification can be achieved.

Continuous Purification

A separate purification chamber holding bulk granular carbon, a carbon canister, or cartridges offers the most flexibility in purification treatment. By means of bypass valving, the amount and rate of flow through the carbon can be regulated to achieve optimum adsorption of impurities without complete depletion of wetting agents and brighteners in the plating bath. It provides for uninterrupted production and fewer rejects. When necessary, the carbon can be changed without stopping filtration of the bath. Filtration should always precede carbon treatment, to prevent dirt particles from covering the carbon surfaces.

CONTINUOUS CARBON TREATMENT METHODS

Carbon Cartridges

Cartridges containing up to 8 oz of either powdered or granular carbon for every 10 in. of cartridge length are available and will fit most standard replaceable filters that employ this type of media. They may include an outer layer, which serves as a prefilter, and an inner layer, which serves as a trap filter. These handy cartridges are ideal for small filter chambers because of the ease and convenience of quickly replacing a conventional depth tube with the carbon tube when necessary. They may also be used with submersible filter systems, but in this case the flow rate could be greatly reduced.

Carbon Canister

Granular carbon may be used in ready-to-use chambers, each with a number of canisters holding up to 10 lb of granular carbon, and placed in line to the tank. A built-in trap filter eliminates migration of the carbon. Prefiltration ahead of the purification chamber will prevent solids from coating the surface of the carbon in the canister, assuring maximum adsorbency. The carbon in the canister can be replaced when its adsorption capacity has been reached. This method of separate purification offers the most flexibility. Any portion or all of the filtrate can be treated as needed by means of a bypass valve after the filter.

Bulk Carbon Method

Granular or bulk carbon is poured loosely around standard depth-type cartridge filters or sleeves, is poured into specific chambers designed for carbon, or is pumped between the plates or disks of other surface media. Since no filter aid is used, fines breaking off from the piece of carbon will have to be stopped by the surface media. Therefore, an initial recirculation cycle without entering the plating tank or recirculation on the plating tank prior to plating is desirable. This

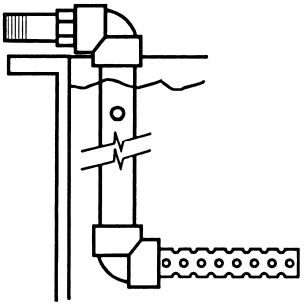


Fig. 8. Suction or dispersion piping system with strainer and siphon breaker. Drill a hole 2 in. below working solution level as a siphon breaker to prevent solution loss due to unforeseen damage to piping, pump, and so on. Chlorinated polyvinyl chloride with screwed connections offers maximum flexibility and ease in installation and may also be used on the return line by eliminating the strainer and replacing it with a longer length of pipe that is open along the full length.

method does not alter the solids-holding capacity of depth-type cartridges, as most of the carbon will stay on the outer surface layer; however, carbon removal is not easily accomplished.

TIPS ON FILTER INSTALLATION

Filtration equipment should be installed as close to the plating tank as possible in an area that affords access for servicing. Equipment that is not easy to service will not be attended to as frequently as required, and the benefits of filtration will not be maximized. The suction line should always have a larger diameter than the discharge to avoid starving the pump (e.g., 1 in. versus in. or 2 in. versus 1.5 in.) Where it is necessary to install the equipment more than 10 to 20 ft away, check the pump suction capabilities and increase the size of the suction piping (1.5 in. instead of 1 in., or 2 in. instead of 1.5 in.) to offset the pressure loss.

Hoses made of rubber or plastic should be checked for compatibility with the different solutions. Strong, hot alkaline and certain acid solutions such as chromium are especially aggressive. The use of chlorinated polyvinyl chloride (CPVC), polypropylene, or other molded plastic piping for permanent installation is becoming more common. Some plastics are available with socket-type fittings, which are joined with solvents. Their chemical inertness and temperature capabilities are excellent. Iron piping, lined with either rubber or plastic, is ideal but usually limited to use on a larger tank capable of justifying the investment. It should be pointed out that whenever permanent piping can be used in and out of the tank a more reliable installation will exist, since there is no shifting to loosen fittings, and collapsing or sharp bending of hoses is eliminated. The suction should be located away from anode bags, to avoid their being drawn into the line and causing cavitation. Strainers on the suction are always advisable.

It is also desirable to drill a small opening into the suction pipe below the normal solution operating level on permanent installations so that, should any damage occur to the system, the siphon action or suction of the pump will be broken when the level reaches the hold (Fig. 8). This provides added safety during unattended operation. Whenever automatic equipment is operated, some provision must be made to protect against unforeseeable events that could cause severe losses. This includes some form of barrier or removable strainer to prevent the suction of parts into the pump. The addition of a pressure gauge is strongly recommended to determine the initial pressure required to force the solution through the filter and also to determine when the filter media needs to be replaced.

When starting up a new filter system, or after servicing an existing system, it is advisable to completely close the valve on the downstream side of the filter; in this way, the pump will develop its maximum pressure, and one can immediately determine whether the system is secure. Sometimes filtration systems are tested on a cold solution and, in turn, will leak on a hot solution and vice versa. Therefore, a further tightening of cover bolts, flange bolts, and so on may be necessary after the filter has been operating at production temperature and pressure. If pump curves are not available, one may wish to check the flow at different pressure readings to determine a reasonable time for servicing the equipment before the flow rate has dropped too low to accomplish good dirt removal.

AIR POLLUTION CONTROL IN THE FINISHING INDUSTRY

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Being responsible for reducing volatile organic compound (VOC) emissions in paint and coating operations seems to be akin to a quest to circumnavigate the globe. At the end of your quest, you are right back where you started. If custom coaters are not able to convert to "environmentally friendly" coating alternatives, such as waterbornes, UV-cure or powder coatings, they must deal with ever-increasing emission regulations through some kind of VOC control technology. Choosing the right equipment for VOC control applications depends primarily on the exhaust air volume and the average concentration of VOCs.

VOC CONTROL PRIMER

VOC Destruction

Thermal oxidation is a process whereby most of the VOCs are broken down and recombined with oxygen to produce water vapor and carbon dioxide. The water vapor and carbon dioxide are naturally occurring and environmentally friendly, therefore safe for venting into the atmosphere. Thermal oxidation occurs by heating the polluted air to an elevated temperature (typically 1,300°F to 1,800°F). At such temperatures, the pollutant molecules spontaneously disassociate and recombine with available oxygen to create the carbon dioxide and water vapor. The efficiency of oxidation and the design of most oxidizers is governed by the residence time, the combustion chamber temperature and the amount of turbulence the air stream sees.

Catalyst Improves Fuel Efficiency

A Catalyst is a substance that promotes oxidation without being consumed by the process. VOC catalyst can be added to the combustion chamber of almost any oxidizer to promote VOC destruction at lower operating temperatures (typically 600°F to 900°F), lowering fuel usage.
Note: Catalytic oxidizers are only suitable for processes whose constituents will not adversely affect the life of the catalyst.

VOC Capture

Concentrators take advantage of a chemical surface phenomenon and the tendency of VOCs and other pollutants to adhere to certain types of materials such as activated carbon and zeolites. Adsorbent media are selected for their tendency to attract pollutants as well as their high surface area — qualities that allow them to trap and hold more pollutants. When emission gases pass through the adsorbent media in a concentrator the pollutants stay behind, trapped in the media.

The pollutants can then be removed from the media by desorption — passing a much smaller quantity of very hot air through the media. The smaller volume of desorption air contains a very high concentration of pollutants that can be destroyed efficiently by oxidation.

CONCENTRATOR/OXIDIZER SYSTEMS

Combining technologies creates "Capture & Control" systems that use an integrated concentrator and final treatment system to process large volumes of process air, concentrate VOCs in a smaller volume of air, destroy the pollutants in the air and use the heat from the destruction process as part of the concentration process.

OXIDATION TECHNOLOGY

The most reliable and acceptable means of destroying VOCs, HAPs, and odors available today is thermal oxidation. Oxidation, typically, is an energy intensive technology wherein a polluted air stream is heated to a high temperature setpoint that is predetermined by the nature of the pollutant. The simplest form of an oxidizer is a direct-fired burner that elevates the air temperature from incoming levels to combustion levels. Because of the high cost of heating the process exhaust stream to the required oxidation temperature most thermal oxidizers incorporate some type of primary heat recovery. Primary heat recovery transfers energy from the hot clean gas stream exiting the oxidizer into the incoming polluted gas stream. This reduces the amount of additional energy required to achieve the oxidation temperatures. There are two widely used methods of recovering this thermal energy, recuperative and regenerative.

Oxidizer Selection Criteria

In order to select which type of oxidizer is most advantageous for a specific application, the following information must be known:

- Process exhaust flow rate: If the process exhaust stream flow rate is below about 3,000 scfm, regenerative systems are generally not practical. This is because the fuel savings gained by the highly efficiency regenerative heat recovery is generally not sufficient to offset the increased capital cost and maintenance of the RTO when compared to a recuperative or direct flame system. At flow rates above approximately 25,000 scfm, direct flame oxidizers are at a severe economic disadvantage because of their very high fuel cost. However, it is not unheard of for direct flame systems of this size or larger to be installed where secondary heat recovery boilers can be used to offset the high fuel cost. Another case where direct flame systems are favored for large air volumes is for emergency or stand-by systems which operate very few hours per year.
- Process exhaust stream temperature: If the polluted waste gas stream temperature is above approximately 600°F, regenerative systems are disfavored because the high temperatures can reduce the reliability and longevity of the valve system. In addition, at these temperatures, there is less difference in fuel consumption to justify the additional cost and complexity. If the exhaust temperature is significantly above 1000°F, recuperative systems are disfavored versus direct flame systems again because the difference in fuel consumption becomes too small to justify the added first cost.
- Pollutant concentration levels: The concentration of pollutants in the waste gas stream can have a major impact on the selection of the

type of thermal oxidizer system. Direct flame oxidizers are capable of handling the broadest range of hydrocarbon concentrations, from parts per billion levels to pure hydrocarbon vapors. For waste gas streams with concentrations over 25% LEL, special considerations are routinely taken to prevent flashback from the oxidizer to the waste generating source. The cost of this flexibility is the high fuel cost for this type of oxidizer. Recuperative and regenerative oxidizers are limited gas streams with less than approximately 25% LEL but for different reasons. For a regenerative system, this restriction is primarily due to the danger a thermal run-away situation. In a thermal run-away, the oxidation of the excessive hydrocarbon concentration causes the combustion chamber outlet temperature to rise. This additional heat is recovered by the heat exchange system, which increases the combustion chamber inlet temperature, causing a further increase in the combustion chamber outlet temperature and so on until an excessive temperature is reached. A regenerative system is vulnerable to thermal run-away because they are capable of auto-thermal operation. This is a situation where the heat produced by oxidation of the pollutants is enough to operate the system with no additional input from the burner. In auto-thermal operation, the burner can be shut down and the oxidizer will sustain operation as long as the hydrocarbon loading is high enough. A recuperative thermal oxidizer on the other hand is not capable of self-sustaining operation. In fact, they are purposely designed to avoid a self-sustaining situation because this type of operation will overheat and damage the heat exchanger. The burner must always operate to provide the additional heat to bring the pre-heated waste gas to the full oxidation temperature. As the pollutant loading increases the burner will throttle back by an amount equal to the heat of oxidation. However, if the burner throttles back too far, the oxidation reaction will not be properly initiated and the combustion chamber temperature will crash.

- Type of Pollutant Process: Exhaust streams that contain high levels of acid or compounds that convert into acids (Chlorine, Fluorine, Bromine, Sulfur, etc.) must be treated with special care. Any of these elements, which are present in many important industrial solvents and cleaning agents will attack metal alloys at high temperatures and can form highly corrosive acids in the presence of water at low temperatures. With special materials of construction and design techniques all types of thermal oxidizers can be made to resist low levels of these elements. However, if the levels of acid are high or unpredictable, a direct flame type oxidizer is most preferred. This is because this type of oxidizer has no heat transfer system to be corroded by the acids.
- Particulate Emission Levels Process: Exhaust streams containing particulate must be given special consideration. There are a great number of waste gas sources that contain both gaseous hydrocarbon pollutants and particulate pollutants. In most cases, the particulate can be filtered out upstream of the thermal oxidizer. However, in many cases, it is possible to avoid the additional complexity and cost of a filtration system through proper selection of the thermal oxidizer and its operation. Particulate can be broken down into two basic cat-

egories, organic and inorganic. An example of an organic particulate is an oil mist from machining operation. This type of pollutant will either accumulate in the ductwork and cooler parts of the thermal oxidizer or penetrate to the combustion chamber. Any particulate that accumulates in the cooler parts may need to be periodically cleaned out. Obviously, provisions must be made in the oxidizer design to allow cleaning. In general, any type of thermal oxidizer is capable of handling purely organic particulate. However, as the total loading increases, increasing amounts of maintenance will be required. One feature of regenerative type systems for these applications is that the can be programmed to perform a thermal self-cleaning or bake out. This process brings heat from the combustion chamber into the lower portions of the heat exchange media and valves and can burn off accumulated organic material. With this feature, regenerative systems are favored in high organic particulate applications because the manpower and disruption to operation is minimal for a bake out compared to cleaning of other types of systems. Any organic particulate that enters the combustion chamber will be oxidized as any other hydrocarbon would. Oxidation of a particle takes longer than a gas because the particle must first be broken down and volatilized before the thermal oxidation reaction can take place. This takes time and therefore, a thermal oxidizer with sufficient residence time to oxidize gaseous compounds, may be inadequate for particulate. In this case, the oxidizer would have elevated hydrocarbons in the exhaust from the partially oxidized particulate and would also show elevated levels of carbon monoxide. If the particulate is fine, less than about 10 micrometers, and of low concentration, less than about 10 grain/standard cubic foot, adequate performance can be achieved with an oxidizer of normal design. It may be necessary to raise the operating temperature by 100°F or so to achieve required emission performance. For significantly higher levels or sizes, some pre-filtration is usually favored. Inorganic particulate presents different challenges. Inorganic particulate can be any of a wide variety of substances ranging from common dust, to soil, metals, paint pigments or salts. Each type has specific characteristics and therefore requires special considerations in oxidizer design. Inorganic compounds can react with oxidizer components, fuse and foul certain parts, accelerate corrosion or cause erosion damage. Because there are such a wide range of possibilities, no general guideline can be given that would cover all inorganic particulate.

- Required Pollutant Control Efficiency: Many federal, state and local VOC and HAP emission limits for surface coating operations are expressed in terms of one or more of the following:
    - lb per gallon minus water
    - lb per gallon coating solids as applied (e.g. as sprayed)
    - lb per gallon of applied coating solids (e.g. auto & light truck)

These limits may be met either by applying coatings meeting these emission limits without add-on controls or achieving an equivalent limit with add-on controls. For auto and light truck surface coating operations, the paint solids transfer efficiency (TE) is part of the calculation. Some state and local regulations

require a minimum TE for certain coating operation in addition to a VOC or HAP content limit.

If a catalytic or thermal oxidizer is used to control VOC or HAP emissions, 95% minimum destruction efficiency is generally required. An overall 90% minimum VOC or HAP destruction efficiency is generally required if a carbon or zeolite adsorber is used to concentrate emissions prior to destruction in an oxidizer. However, 80% combined system destruction efficiencies have been allowed for plastic parts spray booths employing a carbon adsorber in series with a thermal oxidizer.

At least one permitting agency requires a minimum VOC control efficiency for major sources and others allow it as an alternative to laborious record keeping required to demonstrate compliance with individual coating emission limits.

- Ohio Administrative Code (OAC) 3745-21-07 (G) Operations Using Liquid Organic Material requires discharge of organic materials (i.e. VOC) be reduced by at least 85% from applying, evaporating or drying any photochemically reactive material and any liquid organic material that is baked, heat-cured or heat polymerized.

- Section 215.205 22 Illinois Regulation 11427 allows operators of coating lines alternative emission limitations to individual coating emission limits for emissions controlled by an afterburner (thermal oxidizer): 81% (75% for can coating) reduction in the overall emissions of volatile organic material from the coating line, and

Oxidation to carbon dioxide and water of 90% of nonmethane volatile organic material (measured as total combustible carbon) which enters the afterburner.

- Under South Coast Air Quality Management District (SCAQMD) of California (Los Angeles) Rules 1107 Coating of Metal Parts & Products and 1145 Plastic, Rubber and Glass Coating, lines may comply with these regulations using pollution control equipment provided VOC emissions are reduced as follows:
- The control device shall reduce VOC emissions from an emission collection system by at least 95% by weight or the output of the air pollution control device is 50 PPM by volume calculated as carbon with no dilution.
- The owner/operator demonstrates that the system collects at least 90% by weight of the emissions generated by the sources of the emissions.

Other examples of minimum required or allowable VOC and HAP collection and destruction efficiencies can be found in various federal, state, and local regulations.

In many cases the most advantageous type of oxidizer can be selected based on the following general guidelines. In other cases two or more oxidizer types may be practical and a detailed economic analysis based upon your specific costs of fuel and electricity will be required to determine the best selection.

Recuperative Oxidizers

A recuperative oxidizer is a direct-fired unit that employs integral primary heat

recovery. To minimize the energy consumption of the oxidizer, the hot air exiting the combustion chamber is passed over an air-to-air heat exchanger. The heat recovered is used to preheat the incoming pollutant laden air. The primary heat exchangers are usually supplied as either a plate-type or a shell and tube type heat exchanger. These heat exchangers can be designed for various heat transfer efficiencies, but the nominal maximum is 70%. Thus by the addition of a heat exchanger, the net heat load on the burner can be reduced by up to 70% of that required in a DFTO. The addition of the heat exchanger, because it is made of heat corrosion resistant alloy, substantially increases the cost of the oxidizer system. Also, the fan for moving the polluted gas through the oxidizer must be more powerful to overcome the additional pressure drop of the heat exchanger. In most cases, the savings in fuel will more than offset the additional up-front cost within the first two years of operation, however, even with 70% heat recovery, recuperative oxidizers can be expensive to operate, especially if the airflow is large and has dilute concentration levels, unless additional secondary heat recovery can be applied to the customer's process.

Regenerative Thermal Oxidizers (RTOS)

A regenerative oxidizer is also a direct-fired oxidizer that employs integral primary heat recovery. However, the RTO operates is periodic, repetitive cycle rather than a steady state mode. Instead of conventional heat exchangers which indirectly transfer heat from hot side to cold side across the exchanger walls, RTOs use a store and release mechanism. The hot gases exiting the combustion chamber of an RTO are made to pass over a bed of inert and temperature tolerant media with a high heat capacity. The temperature difference between the gas and the media causes heat transfer to occur between the gases and the bed. The heat storage media is either a granular or structured form of heat resistant ceramic. Once the bed has been saturated with heat, the air flow is reversed and redirected by a valve mechanism. Reversed flow allows the cooler process air to pass over the hot bed, and hence become preheated before entering the combustion chamber where the remaining heat is provided by a burner. The hot gas is redirected to a cold bed (one that just completed being an inlet bed) and "regenerates the bed, making it hot and ready for the next pre-heat cycle. In other words, one bed (or chamber) is used as a heat source and one is used as a heat sink. The flow through an RTO must be frequently reversed in order to maximize heat recovery and media regeneration.

The nature of an RTOs heat recovery process requires it to have at least two beds of appropriate heat recovery media. In many applications, the additional step of purging a bed before reversing the flow through it from inlet to exhaust is necessary to maintain very high destruction efficiencies. This purge step creates the requirement for an additional (or odd number) chamber making the RTO more complicated and more expensive than a recuperative oxidizer. RTO systems can utilize more than two beds (operating in parallel) in order to be capable of handling larger air volumes. The primary advantage of an RTO is lower operating costs due to high heat recovery and low fuel consumption. Depending on the mass of media included in an RTO, heat recoveries of up to 95% are common. Because of their capability for high heat recovery, RTOs are often operated in an "auto-thermal" or self-sustaining mode, where the heat content of the VOCs being oxidized is enough to sustain the combustion chamber temperature at setpoint, requiring no external fuel input.

RTOs are a well-proven technology, but are being called on to become more efficient than ever, to reduce operating costs to even lower levels than have traditionally been seen. That challenge has been met by developing improvements in heat transfer media, alternative oxidation technology and fuel usage optimization techniques.

- Heat Transfer Media: Traditionally, the heat transfer beds of an RTO are composed of ceramic saddles, randomly packed into an insulated chamber. The airflow through the saddles is forced to make many changes in direction and velocity. Due to the turbulent nature of the airflow, the pressure drop across the bed increases with the square of the airflow. Dürr's investigations into the fundamental principles of RTO operation led to the development and application of a structured heat transfer media. These investigations indicated that a heat transfer media having straight airflow passages of constant cross-section offer significantly improved performance over traditional saddles by providing more laminar airflow characteristics. The improved performance can be seen in a lower pressure drop across the packed beds of an RTO. Structured packing is a ceramic monolithic block, composed of silica alumna ceramic. Each block is approximately 12" tall, 6" wide and 6" long, and has hundreds of parallel passages, each approximately 1/8" square, extending from top to bottom. It's physical and performance characteristics allow for a higher airflow velocity through a packed bed, resulting in a more compact RTO which is attractive to land-locked plants that may not have the normal space required for an RTO. This higher bed velocity also allows for a unique solution to plants that have existing RTO equipment that may require additional airstream treatment capacity. Increased flow in a traditional saddle packed bed requires an exponential increase in pressure drop and motor horsepower, quickly overloading existing handling capacity. Replacement of an existing saddle bed with ceramic monolith can not only reduce the pressure drop for existing capacity, but also provide almost a 40% increase in incoming airflow capacity with the existing motor and fan, while providing better thermal performance, lowering the natural gas consumption of the RTO.
- Regenerative Catalytic Oxidation (RCO): RCO's are a recent hybrid VOC abatement technology that is gaining acceptance in plants where energy cost are high and the hours of operation are long. An RCO combines the benefits of an RTO with the benefits of catalysis. By adding a precious metal catalyst to the combustion chamber of an RTO system, the catalyst provides hydrocarbon conversion at a much lower operating temperature than an RTO, typically 600°F to 1000°F, which thereby reduces the auxiliary fuel requirements. The precious metal catalyst, like all catalysts, is a substance which accelerates the rate of a chemical reaction, i.e. oxidation, without the catalyst or the substance being consumed. Another benefit of a precious metal catalyst is its ability to eliminate not only VOCs, but also secondary products, notably CO and NOx. In addition, a precious metal-based catalyst is much more resistant to poisoning and fouling than base metal catalysts. Like structured packing, converting an ex-

isting RTO to an RCO is possible, and often beneficial depending on the operating and energy consumption conditions in the plant. Adding a layer of proprietary precious metal catalyst on top of the ceramic media in the RTO's combustion chamber will allow the combustion chamber operating temperature to be lowered to roughly 800°F. In large air volume systems, this fuel savings can be significant. The proprietary catalyst in Durr systems is impregnated in the ceramic media of choice, either saddles or structured packing. In some instances, an RCO system may not be a beneficial choice. These exceptions result from either the presence of a stream that contains organometallic or inhibiting compounds that will cause degradation of catalyst performance. Each VOC stream needs to be examined to ensure there are no catalyst poisons such as silicon, phosphorus, arsenic or other heavy metals. In addition, the catalyst performance could be masked or fouled by particulate in the air stream. However, the catalyst can be recharged relatively easily. It is important to discuss the properties of individual air streams before making any decisions on the applicability of catalyst in an RCO, but for many, the potential for operating cost savings is large.

- Natural Gas Injection (NGI): Typically a natural gas burner system is used to provide the energy required to make-up the heat that is not recovered by a regenerative oxidizer (around 5% of the energy required to reach setpoint). An incoming airstream with a high enough concentration of hydrocarbons, would provide enough energy from auto-ignition of the hydrocarbons for the oxidation process to be self-sustaining, i.e. require no burner operation for make-up energy. Natural Gas Injection (NGI) is a means of artificially creating a self-sustaining condition in an airstream with a low concentration of hydrocarbons. A natural gas burner system is provided and utilized for system pre-heat. Once the heat exchange media is saturated and hot enough to elevate the airstream above autoignition levels, the burner and combustion blower is turned off, and natural gas or methane is safely injected into the incoming airstream, enriching it to the concentration levels necessary for self-sustaining operation. NGI actually improves the thermal efficiency of an RTO because it eliminates the requirement for combustion air being introduced, and thereby mitigates the mass imbalance in airflow between the regenerator bed that is on inlet and the bed that is on outlet. In commercial application, NGI improves an RTO's thermal efficiency by approximately 1% or more overall. Another advantage to NGI is an improvement in NOx emissions from an RTO. The burner is the single biggest contributor of NOx to the exhaust stream of an RTO, due to the high flame temperatures. Eliminating the burner from operating significantly decreases the NOx levels seen in operating RTOs. Due to the lower combustion temperatures of an RCO, NGI is not a tool that is utilized in conjunction with catalyst. However, many existing systems could see a decrease in operating fuel usage, by a simple, low cost retrofit that would install a Natural Gas Injection system to the RTO, especially those airstreams not conducive to catalyst usage.

Concentrators

Rotary concentrators are a continuous adsorption technology commonly applied to very dilute airstreams with relatively low hydrocarbon concentrations. Classified as a capture device, Rotary adsorbers can be used to concentrate the emissions into smaller airstreams with much higher concentrations (typically by a factor of 10 or higher) that can be handled by a smaller oxidation or destruction device much more economically. Continuous adsorption is achieved through the use of rotating media, a section of which is simultaneously desorbed. This design eliminates the need for dual running and stand-by fixed adsorption beds.

The hydrocarbon-laden air passes through the rotary adsorption unit where the hydrocarbons are adsorbed onto an adsorbent media such as activated carbon or hydrophobic zeolite. The large volume of incoming air, now purified by the adsorption process, is exhausted to atmosphere. The hydrocarbons which were adsorbed are then continuously removed from the media by desorption with a higher-temperature, low-volume airstream. This high concentration desorption air is delivered to an oxidation device for destruction.

Concentration of hydrocarbons into a smaller airstream is a significant benefit to operating costs to a destruction device. By decreasing the airflow, the device is inherently smaller and less costly to purchase. By increasing the concentration, the auxiliary fuel benefit of the hydrocarbons is increased, in many cases, almost to the level of self-sustaining operation, where the customer's natural gas requirements are virtually eliminated. Traditionally, concentrators were applied and justified on very large airstream volumes, but recent commercial applications have been on airstreams of 30,000 scfm and smaller.

Media Choices

The key to effective adsorption is the medium that is used. The most widely used medium is activated carbon because it is very effective, readily available and long lasting. Zeolite has also found a niche due to higher removal efficiencies for low molecular weight, polar, solvents.

Activated Carbon

Being relatively inexpensive and lightweight, with pores ranging from 1 to 50 Ångstroms (Å), carbon can adsorb most paint solvents and even semiVOCs (SVOCs) such as plasticizers. Though widely used and preferred, activated carbon is not without disadvantages. The three primary drawbacks are:

1. Its combustibility, with the potential to promote a fire when heated above 600°F.
2. Its hydrophobic structure, which requires relative humidity control. Carbon's adsorption capacity drops significantly at 50 to 60% relative humidity. Reheat coils are often required, especially when controlling a wet venture paint spray booth.
3. Impurities that naturally occur in carbon. These impurities can act as catalysts and promote polymerization or oxidation of solvents such as methyl ethyl ketone (MEK) and cyclohexanone, resulting in byproducts that cannot be desorbed or that might be hazardous.

In certain applications, a granular activated carbon (GAC) pre-filter is installed upstream of the carbon adsorption media. A GAC prefilter, often termed a sacrificial bed, adsorbs high boiling VOCs or SVOCs. GAC protects the activated carbon media from being saturated with compounds that can not be completely desorbed by the limited desorption temperature (250°F) typically used with carbon media. A GAC bed also dampens fluctuations in VOC content, typical of paint spray booth applications, providing a relatively steady VOC concentration to the downstream media.

- Hydrophobic Zeolite: Zeolites are sometimes called molecular sieves because of their crystalline framework with pores and interconnecting voids. The resulting homogeneous pore size prevents molecules larger than a certain size from entering the lattice. By varying the structure and pore size, the selectivity for various size solvent molecules can be achieved. Synthetic zeolite has a much greater adsorption capacity than carbon at low solvent concentrations, but carbon has a higher capacity at high concentrations. Hydrophobic zeolite, a synthetic porous silicate, is non combustible and capable of withstanding temperatures as high as 1,100°F when coated on a ceramic, honeycomb structure. It can be desorbed at 400° F, the working limit of the desorption section seals. A higher operating temperature allows the removal of solvents with boiling points above 175°C (350° F). Often, versatility is sacrificed for selectivity. Synthetic zeolite has a lower capacity for some common solvents (e.g., xylene and high flash aromatic naphtha 100). Because activated carbon has a wide range of pore sizes it does not exhibit this type of selectivity.

The two absorbents can be viewed as complimentary rather than competing technologies. One can take advantage of their different adsorption characteristics and use carbon and zeolite together, both as separate phase and mix media, to control complex VOC streams at coating and other manufacturing facilities. In many cases the most advantageous type of media can be selected based on general guidelines; however specific performance guarantees must be developed from laboratory analysis of individual process conditions. In many cases, one or more concentrator types may be practical and a detailed economic analysis based upon your specific costs of fuel and electricity will be required to determine the best selection.

ALTERNATIVE STRATEGIES

Alternative technologies have been developed to oxidize solvents without the use of high temperatures.

Ultraviolet Light, Ozone Oxidation (UV/OX) Systems

This technology has been used in a limited number of paint finishing applications. Solvent-laden air is fed into a chamber and exposed to high-intensity ultraviolet (UV) light. High-intensity UV light prepares the solvent molecule for oxidation. The air is then scrubbed with a high-intensity water-wash scrubber. Much of the solvent is transferred to the scrubber water. The water contains a strong oxidant (ozone), which converts the solvent to carbon dioxide and water. Solvent that is not removed in the scrubber passes through a two-bed carbon system. One bed adsorbs solvent while the other bed is in a solvent de-

struction mode. Ozone is injected into this bed and the solvent is oxidized right on the carbon. No nitrogen oxides or carbon monoxide are formed in this process, and high destruction efficiencies are possible. Wet scrubbing can remove particulate as well as VOC. UV/OX systems are complicated, with many dampers, valves, and motors. Systems are large, and operating costs to produce ozone can be high. These systems have not been proven on very large airstreams. Another disadvantage is that a wastewater stream is produced.

Biofiltration

Biofiltration units have been successful in abating odors and some VOC streams. Large chambers charged with bacteria are used to convert VOC to carbon dioxide and other compounds. No nitrogen oxides are created with biofiltration and energy consumption is very low. However, bacteria need a relatively constant supply of solvents to remain active. Very large amounts of space are required and very little past experience in paint applications is available.

CONCLUSION

Applying the Right Solution

It is quite clear that no one solution can be applied universally to all VOC abatement scenarios. The ideology of "One Size Fits All" is false and potentially costly. In choosing the right technology, it is important to examine both the process and the airstream constituents to be abated. A careful review of current and future regulations, along with local site considerations, i.e. utility costs, space constraints and local regulations should be used to select the appropriate solution to the end user's problem.

For paint/coating operations, effectively meeting today's stricter VOC regulations is an ongoing challenge. For larger operations, meeting the challenge becomes a matter of improving overall system efficiencies and economics while retaining enough flexibility to adapt to new coating formulations. For smaller, previously unaffected operations, the challenge involves incorporating a new system into the overall operation and investing in new equipment. Careful consideration must be given to future growth and flexibility while working within the constraints of economic resource limitations. A well-planned environmental system can save many thousands of dollars, which can make a big difference to finishers trying to operate in a competitive industry.

WATER POLLUTION CONTROL FOR PAINT BOOTHS

BY ALAN MONKEN

As a nonrenewable resource, water and its conservation are of prime importance in the metal finishing industry. The reduction and control of water pollution in the manufacturing process is an important area for improvement; one of the most critical areas of industrial water usage is the paint shop. Current technology can be utilized to reduce water consumption and improve the efficiency of water use. To put this technology in perspective, it is necessary to explore the use of water in the paint shop, the available chemical means to deal with water pollutants, and the mechanical means of removing these pollutants.

THE PAINT SHOP

The function of the paint shop is to apply an organic coating (i.e., paint) to a substrate (i.e., metal or plastic) for protective and decorative reasons. The paint can be applied in various forms, including dry powder, solvent-diluted formulations, and waterborne formulations. The application method can vary widely, two of the most common being through spraying or through immersion. In the case of immersion or dip-paint systems, very little paint waste is generated. The drawback to immersion painting, however, is that variations in paint colors and types are severely limited within the same operation. Spray systems allow a great deal of flexibility in the types and colors of coatings that can be applied.

The downside of spray systems is that not all of the paint sprayed comes into contact with the work surface. The paint that misses the production part is commonly known as overspray. If the process being used is powder painting, the *oversprayed* paint can most typically be collected and reused (the ability for capturing this excess powder typically is designed into the powder paint spraying system or booth). If the process involves liquid paint, however, the paint overspray quickly changes from an asset to a liability as it becomes paint waste. Although it is possible to collect this oversprayed paint on dry-filter media, the most common collection/removal method is the use of the waterwash paint booth.

WATERWASH PAINT BOOTHS

The primary function of a paint booth, whether wet or dry, is to remove the paint overspray from the air of the work environment; secondarily, it functions to remove the paint solids from the air stream, allowing any volatile solvent vapors to be expelled from the work area. Dry-filter booths make use of media sometimes resembling conventional furnace dust filters to screen out the tacky paint solids,which are actually the organic portion of the paint responsible for providing the coating. This media can quickly plug, reducing the effectiveness of the removal process. The media, once saturated with paint, is disposed of, typically as flammable waste. Waterwash booths perform the same function but use water as the medium of capturing the paint overspray and the resultant waste material.

Although there is a wide variety of variations in waterwash paint booth styles and types, the two basic categories of design are side-draft and downdraft booths. *Draft* here refers to the way the air movement is directed through the system to

draw the paint overspray in for capture. Side-draft booths, most common in small noncontinuous metal finishing and manufacturing operations, typically function by pulling a mixture of paint overspray and air through a mobile water curtain, using the action of the water to "scrub" the paint solids from the water. This water is recirculated from a holding tank and continuously is cascaded down the "waterfall" wall.

A similar mechanism can be used in the downdraft paint booth, which is most common in larger continuous operations, such as automotive assembly plants. The downdraft system makes use of a downward airflow, most typically through a steel floor grating, into a mobile flood sheet (much like a horizontal "waterfall") or pit of water. Downdraft systems normally contain much larger volumes of water than side-draft systems, making the treatment and conservation of this water even more critical.

COMMON PAINT-RELATED WATER POLLUTANTS

In the case of either side-draft or downdraft systems, the recirculated water comes into contact with a wide variety of potential pollutants from the paint overspray. Many of the materials in the paint, particularly in solvent-based formulations, are not particularly compatible in water systems. The solvents, which would include xylene, toluene, and methylene chloride, are typically not water soluble but can be water miscible (i.e., mixable). At any rate, most of these solvents are volatile and will evaporate over time to exit through the air exhaust. The organic resins making up the bulk of the paint coating are insoluble in water and tend to stay tacky if not treated with some additional material introduced into the water.

If left untreated, tacky sludge can plug up recirculation pipes and pumps (as well as adhere to any and all surfaces of the booth), reducing overall efficiency. Other additives in the paint formulation, such as film-forming/wetting agents, may or may not be soluble in the water and will be present in varying degrees. Some pigments or other inorganic components, such as zinc or chromate compounds, may be partially or completely soluble in water. These inorganics, especially the zinc and chromium salts found in many primers, can pose major problems in disposal. The key to reducing or removing any of these pollutants is to find a way to either solubilize or detackify the paint solids and to collect and remove the dissolved solids (if possible).

Water-based paints, unlike solvent-based formulations, dissolve or disperse readily in water. Because of this dispersibility, caused impart by the relatively small particle size of the waterborne pigments and resins, water-based paints can often be difficult to physically remove from the system. The problem then is one of solids concentration and removal, rather than detackification.

PAINT DETACKIFICATION

A number of methods have been developed to chemically treat the sticky organic paint sludge collecting in waterwash paint booths. Reviewing these detackification systems both historically and in terms of increasing effectiveness, they include caustic/hydroxide treatments,metal salts programs, clay-based programs, and acid colloid programs.

Caustic/Hydroxide Treatments

The use of caustic-based treatments (most commonly in the form of sodium hydroxide) represents the oldest chemically based treatment for detackification. These products work well with lacquers (paints cured by solvent loss), which made

up many low-solids paints in the past. The basic principle of detackification is the cleavage of ester linkages found in the fatty acid-based resin by hydroxide. This results in the formation of a metal-based soap, which emulsifies any remaining solvents in the paint. The remaining material, with no solvent present, cures and hardens into a mass for "easy" removal.

The drawback of the caustic-based program is that, as paint technology has advanced, with changes to higher solids levels (primarily for reasons of environmental compliance) and catalyzed curing, this type of treatment no longer fully reacts with the components of the paint. This results in only partially killed paint, which causes most of the same problems as "live" paint. To combat this problem, caustic-based programs containing some insoluble inorganic material (such as lime) were developed. The insoluble material helps to capture some of the unkilled mass of the paint, essentially embedding it. Even these modified programs are inefficient, however, as the solids level of the paint increases past 25%.

Metal Salts Programs

Metal salts products primarily make use of aluminum and zinc salts combined with a source of alkalinity to form either catalyzed insoluble metal soaps (somewhat similar to the treatment with caustic) or suspended metal complexes, which can be removed by treatment with an additional polymer.

The limitation of this type of treatment is that, except in the case of alkyd-based, air-cured paints, the pH control of the system is very crucial to proper operation. Fluctuations in pH level can easily cause disruption of the program, resulting in live paint and settling solids.

Clay-Based Programs

Clay-based products primarily represent a physical, rather than chemical, method of paint detackification. As bentonite clay absorbs water, it swells to a large irregularly surfaced material. Sticky paint particles entering the water containing this clay adhere to the outside surface and are, in turn, covered by other clay particles. This results in a large detackified mass. An amine is often fed to increase the paint's tendency to disperse prior to contact.

Although the clay itself is relatively inexpensive as treatments go, large amounts of clay or clay slurry are often required to maintain good detackification. This produces voluminous amounts of sludge, as compared with other treatment types. In addition, both water and solvent are often trapped in the clay matrix, making it difficult for landfill and limiting the ability to dewater to a range of 20% to 25% maximum. Clay programs also typically have problems with foaming and biological contamination, due to the entrapment of paint and water in the clay sludge.

Acid Colloid Programs

The acid colloid treatments function on the principle that certain mixtures of hydrophilic (water loving) and hydrophobic (water hating) materials can form stable suspensions under acidic conditions but precipitate as associated complexes as the pH increases. There are three detackification programs currently used based on this principle: silicate amine programs, silica amine programs, and melamine-formaldehyde programs. The basic principle is to feed th e product into the system at a raised alkalinity level to form the associated complex. The hydrophobic end orients onto the hydrophobic paint particle, with the hydrophilic end sticking into the water phase.This effectively allows the paint particle to be coated with a thin film of water that prevents its surface from adhering to other surfaces.

Silicate Amines

In this treatment, the hydrophilic portion is a polyamine and the hydrophobe is a silicate (usually sodium metasilicate). These materials are fed separately to the booth in a fixed ratio based on the paint overspray rate. (Most typically 4 to 13 parts of silicate to 1 part of polyamine and both at 5% to 15% based upon overspray.) The pH level is critical, since too high a pH can cause the complex to redissolve.

The main drawback in silicate amine treatments is that they do not disperse paints very well, nor do they provide instantaneous detackification. Because of this, it is not uncommon to find sticky deposits in the back sections of spray booths where good mixing does not occur. Better detackification usually takes place as the system runs longer.

Silica Amines

The silica amine program is very similar to the silicate amine treatment. The primary difference is that it utilizes an aqueous colloidal silica sol as the hydrophobe. Colloidal silica can be thought of somewhat as a nonswelling clay. The silica sol is fed at a ratio of 1 to 3 parts to each part of polyamine. Since the pH of these materials is essentially neutral, an alkalinity source (usually potassium hydroxide) is fed to bring the system pH to 8.0 to 9.0. The primary drawback of this program is that under conditions of high shear, such as might take place with a centrifuge separator, the small size of the silica might not allow itself to fully embed onto the paint, resulting in partially killed sludge.

Melamine Formaldehyde

This copolymer was originally developed by Du Pont in the early 1940s. It makes use of its unique organic structure to act to detackify paint. The alternating melamine and formaldehyde in the polymer chain form a two dimensional netlike structure, the melamine portion acting as the hydrophobe and the formaldehyde functioning as the hydrophile. Under alkaline conditions, the compound forms an associated complex.The melamines orient on the surface of the paint while the formaldehyde groups attract the water layer that prevents the paint from sticking. Because both of these groups are on the same molecule, the effect of detackification is nearly instantaneous. Also, because the size of the groups is small relative to that of silicate or silica amine, the melamine formaldehyde coats the paint particle much more effectively.

One of the drawbacks of melamine formaldehyde treatment is the relative fragility of the coating. Because of this, it is necessary to disperse the paint well. Under conditions of high shear the coating can be ruptured, releasing sticky paint. The other fact to consider is that because of the sensitivity of this treatment to waterborne particulates, the cleaner the system, the more effective the melamine formaldehyde is in killing the paint. As the solids loading increases, the level of detackification decreases and the ability to form a good floc is affected.

SLUDGE REMOVAL METHODS AND EQUIPMENT

Once the paint sludge has been detackified or otherwise concentrated, it is necessary to use some mechanical means to remove it from the water. The methods used to remove the captured paint overspray from paint booths vary widely in type, effectiveness, and cost. A great deal of the choice as to which method is selected is dependent upon the type of booth, the amount of paint sprayed, the desired end results of the sludge removal, and the money available for equipment. Options available for side- draft and downdraft systems will be examined separately, in terms of both manual and automatic methods.

Side-Draft Systems

In smaller booths, the most common method of sludge removal has historically been skimming. Some portion of most solvent-based paints will usually float if untreated; caustic-based treatments will typically result in partial float/partial sink on a continuous basis, especially when a flotation aid is used. Many users of small booths were, therefore, accustomed to continual skimming of floating material from their systems.

With the advent of paint-dispersing polymer treatments, continuous manual skimming is unnecessary. Elimination of this process reduces much of the daily labor and its associated costs. In side-draft systems, use of a polymer paint detackifier normally keeps paint in a suspended, dispersed state, allowing for flocculation and flotation on a batch (periodic) basis. Manual skimming, with screens or rakes, is still possible at this point. Manual skimming has the next-to-lowest capital cost (the lowest being passive settling, which will be discussed in detail in the downdraft section) but is also labor intensive.

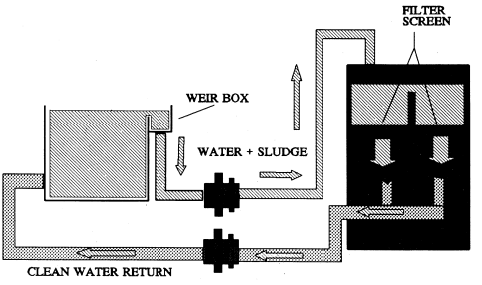


Fig. 1. Tank-side weir for removing floating sludge.

The next level of sophistication in side-draft sludge removal would be the use of semiautomatic or automatic equipment to remove the floating waste. One way of reducing labor and eliminating manual skimming in batch flocculation clean outs would be to use a wet-vacuum filtration system. This basically consists of an industrial wet-vacuum head on a steel drum containing a burlap (or other coarse filter cloth) bag. The floating sludge (and some water) is vacuumed from the top of the booth tank. The paint sludge should collect in the bag, while the water is drained (or pumped) from the bottom of the drum back into the booth. This method can also be used for sludge settling out on the booth tank bottom, although the *settled sludge must be completely detackified*. Another method for removing periodically produced floating sludge is the use of a tank-side weir (see Fig. 1) In essence, a small weir is welded onto the side of the booth tank, allowing floating material to overflow from the booth and be pumped to a filtering tank (or other system) for dewatering.

Side-draft booths can also be equipped for automatic *continuous* removal of floating sludge, using equipment generically referred to as a consolidator (see Fig. 2). This type of system pumps water from the booth into a separate tank. As the water is pumped in, a flocculating polymer is injected into the water, causing the detackified paint sludge to float to the top where it is skimmed off by a continuously moving blade. The clean water is cycled back into the booth. Paint sludge can also be removed continuously without flocculation/floating using filtration methods. The simplest filtration equipment consists of filter beds utilizing paper or cloth media. These systems allow the solid material to settle out on the filter media,with the water draining to some collection unit where it can be returned to the booth. Although this type of system has low labor and capital requirements, it is often very cumbersome, which can be a problem since space around a painting area is usually at a premium. Gravity filtration systems are also slow and restricted as to through put volume, which makes them suitable for only low levels of water or sludge to be processed.

Vacuum filtration, such as that done using diatomaceous earth filters, is effective on completely detackified materials, but can add to the overall volume of waste produced due to the contributions of the disposable media itself.

Centrifugal methods of sludge removal/dewatering are somewhat more expensive to purchase and install than skimming or filtration equipment but can make up the difference in cost with their performance. The two most commonly encountered centrifugal separator types are the hydrocyclone and the centrifuge. Hydrocyclones (see Fig. 3) are basically solids-concentrating devices. Liquid (in this case, paint-booth water) enters the hydrocyclone under pressure and spins around the inside surface of the cone. This spinning imparts an increased force of gravity to the liquid, which in turn causes the heavier solid particles to be pulled outward (by the centrifugal force) to the walls of the cone. The opening at the bottom releases part of the pressure, which causes the lighter liquid to be pulled back upward through the cone exit in a vortex much like a tornado (hence the "cyclone" part of the name). The solids (and some water) exit at the bottom. Because of the fact that some water does exit along with the paint sludge solids, hydrocyclones by themselves are not efficient dewatering devices. Typically the sludge and water exiting the cone drains into a drum or container where it is further expected to separate due to gravity. Several of these systems have been designed with secondary filtration systems (such as filter belts) to further dewater the sludge. These systems are effective if the paint remains fully detackified at all times. Any tacky paint entering the system can cause problems and plugging of both the cone and the belt.

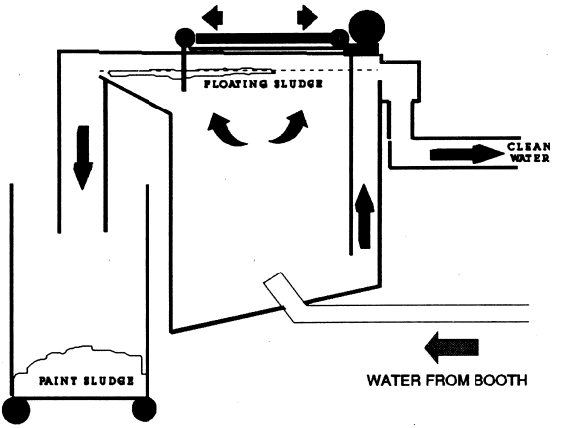


Fig. 2. Consolidator for continuous removal of sludge from side-draft booths by floating sludge.

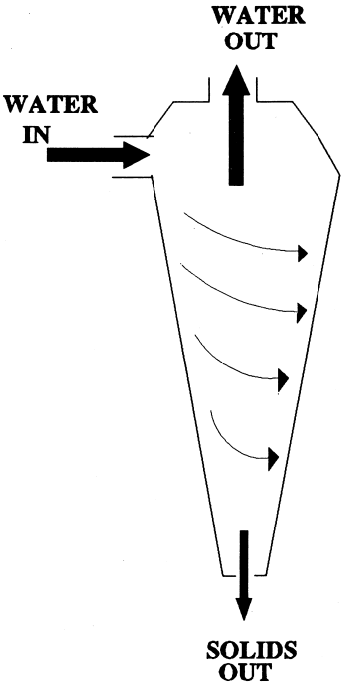


Fig. 3. Principle of hydrocyclone separators.

Centrifuges work on the same principle as the hydrocyclone except that, instead of the water spinning through the cone, the water is pumped into a spinning drum

(much like a clothes drier set on end), which imparts the centrifugal force that "throws" the water out of the solids. A cake of solid material then builds up on the walls of the drum. In the simplest of these systems, the centrifuge (see Fig. 4) is allowed to operate until the drum is full, after which the drum is removed and manually emptied. The more elaborate systems will periodically go through a "cleaning" cycle where the solids will be automatically scraped from the drum and allowed to fall into a container. These systems can produce sludge at a level of 85% solids or more (with some paints), as compared to the average of 40% to 60% solids from a hydrocyclone. The major downside of this is, as previously mentioned, the high equipment cost. A fully automatic system will cost upwards of $35,000, as compared to the $15,000 for a hydrocyclone.

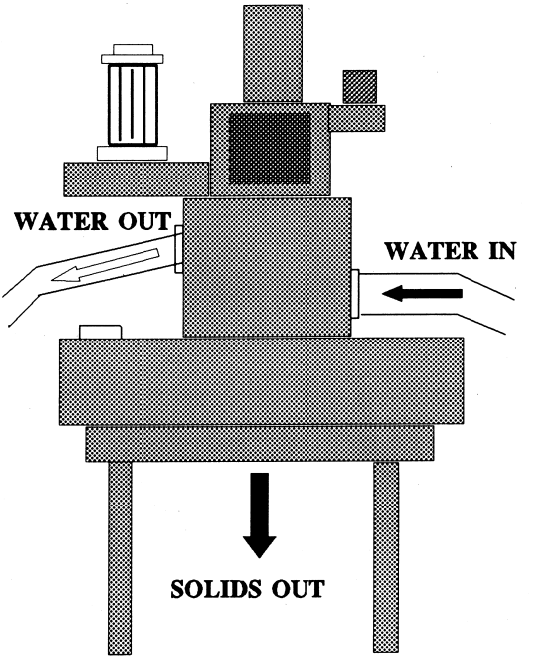


Fig. 4. Centrifuge system for sludge dewatering.

Since these centrifugal-type systems function by pulling solids directly from the booth water, it is vital to maintain uniformity of the water through agitation and circulation. To assure complete agitation, many of these centrifugal systems are packaged with booth agitation equipment, which may include some type of tank bottom sprayers. Since polymeric detackifiers tend to settle out in still water, the addition of bottom circulation may enhance the operation of the chemicals, not only with centrifugal systems but in all operations.

Depending on the method chosen and its efficiency, the system water can be virtually free of contaminants after treatment. With an efficient method of solids removal, the water can be reused in the booth for sometime, conserving water usage and reducing disposal costs. The selection of the chemical treatment program and sludge removal system is dependent upon the type of paint, type of booth, and the money available. Virtually any level of water quality is achievable, given that capital is available; for example, distillation equipment can be purchased for complete solvent removal from water and infrared drying systems are available to reduce paint sludge to a dry powder to minimize the cost of disposal. Most companies, however, do not have unlimited capital to spend on paint booths or the related products and equipment for water clean up. Using the information provided here and an understanding of the particular system in question, an end user should be able to pick the right chemical and mechanical means to minimize the water pollutants coming from the paint shop. Doing so will reduce overall operating costs, reduce water consumption, and help in conserving one of the most important natural resources.

WASTEWATER TREATMENT SYSTEMS FOR FINISHING OPERATIONS

BY ALAN MONKEN

One of the most common growing areas of concern in organic finishing operations is waste disposal. Where wastewater discharge into municipal sewers was once common place, greater and greater restrictions are being placed on any effluent from manufacturing operations, not only for obvious problem areas such as plating operations, but also for water once considered innocuous, such as spray washer rinse stage overflow. In some situations, it is possible to conserve water usage/discharge with filtration systems; it is also possible to find waste haulers to remove contaminated water from the plant. However, both can be costly and neither is a long-term answer to the ever-increasing regulations governing disposal of industrial waste. The best solution is to pursue installation of an in-plant treatment system, putting the control and reduction of contaminants in any effluent directly in the hands of the manufacturer. Before doing so, however, it is necessary to determine what types of materials may be entering your waste stream and the methods available to treat/remove them.

SOURCES AND TYPES OF WASTE CONTAMINANTS

The type of operation at each individual finishing shop largely determines the types of materials that will enter the waste stream, and the type of treatment that will be required for the resultant waste influent. The types of operations typically found include metal forming processes such as drawing, stamping, and bending, chemical treatment processes such as plating and phosphatizing, and coating processes such as painting.

Metal Forming Operations

In metal fabrication there are a number of processes that may been countered. One of the most common is drawing, the process by which sheet metal stock (or other material) is formed in a press into a cup like or box like shape. During this process lubricants known as drawing compounds are normally required to prevent scoring and damage from the metal-to-metal contact between the stock metal and the die.Coolants may be required for this process due to the heat of friction produced, which can reduce die life. These lubricants and coolants are normally oil-based compounds, either "natural" (i.e., petroleum or animal-fat derived) or synthetic. In addition, metal can be drilled, cut, forged, stamped, or cast, each of which may require additional coolants or lubricants. While these coolant and lubrication systems are typically closed (i.e., not directly tied to the wastewater stream), residue from these materials normally must be removed from the work in process.

Paint Pretreatment Operations

In metal fabrication operations the normal sequence of events in production is formation of raw metal stock into component parts, which are assembled and, most typically, painted. After the forming process it is necessary to go through several pretreatment steps prior to painting, including chemical or physical treatment to remove rust or other surface defects (such as mill scale) resulting from

the forming process or handling; cleaning of the parts or assembled product with oils, greases, and other soils present due to the forming processes (such as drawing compounds and lubricants); and conversion coatings (such as iron and zinc phosphates), which are applied to promote enhanced paint performance and provide corrosion inhibition. A similar sequence of events is used in plastics manufacture, with cleaners, alkaline and acidic, used to remove shop soils and mold release agents, and conditioning agents applied to promote better paint adhesion. Because most of these processes are aqueous-based, a number of opportunities exist for contaminants to enter the waste stream. From the derusting or pickling operations, extremely low pH solutions, often high in iron and other dissolved metals, require eventual disposal. Alkaline cleaner solutions contain surfactants, which are present to help remove/disperse oils and greases but can themselves add to the organic pollutants requiring removal in waste treatment. In addition ,the more alkaline caustic-based cleaners require pH neutralization when treated for disposal.

These cleaners may also contain chelants, which are chemical compounds present to tie up metal fines and particulates in the water solution. When sent to treatment, these chelants may prevent the easy precipitation of metals. The tank solutions of alkaline cleaners will also contain high levels of oils and greases coming from the drawing compounds, etc., being removed as soils.

Conversion coating baths are typically at a low pH during use. Depending on whether the process is iron or zinc phosphating, there will be a high concentration of that particular metal when the tank is dumped; in either case, there will be a large amount of phosphates, both soluble and insoluble (in the form of sludge).

In cleaning and prepaint treatment systems one of the most important process steps is the clear water rinse. These rinses may be continuously overflowed or recirculated, or a combination of the two.The rinse stages will gradually become contaminated with the same materials as the chemical process stages due to carry over and drag-out from stage to stage.

The final stage of a multiple stage washer often is used to apply a rust inhibitory material or other final sealing rinse material. These treatments can include chromium, zinc, and other exotic metals, which may require special treatment for removal.

Paint Operations

Once the formed parts are cleaned and pretreated, they are ready for painting.

Sprayed liquid paint is applied in an apparatus called a spray booth,which is typically a water system. Although these booths are closed systems, with the sludge removal taking place at the booth site, there maining water from cleanout of the booth is often pumped directly to waste treatment for disposal. This water may have a high pH (if caustic-based detackifying chemicals are in use) or high dissolved solids (if a polymer system is in use). Surfactants, miscible solvents,and other debris may also be present. When water-based paints are sprayed, it may be more practical to continuously cycle the dispersed paint-and-water mixture directly to waste treatment. The waste treatment scheme has to be adjusted to account for this other material.

ADDITIONAL SOURCES OF OPERATIONAL CONTAMINANTS

There are a number of other processes, which may be in use inorganic finishing operations that will significantly impact waste treatment.

Electroplating generates copious amounts of wastewater to be treated, normally for removal and/or destruction of materials such as chromium,cyanide, nickel, cadmium, copper, lead, and zinc. The wastewater from such systems is usually at the extremes of the pH scale depending upon which stage is being treated, thus requiring neutralization. Processes such as aluminum anodizing will also produce significant amounts of pollutants, similar in some cases to electroplating systems, with high amounts of hexavalent chromium and other metals to be removed and highly acidic and alkaline wastewater to be neutralized.

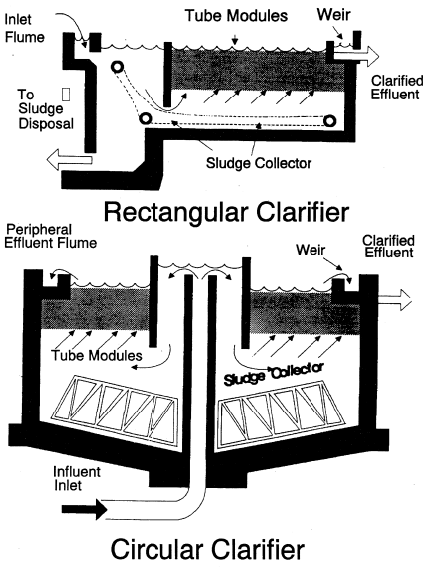


Fig. 1. Clarifiers

WASTE TREATMENT SYSTEMS

Waste treatment systems are put into place to remove the various pollutants entering the waste stream from plant operations. These systems have grown in sophistication over time from simple settling ponds to complex osmotic filtration units. The typical waste treatment system consists of a series of tanks in which wastewater can be collected and chemically treated as necessary to remove contaminants. Depending on the rate of water flow, the system may be continuous or may involve batch treatment. (As a rule, systems in which spray washer rinse run-off and "dumped" washer stages are the prevalent material in the waste stream can typically be treated on a batch basis; systems consuming large amounts of water on a continuous basis, such as electroplating or electrocleaning lines, are often treated in a continuous system.) In the case of materials such as hexavalent chromium a dedicated tank might be necessary for segregation/treatment of a particular pollutant. The material can then be treated, adjusted, and, quite possibly, removed from the water, which then moves on in the treatment system. Other tanks may simply be used for pH adjustments, such as those to neutralize highly acidic or alkaline materials. Once the wastewater is adjusted to the desirable state, it moves into the area of solids removal. This may be done through physical filtration,such as a sand filter system, or through gravity separation, such as would be done in a settling pond. Commonly, however, the particles/pollutants remaining in the water at this point either are not heavy enough to rapidly settle in a simple still pond or are not in a form to ever settle under normal means. To facilitate this process, inorganic materials such as lime or alum can be added to help flocculate the solid pollutants, bringing them together in a mass. Organic polymers can also be used to coagulate the smaller particles, as can combination products made up of polymers and inorganic salts. To further facilitate the settling of these pollutants, a piece of equipment known as a clarifier is used. The

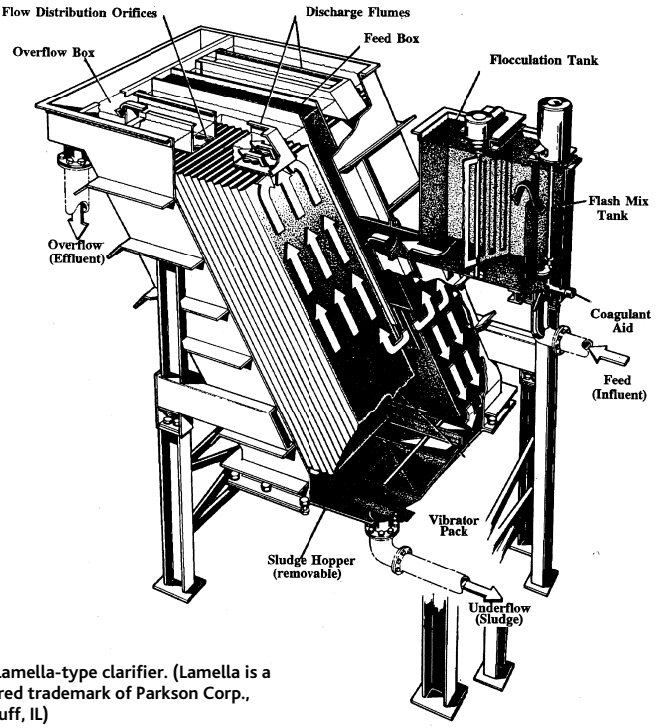


Fig. 1. Lamella-type clarifier. (Lamella is a registered trademark of Parkson Corp., Lake Bluff, IL)

overall purpose of this type of equipment is to remove solids from water streams by gravitational settling in a relatively small area. In much the same way that the polymeric detackifier/flocculent programs remove paint solids,the basic principle involves capturing lightweight dispersed solids and increasing their density/weight with the organic polymers or inorganic materials.

Clarifiers come in various designs, ranging from large rectangular pits to circular tanks (see Fig. 1). The larger circular clarifiers are quite common in continuous treatment type systems with daily flow rates in excess of 250,000 gal/day. For smaller systems, as are typically found in metal fabrication operations, the lamella-type clarifier is quite common (see Fig. 2).The lamella makes use of stacked flow plates to effectively increase the settling surface area to equal that of a much larger tank-type clarifier, resulting in a system that will separate a large amount of solids while requiring a relatively small amount of floor space.

The basic mode of operation followed in industrial waste treatment is:

1. The water stream containing spent detergent solutions, rinse solutions, waste process water, and any other waterborne waste materials is cycled into the treatment system, either continuously or in a batch process;
2. Chemical additions are made to the wastewater, including adjustments to pH and reduction of metals such as hexavalent chromium;
3. Treatment chemical additions are made to the adjusted wastewater to aid precipitation (settling) of solids; this treatment may consist of addition of in-

organic materials, such as alum or ferrous sulfate, or organic polymers, or some combination of the two;

4. The precipitated solids are pumped from the clarifier to a secondary system for further dewatering; the dewatering system may be anything from a sludge consolidation pit to a plate and frame filter press.

The waste treatment system allows suspended solid pollutants to settle out of the water stream for collection and, in addition, can remove dissolved, dispersed, or otherwise-distributed contaminants by treating them (typically chemically) to separate them from the water in the waste stream. Examples of these contaminants include oils and greases dispersed by surfactants and metals made soluble by chelants. Once these dispersed materials have been "destabilized," the normal methods of collection in the waste treatment system allow the "solids" to settle out. Other additives such as polymers are added to increase the settling rate of the "solids" by increasing the density/weight of the particles. The net result is the removal of all materials infiltrating the water stream from the point of entering the facility to the point of leaving it. With the ever-increasing regulations concerning the contents of discharged water, it may often be the case that the effluent water is of a higher overall quality than the influent. These systems can be run effectively with a minimum of effort on the part of the organic finisher by recognizing what pollutants enter the stream within the plant and how each impacts the treatment program. By working with the various chemical suppliers within the functional areas, problems of treatment for the finisher should be minimized and discharge limits in all areas easily met.

WASTEWATER TREATMENT FOR ELECTROCOATING

BY GORDON S. JOHNSON
TTX ENVIRONMENTAL, STURGEON BAY, WIS.

Because it is an immersion process, electrocoating employs the use of a large amount of water. Typically, pigment, resin, and additives make up only 10 to 15% of the contents of an electrocoating paint tank. Electrocoating is also an extremely efficient coating process due to recycling of paint through ultrafiltration, with usage typically ranging from 95 to 99%; however, the small amount of paint, which may at some point elude deposition, must be extracted from the waste stream prior to discharge.

Wastewater treatment strategies for electrocoating — like those for pretreatment stages — are based on three main considerations: (1) removing impurities from the process tanks; (2) retaining useful materials in the process tanks; (3) minimizing the impurities for disposal.

Waste streams from other sources, i.e., pretreatment stages, may not be initially compatible for treatment with electrocoating paint wastes. Problems arise often enough to warrant conservative strategies — the most basic of which is to separate the different wastes for differing methods of treatment before combining the resultant waste streams for common disposal (Fig. 1). Cleaning wastes are one category. Zinc and iron phosphate conversion coatings and their rinses are another. The chrome seal and the rinse(s) for that stage area third category. Finally, there are the E-coat paint wastes themselves.

Treatment for pretreatment wastes has been examined elsewhere in this publication. Here, we will consider treatment strategies specific to the electrocoating process.

ELECTROCOATING WASTES

As was previously stated, E-coating is an extremely efficient process in which 95% or more of the components (resin, pigment, and other additives) entered into the paint tank will eventually find themselves applied and cured on the product. Except in rare cases of catastrophic tank contamination, the amount of paint solids requiring waste treatment on a regular operating basis is typically very small.

Solution from the paint tank continually undergoes ultrafiltration (UF) to prevent process contamination and produce final rinse makeup. Typically fronting the UF units are one or more bag filters of increasing filtering capabilities, which remove foreign particulates that have entered the paint bath. After ultrafiltration, the paint itself is returned to the tank while the permeate is pumped into the final post rinse. The post rinses counterflow back to the paint tank, returning excess paint to the electrocoating stage.

Ultrafiltration is not considered a portion of the waste treatment system, although a small amount of paint will be removed from this closed loop when the bag filters are replaced. The bag filters are disposed of along with concentrated paint wastes.

The main sources of paint waste are tears in anodes, tank cleaning and ultrafilter cleaning operations, spillage, and final post rinse dumping in situations where reverse osmosis (RO) water is used as tank makeup.

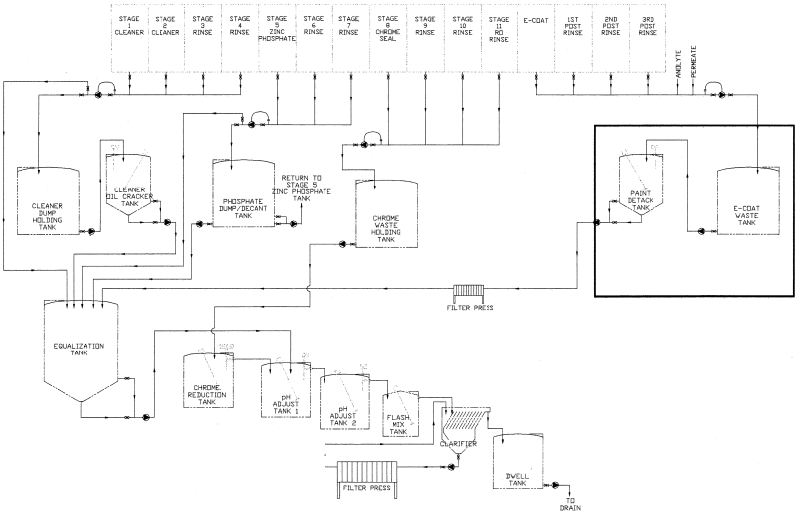


Fig. 1. This drawing represents a complete waste treatment strategy for electrocoating systems. Waste streams from cleaning, phosphating, chrome sealing, and coating operations are initially segregated for individualized treatment before combining pH adjustment and flocculation for solids removal. Segregated paint treatment stages are shown in the box at the upper right.

Solutions containing paint wastes are first pumped to the E-coat waste tank, a storage container dedicated to that purpose. Because the volume is low, they are treated on a batch basis in the paint detackification tank. When cathodic paint is present, a detackification polymer is dissolved into the solution and the pH is raised to approximately 9.0. The paint destabilizes and becomes a small curdlike substance that is no longer tacky. If anodic paint is treated, the pH is lowered to 4.5 after addition of the detackification polymer. The paint will again destabilize and form a curd.

The detackified paint curd is separated from the liquid portion of the paint by a dedicated filter press or some other filtering device. The filter cake can be reduced in volume by further dewatering or evaporation. In any case, it must be disposed of properly as it may bea RCRA hazardous waste under federal code 40 CFR 261.31, FO19. Liquid remaining after the filter press step is sent to the equalization tank where it is mixed with waste solutions from pretreatment processes before further treatment in a common waste stream including pH adjustment and clarification.

During tank cleaning operations, the solution in the electrocoating tank or any of the post rinses are pumped to the E-coat waste tank for storage. The remaining paint wastes cleaned out the tank are flushed directly to the paint detackification tank for treatment. The contents of the E-coat waste tank can then be returned to the tank from which they originated.

Proper handling of waste products created by the cleaning, pretreatment, and painting processes is an extremely important part of the entire electrocoating equation. Waste treatment strategies must focus on removing impurities from the system while retaining paint chemistry. Although small in volume, paint wastes are registered substances, which must be segregated and removed from the waste stream prior to proper disposal of the solids and pH-adjusted discharge of treated liquid components.

CONVERSION OF PLATING LINE RINSES TO A CLOSED-LOOP DEIONIZATION SYSTEM

BY DAVE FISTER, SENIOR STAFF ENGINEER, NEW YORK STATE POLLUTION PREVENTION INSTITUTE AT ROCHESTER INSTITUTE OF TECHNOLOGY, ROCHESTER, N.Y.

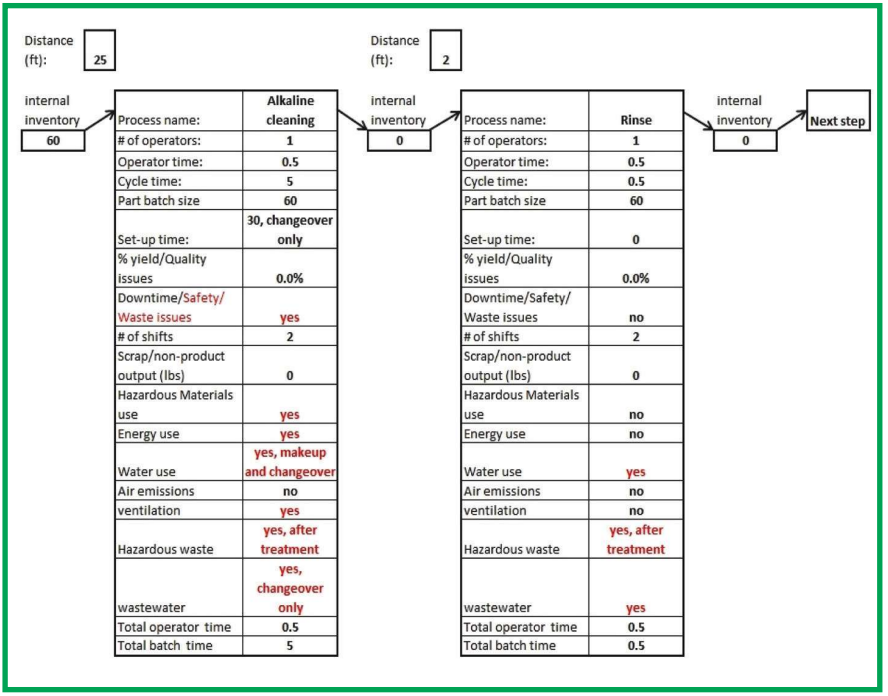
Background. An upstate New York manufacturing company (Company XYZ) has a captive plating shop with hard chrome, black oxide, and copper plating processes.

The chrome, copper and black oxide plating lines all have rinse tanks to remove any heavy metal residue or other chemicals as parts move from tank to tank. Since regulatory requirements limit the amount of dissolved heavy metals and other effluents that can be released into the sewer system, Company XYZ also has in-house wastewater treatment capabilities to remove dissolved metal from their rinse water. Their method for accomplishing wastewater treatment was changed dramatically in early 2011, resulting in plating process improvements and electricity reductions.

Overview. Company XYZ worked in collaboration with NYSP2I (New York State Pollution Prevention Institute) on a Lean, Energy & Environment assessment, which resulted in an opportunity to convert their rinse waste processing in their plating lines and chrome exhaust scrubber. This consisted of eliminating the existing electro-precipitation process and moving to a reverse osmosis, deionization system (RO-DI). The results were consistently cleaner rinse water, reduced electricity use, and reduced maintenance on the chrome exhaust scrubber. The annual electricity savings, scrubber maintenance savings, added cost of resin column generation resulted in a net annual savings of $21,627 with an expected simple payback of two and a half years (after the NYSERDA capital rebate of $25,000). Total capital cost, including new equipment purchase and old equipment removal, was approximately $80,000.

Lean, Energy & Environment (LE2) Approach. A Lean, Energy and Environment (LE2) approach was used to identify environmental and energy savings for Company XYZ. LE2 combines two programs previously developed by the U.S. Environmental Protection Agency; the Lean and Energy program, and the Lean and Environment program. The Lean and Energy program offers practical strategies and techniques to Lean implementers about how to improve Lean results while reducing energy use, costs, and risk. Similarly, the Lean and Environment program offers practical strategies and techniques to Lean implementers about how to improve lean results while achieving environmental performance goals. LE2 combines both of these programs into a single assessment program.

Energy waste and material waste are non-value added aspects of manufacturing, just as much as labor waste. The use of all three aspects of manufacturing allows



Process name:	Alkaline cleaning
# of operators:	1
Operator time:	0.5
Cycle time:	5
Part batch size	60
Set-up time:	30, changeover only
% yield/Quality issues	0.0%
Downtime/Safety/ Waste issues	yes
# of shifts	2
Scrap/non-product output (lbs)	0
Hazardous Materials use	yes
Energy use	yes
Water use	yes, makeup and changeover
Air emissions	no
ventilation	yes
Hazardous waste	yes, after treatment
wastewater	yes, changeover only
Total operator time	0.5
Total batch time	5

Process name:	Rinse
# of operators:	1
Operator time:	0.5
Cycle time:	0.5
Part batch size	60
Set-up time:	0
% yield/Quality issues	0.0%
Downtime/Safety/ Waste issues	no
# of shifts	2
Scrap/non-product output (lbs)	0
Hazardous Materials use	no
Energy use	no
Water use	yes
Air emissions	no
ventilation	no
Hazardous waste	yes, after treatment
wastewater	yes
Total operator time	0.5
Total batch time	0.5

Figure 1. Simple example of a lean value stream map with energy and environmental components added.

a company to find significant waste across their entire manufacturing process by combining labor, materials, energy, and environmental components to each process step.

For Company XYZ the primary focus of the LE2 was on the energy and waste aspect of their plating operation and less on the lean aspects of the operation since energy and environmental issues were dominant. Partial capital funding and engineering funding was provided by a combination of funds from the New York Department of Environmental Conservation (engineering funding) and the New York State Energy Research and Development Authority (capital funding assistance).

Figure 1 is an example of two plating process steps using lean but also including energy and environmental items. Lean typically focuses on operator time, distance of part travel, lags between operations, scrap, etc. Figure 1 shows the energy and environmental opportunities in red. For energy, there are direct electrical costs associated with ventilation fans and tank heating. There are indirect costs associated with heating or cooling of make-up air from the exhaust ventilation. There are secondary energy costs not shown in this example for pumping wastewater to waste treatment, wastewater mixing, and sludge presses that would be typical of a plating operation.

There are costs of hazardous materials used in the alkaline cleaning operation such as the purchase costs, protective equipment for operators, neutralization



Figure 2. Reverse Osmosis System, 3,200-gallon per-day output at Company XYZ.

chemicals in wastewater treatment, and sludge disposal as a hazardous waste or regulated waste. Finally, in the rinsing process there is the cost of water in purchasing, sewer charges, and treatment and testing costs before disposal to sewer.

Original Rinse Water Treatment Process and Associated Costs. Company XYZ's original rinse water treatment to remove dissolved metals was with electro-precipitation. (Electro-precipitation is a technology using a combination of oxygen from air and electrochemical reactions at the anode and cathode that causes dissolved metals to precipitate out of solution and form a sludge.) The process does not require chemical additives, unlike other methods of treating dissolved metals. Company XYZ would recirculate the treated water back through their rinsing system and their scrubber until sufficient salts built up in the water to cause rinsing problems. The system used significant amounts of compressed air to oxygenate the water and significant electricity—both for pumping water through the system and for the precipitation electrodes. This system also treated the scrubber water from the chrome exhaust system in the same way. Chrome mist from the chrome plating tanks was captured by the scrubber water. This scrubber water required treatment in the same electro-precipitation system to remove the chromium. The total energy consumption of the electro-precipitation water treatment was 192,196 kWh per year at a total electricity cost of $16,041 per year. The annual cost for disposal of the hazardous sludge from the electro-precipitation process was approximately $7,900.

Another cost was scrubber ball disposal twice a year due to biofouling associated with high mineral and organic content of the recirculated electro-precipitation water. The electro-precipitation process cannot remove organics and the acid and alkaline rinses produce salts, which also cannot be removed by this process. The cost of scrubber cleanout labor, scrubber ball replacement, and scrubber ball disposal as hazardous waste was approximately $22,400 per year. Therefore, the total costs associated with the electro-precipitation process were $46,341 per year.

The original electro-precipitation treatment process had the following electricity consuming components, which ran 24 hours a day and 7 days per week:

- **(3) 1 HP Water Circulation Pumps**
- **(1) 2 HP Water Circulation Pump**
- **(1) 1 HP Reactor Pump**
- **(1) 1 HP Filter Pump**

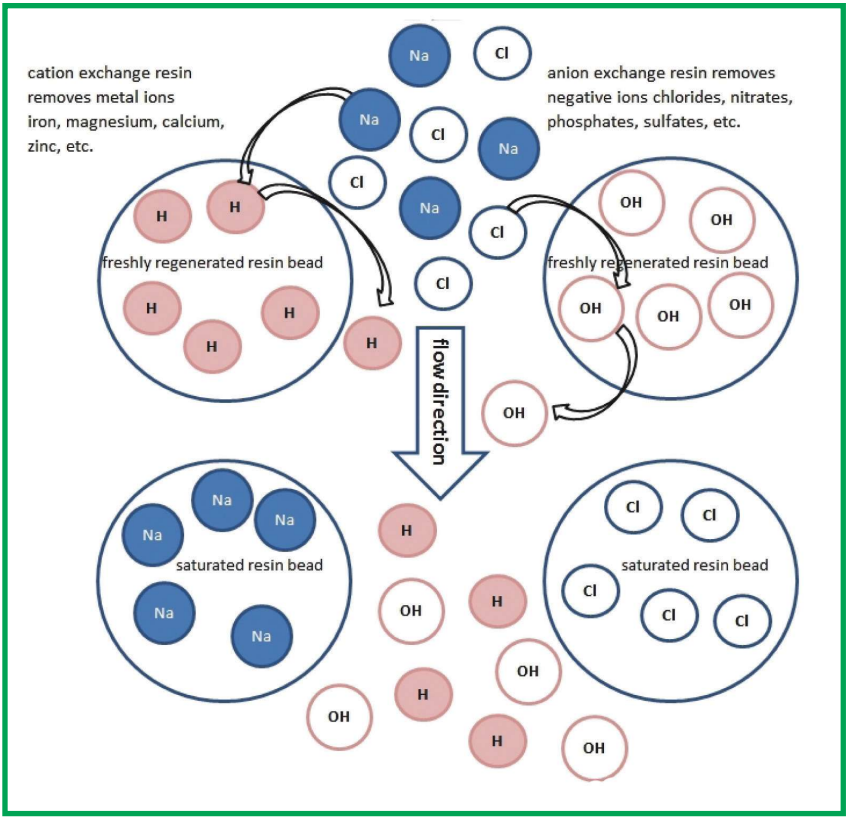


Figure 3. Mixed-bed DI system showing anion and cation exchange on the resin beads.

- **(1) 5.8 HP Sludge Blower**
- **Compressed Air (from main system)**
- **Electrode rectifier**

The electro-precipitation allowed salt and organic build-up so the rinse water system was drained and replenished on a regular basis to keep the contaminant levels down. Due to this drain-and-replenish cycle, the rinse water quality gradually degraded after the replenishment process. Therefore, the rinse water had to be monitored to prevent poor rinsing of parts and chemical contamination of the plating tanks by dragout from the rinses.

New Rinse Water Treatment Process. The new process starts with a reverse osmosis system to pretreat the incoming city water. This water serves as make-up water for tank evaporation and tank changeovers.



Figure 4. DI system for one of the plating rinse tanks.

An RO system (reverse osmosis) has a membrane that is permeable to water and a small percentage of ions, typically less than 5% of the total ion loading. The primary purpose of the RO system as a pretreatment for Company XYZ is to remove the hard water ions such as magnesium and calcium before this water is used in the various plating line tanks. If the city water was used directly in the plating rinse tanks, the magnesium and calcium would be removed by the ion-exchange system but would needlessly reduce the life of the ion exchange resins.

Figure 2 shows the RO system at Company XYZ. It should be noted that a typical RO system is about 50% efficient since it relies on pressure to push the pure water through the RO membrane (against the osmotic pressure), leaving the hard water ions behind. Therefore, 100 gallons of incoming water produces about 50 gallons of low ion water and 50 gallons of high ion wastewater.

Each rinse tank and the chrome exhaust scrubber have dedicated sets of ion-exchange columns (DI) to remove dissolved metals and other ionic impurities as the water in each system recirculates through the tank and the columns. The pump on each DI tank is very small, resulting in low electrical use. The DI units start with particulate filters, followed by carbon filters for particulate and organic material removal. Next, water is passed through the DI columns to remove the dissolved metal ions and other cations and anions. These columns eventually become saturated with ions and must be sent out for regeneration where the ions are stripped off the active sites on the DI resin and are ready for another cycle of use. Only the DI columns used for the chromium and copper plating rinses go out as hazardous waste compared to the previous process, where the sludge from all the tanks went out as hazardous waste since there was no rinse water segregation. (Figure 3 shows schematically how the active sites on the DI resin beads act to pick up anions or cations from the rinse water.)

The DI systems remove the metal ions from the plating tank rinses and the metal ions and salts from the cleaning rinses and acid rinses. Regenerating the ion exchange columns is the means of removing the metals from the resin columns and allows the columns and resins to be reused. There are transportation and treatment costs associated with each column regeneration, and costs approximately $300 per DI column regeneration. Figure 4 shows one of the skid-mounted DI systems at Company XYZ used for one of the rinse tanks. Since the column regeneration costs are a major portion of the new system's operating cost, conservative estimates were used to determine the DI tank life. All the DI tanks have lasted longer than the estimates.

There was one start-up issue that caused the scrubber DI tanks to have a much shorter life. Fine "silt" from the scrubber was being flushed out during start-

up and caused physical plugging of the DI tanks. After the initial purge of the scrubber, the tanks no longer had problems.

The electricity utilization of the new system is almost an 80% reduction compared to the old system, primarily due to the elimination of compressed air and the overall reduction in pump sizes. Table 1 summarizes the electricity use of the old electro-precipitation system compared to the new system.

The RO/DI treatment process has the following electricity consuming components which run only during plating line operation (24 hours, 6 days/week):

- **(7) 1/4 HP Rinse Tank Water Recirculation Pumps (small tanks)**
- **(1) 1/2 HP Rinse Tank Water Recirculation Pump (Chrome)**
- **(1) 1 HP Cleaning Tank Recirculation Pump**
- **(1) 5 HP RO Pump**

Although the RO pump is relatively large compared to the other motors (5 HP), it is utilized approximately 50% of the time compared to the old system's large pump (5.8 HP), which ran continuously.

CONCLUSIONS

Table 2 is a summary of the costs and operating expenses associated with the original system of water treatment using electro-precipitation and the operating costs associated with the RO/DI system. As shown, the main operating expense of the new RO/DI system is the cost of regenerating the DI columns, estimated at $12,000/year since the system has been running since April 2011. This

Electricity Costs: Original Water Treatment System Compared to New RO-DI System		
	kWh/year	Cost ($/year)
Total Electricity Consumption by Electro-Precipitation	192,196	$16,041
RO/DI System		
RO/DI Water Treatment System to Replace Electro-Precipitation	37,517	$3,114
Total Electricity Saved:	**154,679**	**$12,927**
Cost per kWh is $.083 (blended cost)		

Table 1. Annual electricity savings.

Annual Costs ($.083/kWh)			
	Original Electro-Precipitation	New RO/DI	Net Savings
Electric, pumps, etc.	$7,160	$3,114	$4,046
Electric, compressed air	$8,881	$0	$8,881
Sludge Disposal/Column Regeneration	$7,900	$12,000	(-$4,100)
Scrubber Maintenance	$22,400	$9,600	$12,800
Totals	**$46,341**	**$24,714**	**$21,627**

Table 2. Summary of operating costs, old system, new RO/DI system.

new expense is offset by the reduced electrical use both in pump motors and in compressed air use (savings of $12,927/year) along with the elimination of sludge disposal ($7,882/year). Scrubber maintenance costs are expected to go down by 50–75% (from every 6 months to up to two years between maintenance cycles) due to a reduction in biofouling by reducing organics in the scrubber water.

The combination of environmental improvements, including elimination of hazardous sludge waste and reduction in electricity consumption, resulted in a total annual operating cost savings of $21,627 for Company XYZ. The simple payback after the NYSERDA rebate is expected to be two-and-half years. The overall process control of each rinse tank is much easier with a simple DI tank exchange after the tank reaches saturation. Overall rinse water cleanliness is noticeably better, with even the chrome rinse tanks being clear rather than yellow from the chromic acid dragout.

ACKNOWLEDGMENTS

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Disclaimer: Any opinions, findings, conclusions or recommendations expressed are those of the author(s) and do not necessarily reflect the views of the Department of Environmental Conservation. NYSERDA has not reviewed the information contained herein, and the opinions expressed in this report do not necessarily reflect those of NYSERDA or the State of New York.

BIO

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THE OPERATIONAL BENEFITS IN DELISTING HAZARDOUS WASTES GENERATED BY THE FINISHING INDUSTRY

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The U.S. Code defines a hazardous waste as:

(1)...a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may—

a. cause, or significantly contribute to, an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or
b. pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.[i]

Further, the Resource Conservation and Recovery Act or RCRA defines hazardous wastes as:

(1) Wastes that are contained on an EPA List (e.g., electroplating wastes like F006, F009, and F019), or
(2) Wastes that are characteristically hazardous (e.g., corrosive, ignitable, reactive), or
(3) Wastes that are mixtures of hazardous wastes and solid wastes (e.g., a mixture of F019 wastes and filters), or
(4) Wastes that are derived from hazardous wastes (e.g., wastewater treatment plant sludge from a process that meets the definition of a F006 waste).ii

Metal finishing processes frequently generate objectionable by-products that might include, for example, air emissions, wastewater treatment plant sludges, characteristically hazardous corrosive wastes, organic halogenated solvents, and cyanide. An overview of the wastes typical of the metal finishing industry is provided in Table 1.

It is not unusual for waste disposal to be one of the more costly operating expenses at a metal finishing plant. Managing hazardous wastes at a plant is also a very resource-intensive activity. Tasks such as labeling, storing, manifesting, training, signage, spill response, closure, and long-term liability are all integral to the proper management of hazardous wastes. The most common waste codes applicable to the metal finishing sector are F-Codes F006, F009, and F019. F006 and F009 deal with electroplating while F019 pertains to the chemical conversion coat-

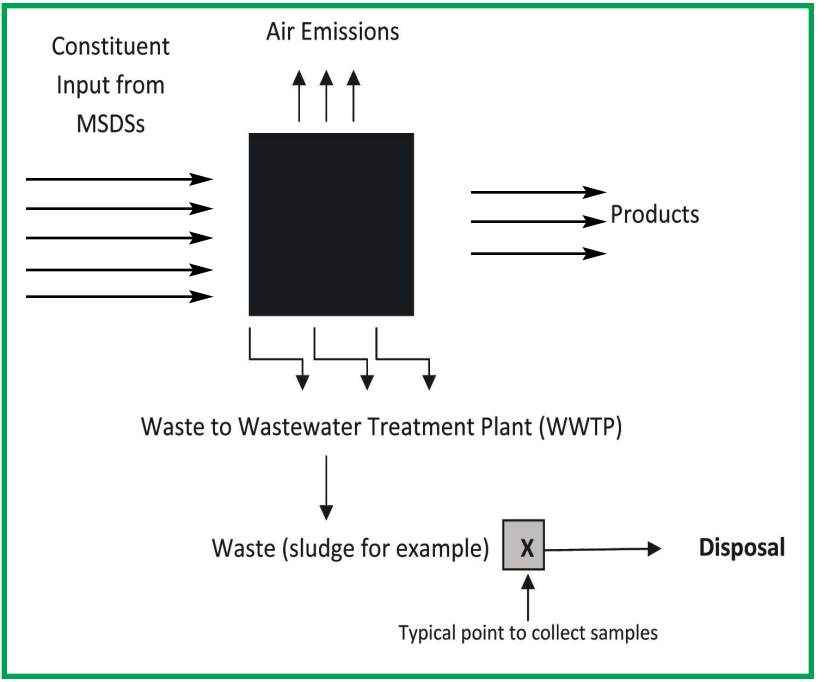


Figure 1. Mass Balance Approach Used for an Engineering Analysis

ing of aluminum. It is not uncommon for facilities to spend well over $100,000/year dealing with these F-coded wastes. Disposal costs, including all the tasks referenced above—plus transportation and state fees—can run to well over $200/ton.

One way around these high disposal costs is to go through the process of excluding or delisting the waste from consideration as hazardous. Regulations at 40 CFR 260.22 outline in general what is required to delist a waste. Major components of a delisting include: identifying constituents of concern, preparation of a sampling and analysis plan, preparation of a quality assurance project plan, close coordination with the regulatory authority having jurisdiction (either an EPA Region or a State agency), and publication of proposed and final rules in the *Federal Register*.

Hazardous Waste Delistings. Delistings are primarily handled out of an EPA Region with Regions 4, 5, and 6 performing the most delistings. Some states, however, have jurisdiction to perform delistings (e.g., Georgia, Indiana, and Pennsylvania) and in such cases you will want to coordinate your activities with the state environmental agency.

There are a number of resources you will want to review prior to undertaking a hazardous waste delistings. A few of these are listed in Table 2.

Process	Material Input	Air Emission	Process Wastewater	Solid Waste
Surface Preparation				
Solvent Degreasing and Emulsion Alkaline and Acid Cleaning	• Solvents • Emulsifying agents • Alkalis • Acids	• Solvents • Caustic mists	• Solvent • Alkaline • Acid wastes	• Ignitable wastes • Solvent wastes • Still bottoms
Surface Finishing				
Anodizing	• Acids	• Metal ion-bearing mists • Acid mists	• Acid wastes	• Spent solutions • Wastewater treatment sludges • Base metals
Chemical Conversion Coatings	• Dilute metals • Dilute acids	• Metal ion-bearing mists • Acid mists	• Metal salts • Acid • Base wastes	• Spent solutions • Wastewater treatment sludges • Base metals
Electroplating	• Acid/alkaline solutions • Heavy metal-bearing solutions • Cyanide-bearing solutions	• Metal ion-bearing mists • Acid mists	• Acid/alkaline • Cyanide • Metal wastes	• Metal • Reactive wastes
Plating	• Metals (e.g., salts) • Complexing agents • Alkalis	• Metal ion-bearing mists • Acid mists	• Cyanide • Metal wastes	• Cyanide • Metal wastes
Miscellaneous (e.g., polishing, hot dip coating and etching)		• Metal fumes • Acid fumes • Particulates	• Metal • Acid wastes	• Polishing sludges • Hot dip tank dross • Etching sludges • Scrubber residues

Table 1. Process Inputs and Pollution Generated by Metal Finishing[vii]

Major Steps in a Delisting. There are at least 12 (twelve) major steps in a typical delisting. These major steps, along with some information on timing, are included in Table 3. It is assumed that close coordination with the controlling regulatory agency will be a part of every step identified in Table 3.

Steps 1 and 2 — Identifying Constituents of Concern. There is perhaps no other step in securing a delisting that is more important than identifying the constituents of concern (COC). The process involves reviewing a number of regulatory lists (e.g., Appendix VIII and Appendix IX)iii to determine if a given constituent is in the subject waste. For one list of chemicals in particular, Appendix VIII, it is difficult to identify all of the chemicals on the list because either standard methods do not exist, or the procedure is incredibly expensive, or the method will not work in the matrix of the waste sample. Either way, it will be important to establish with the regulatory authority the total universe of chemicals to include in your review. One thing the petitioner (the entity conducting the delisting is termed the petitioner) should keep in mind is that it is your responsibility to provide a complete and thorough characterization of your waste. Ultimately, it is not uncommon for the petitioner and the agency to settle on analyzing for all constituents (~ 222

Document Title	URL
EPA RCRA Delisting Program Guidance Manual for the Petitioner, US EPA, March 23, 2000.	http://www.epa.gov/region6/6pd/rcra_c/pd-o/delist23.pdf
Delisting Risk Assessment Software	http://www.epa.gov/Region5/waste/hazardous/delisting/dras-software.html
Guidance for Quality Assurance Project Plans - EPA QA/G-5, EPA/240/R-02/009, December 2002	http://www.epa.gov/quality/qs-docs/g5-final.pdf
RCRA Hazardous Waste Delisting: The First 20 Years, U.S. EPA, Office of Solid Waste, June, 2002	http://www.epa.gov/osw/hazard/wastetypes/wasteid/delist/report.pdf
User's Guide Delisting Risk Assessment Software (DRAS) Version 3.0, October 2008	http://www.epa.gov/Region5/waste/hazardous/delisting/pdfs/dras-uguide-200810.pdf

Table 2. Typical Delisting References

Step Number	Description of Step	Approximate Time to Complete (months)
1	Identify constituents of concern and hazardous waste characteristics	3-6
2	Identify constituents of concern for special waste categories	3-6
3	Conduct an engineering analysis to complete your list of constituents of concern	1-2
4	Use generator knowledge to identify constituents of concern that ARE NOT in the waste	1-2
5	Identify Analytes	1-2
6	Select appropriate analytical methods	1
7	Identify appropriate QA/QC methods in a quality assurance project plan (QAPP)	1-2
8	Gather data following the approved sampling & analysis plan	1-2
9	Analyze data, run the DRAS risk assessment model, and begin preparing your delisting petition	3-6
10	Submit delisting petition to appropriate regulatory agency	3-6
11	Regulatory agency prepares proposed rule and publishes it in the *Federal Register*, for example	3-6
12	Regulatory agency prepares final rule and publishes it in the *Federal Register*, for example. At this point the waste is delisted and can be disposed as a non-hazardous waste.	2-4
	TOTAL TIME	**23-45**

Table 3. Major Steps in Performing a Hazardous Waste Delisting

Section	Purpose
Executive Summary	Summarize the petition
Certification Statement	Certification Signature by Plant Manager per requirements at 40 CFR 260.22
Administrative Information	Facility level information – e.g., location, contact information, waste identification, and requested action to delist a certain number of cubic yards of waste
Waste and Waste Management Historical Information	Basis for waste listing, historical waste handling procedures, and waste generation rates
Facility Operation	Overview of manufacturing operations, overview of pertinent systems, and overview of wastewater treatment plant systems
Chemical Review	Review of MSDSs
Waste Sampling Procedures	Procedures for sampling the waste and exceptions
Analytical Methods	Methods used to analyze waste samples
Summary and Discussion of Results	Statistical analysis of results and input of results into the DRAS model. Results are summarized and a PASS or FAIL decision is made.
Conclusions and Recommendations	Conclusions and Recommendations
Appendices	Include any significant correspondence, chemical reviews, data validation reports, and validated data results.

Table 4. Major Parts of a Hazardous Waste Delisting Petition

chemicals) on Appendix IX.

An important document that the petitioner must prepare is the Sampling and Analysis Plan (SAP). The SAP lays out specifically what will be analyzed for, the number of samples, the analytical techniques, and data analysis methods that will be used. The SAP is a living document in that the petitioner and the agency will probably go through several iterations before a final SAP will be produced. You cannot proceed with the overall process until you have an agreed upon SAP.

There are lists of chemicals that are expected to characterize certain wastes (e.g., petroleum refinery wastes) and those chemicals should be incorporated into your SAP.

Steps 3, 4, and 5 — Engineering Analysis, Generator Knowledge and Identifying Analytes. There are several additional ways to modify the COCs list. One way is to conduct an engineering analysis that essentially involves conducting a mass balance around major process units at the facility undergoing the delisting. This is typically done by using a plant's chemical management system to assemble the list of potential inputs to a process. Essentially you take a process unit and treat it as a black box with chemical inputs, and product, and waste outputs. Material Safety Data Sheets (MSDSs) are extremely useful in conducting this phase of the analysis. By lining up the constituents, as displayed on an MSDS, you can approximate a mass balance around a given process unit. An example of this is provided in Figure 1.

As with the characterization of any RCRA waste, the petitioner can use generator knowledge to add to or subtract from the COC list. Frequently, generator knowledge is the best type of information to use in making a determination as to what to test for or what not to test for. For example, a person familiar with a plant's layout will likely be able to know quite quickly rather or not a particular waste flows into a sewer pipe that eventually makes it to the WWTP.

You are now at a point where the list of COCs should be fairly complete and you have identified all analytes that may be in the waste.

Steps 6 and 7 — Select Analytical Methods and Prepare QAPP. The standard reference for collecting and analyzing waste samples is the series of some 200 methods referred to as SW 846. iv This again is a very important point of coordination with the agency so that everyone is on the same page when it comes to not only what is being analyzed for but how it will be determined. What method is selected can frequently determine the sensitivity of the final analytical result. For example, you would want to select a method that had a reporting limit of 0.001 mg/l over one that had a limit of 0.1 mg/l if the point for comparison from the risk assessment model (see later section on the use of the DRAS model) was 0.01 mg/l.

In conjunction with selecting the analytical methods it is also very important to decide upon the quality assurance and quality controls that will accompany each piece of data. A Quality Assurance Project Plan (QAPP) describes the activities of an environmental data operations project involved with the acquisition of environmental information whether generated from direct measurements activities, collected from other sources, or compiled from computerized databases and information systems.v The QAPP documents the results of a project's technical planning process, providing in one place a clear, concise, and complete plan for the environmental data operation and its quality objectives and identifying key project personnel.

Steps 8 and 9 — Data Collection and Analysis. The SAP will specify the what, where, and how of collecting representative waste samples. The term representative here is very important in that above all else the samples collected need to truly represent the waste. Factors such as waste variability over time, production variables, waste treatment variability, and potential for system upsets are all important to account for in your approach to data collection.

Data analysis can be quite complicated or rather straightforward. Typically if you have a large dataset, say, greater than 15 samples, you can perform fairly robust statistical evaluations using some rigorous data mining efforts. The agency should be consulted beforehand regarding what approach they will endorse regarding data analysis. If your budget will only accommodate a small sample size, say, six (6) samples, the agency will require that for a given analyte the maximum observed value should be used versus, for instance, a mean value or some other statistically derived exposure endpoint.

Once you have analyzed the data and arrived at an exposure point concentration for each of the constituents of concern, you are ready to run the DRAS model. The **D**elisting **R**isk **A**ssessment **S**oftware (DRAS) model was developed by EPA Region 6 and improved and modified by Region 5. DRAS performs a multi-pathway and multi-chemical risk assessment to assess the acceptability of a petitioned waste to be disposed into a Subtitle D landfill or surface impoundment. DRAS executes both forward- and back calculations. The forward calculation uses chemical concentrations and waste volume inputs to determine cumulative carcinogenic risks and hazard results. The back-calculation applies waste volume and acceptable risk and hazard values to calculate upper- limit allowable chemical concentrations in the waste.[vi] The DRAS 3.0 model is available on EPA Region 5's website. The results of running the DRAS model ultimately determine whether you will be able to get your waste delisted. If you pass the DRAS model then you incorporate your findings into your petition. If you fail the DRAS model (i.e., you exceed a DRAS calculated limit for a given chemical) you need to consult with the agency to determine next steps.

Steps 10, 11, and 12 — Preparing and Submitting the Petition and Publication in the Federal Register. The culmination of all of the previous steps is the preparation of a delisting petition. The petition is the petitioner's main product for delivery to the agency for review and consideration. The major sections of a delisting petition are outlined in Table 4.

A typical delisting petition will be well over 500 pages and frequently over 1,000 pages long. The petition is aimed at providing all of the information necessary for the agency to make an informed decision regarding the requested delisting for the waste.

CONCLUSIONS

For metal finishing plants with significant generation rates of hazardous wastes, it may be wise to look at a hazardous waste delisting as a way to avoid high disposal costs. Once a facility is delisted the subject waste can be disposed in a Subtitle D landfill where the costs are frequently 4-8 times cheaper. Further, many of the headaches that go along with handling hazardous wastes (e.g., manifesting, training, spill response, closure, etc.) go away or are substantially reduced.

REFERENCES

iUnited States Code at 42 USC § 6903 (5).

iiSee 40 CFR 261.3

iiiFor Appendix VIII see 40 CFR 261 and for Appendix IX see 40 CFR 264.

ivTest Methods for Evaluating Solid Wastes – Physical/Chemical Methods

vGuidance for Quality Assurance Project Plans EPA QA/G-5, EPA/240/R-02/009, December 2002

viUser's Guide Delisting Risk Assessment Software (DRAS) Version 3.0 October 2008 U.S. viiEPA Region 5 Chicago, Illinois

viiEPA. 1995b. Metal Plating Waste Minimization. Arlington, VA: Waste Management Office, Office of Solid Waste.

BIO

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IMMERSION HEATER DESIGN

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The immersion heater represents a sound, economical method of heating process solutions in the finishing industry.

Classical heater installations consisted of hanging a steam coil on one tank wall, sized to heat up water to a "rule-of-thumb" temperature in two hours. While this method has proved adequate in providing heat and covering a multitude of oversights, it has also proved unsatisfactory with regard to energy costs and control. As the cost of energy rose, the finisher increased heat-up times in an attempt to conserve energy. Soon, heat losses prevented achieving desired temperature levels so tank insulation, covers, and other methods of loss conservation were added. Again, adequate solutions to most of the challenges were found, but the hanging steam coil remained unchanged. Today, we have the knowledge that allows us to adequately plan, design, install, and operate economical, efficient heating systems.

Molecular activity, chemical solubility, and surface activity are enhanced through temperature elevation. The reduced solution surface tension, low vapor pressure of some organic addition agents, and heat-sensitive decomposition or crystallization of other additives are major considerations that modify the benefits gained as solution temperature rises. To achieve a proper balance of all these factors, while providing economical installation and operation, it is necessary to analyze the individual heating requirements of each process. Your best source of process information is your process chemical supplier, which can tell you:

1. Recommended materials of construction.
2. Maximum (minimum) solution temperature.
3. Maximum heater surface temperature.
4. Specific heat of the process solution.
5. Specific gravity of the process solution.
6. Recommended heel (sludge) allowance.

To size the heater, first determine the tank size: space required for the part, parts rack or barrel, space required for busing (anodes), in-tank pumps and filtration, sumps, overflow dams, level controls, air or solution agitation pipes, and any other accessories. From this data, a tank size and configuration can be determined.

Calculate the weight of solution to be heated. For rectangular tanks:

$$\text{Weight} = L \times W \times D \times \text{S.G.} \times 62.4\ \text{lb/ft}^3$$

where L, W, and D are length, width, and depth in feet (substitute 0.036 lb/in.^{3} for dimensions in inches). S.G. is the specific gravity of the solution (water is 1.0). For cylindrical tanks:

$$\text{Weight} = R^2D \times \text{S.G.} \times 62.4\ \text{lb/ft}^3$$

where R is the radius of the tank.

Calculate the temperature rise required by subtracting the average (or lowest)

Solution Temperature (°F)	*Nonventilated Losses (BTU/hr/ft²)*	*Ventilated Losses (BTU/hr/ft²)*
100	170	290
120	340	560
140	615	995
160	900	1,600
180	1,590	2,750

Table I. Heat losses from Liquid Surfaces

ambient temperature from the desired operating temperature (if the shop temperature is kept very cool during winter months, it might be wise to use this temperature as the average ambient temperature).

Temperature rise = T operating minus T ambient [To - Ta = T rise]

Determine an adequate heat-up time to suit your production requirements. The traditional 2-hour heatup may prove costly and unnecessary since using this value usually provides a heater more than twice the size necessary for heat maintenance. A 4- to 6-hour heatup more closely approximates the heat maintenance value but may impose production constraints deemed impractical. Long heat-up times can be overcome through the use of 24-hr timers; however, unattended heat-starts carry the responsibility of tank liquid level monitoring and approved overtemperature safety shutoffs.

With this data, the initial tank heating requirements can be determined. A BTU is the amount of heat required to raise one pound of water one degree Fahrenheit. A BTUH is that amount per hour.

Initial BTUH(Q) = Weight × Trise × s.h./Heat-up time

where s.h. is specific heat. This should be the actual value from the process supplier (water is 1.0).

Calculate the approximate heat loss from the tank surface and tank walls. (Use the data shown in Tables I and II.)

The losses from the tank surface can represent the most significant loss affecting heater sizing. The addition of even a partial or loose-fitting cover will reduce these losses. The tank surface area is simply the width in feet times the length in feet. You can use inches instead of feet, but then must divide the results by 144 to obtain square feet.

If you install partial covers, such as removable covers extending from the tank edge to the anode busing, use the remaining "open" dimensions. The covered

Solution Temperature (°F)	*Metal Tank or Thin Plastic (BTU/hr/ft²)*	*Insulated Tank or Heavy Plastic (BTU/hr/ft²)*
100	170	290
120	340	560
140	615	995
160	900	1,600
180	1,590	2,750

Table I I. Heat losses from Tank Walls and Bottoms

Cover Style	*Still Air*	*Ventilated (150 fpm)*
Loose partials	Metal tank values, shown in Table II	Twice that for still air
Insulated	Insulated tank values, shown in Table II	Same as still air
Floating balls	0.25 times the value obtained from Table I	Twice that for still air

Table III: Cover Loss Values (BTU/hr/ft²)

area uses the reduced loss values shown in Table III. The use of partial covers reduces exhaust volume requirements and associated energy demands as well.

Air agitation can be said to primarily affect losses from the tank surface. Breaking bubbles increase the surface area and expose a thin film of solution to accelerate evaporative losses. Air agitation spargers sized at one cfm per foot of length affect a 6 in. (ft) wide path along their length. Thus, a three foot by four foot tank surface with two lanes of air agitation running on the four foot dimension has:

3 × 4 = 12ft² surface plus 2 × ½ × 4

= 4 ft² agitation increase, a total 16ft² effective

Multiply the effective area by the values shown in Table I. Be sure to deduct any cover area (if used) and use the reduced loss values shown in Table III.

The tank wall area equals the tank length in feet, times the depth of solution in feet, times two plus the tank width in feet, times the depth of solution in feet, times two plus the tank length in feet, times the tank width in feet. L × D × 2 + W × D 2 + L W = wall area. (You can use inches instead of feet but you must divide the result by 144 to convert into square feet.) Multiply the tank wall area times the values shown in Table II.

Calculate the heat loss through parts being immersed. Racks per hour, times the weight of the loaded racks, times the specific heat of the parts (use 0.1 for most metals, 0.2 for aluminum), times the temperature rise (use the same value used in calculating the tank temperature rise).

racks/hr × weight/rack × s.h. ´ T rise

A plastic or metal plating barrel must be included with the parts weight. A metal barrel has a specific heat value close to the average parts (0.1), and can be included in the parts weight, but a plastic barrel has a specific heat of 0.46 and will require an independent calculation. Weight of barrel, times barrel loads per hour, times the specific heat of the barrel, times the temperature rise.

barrels/hr × weight/barrel × 0.46 × T rise

Add to this the parts per barrel

barrels/hr × weight of parts/barrel × s.h. × T rise

The heat loading and the actual heat-up time for immersed parts are distinct values. The heated solution can lose temperature to the immersed parts in a matter of seconds. This heat loss is replaced by the heater. To determine the temperature drop of the process solution, divide the heat loss through parts (barrels) being immersed by the weight, times the specific heat of the solution.

Heat loss (parts)/[Weight (solution) × s.h. (solution)] = Temperature drop

Calculate the heat loss through solution additions such as drag-in and make-

up water when working on small process tanks with high operating temperatures. In some operations, it is customary to replenish evaporative losses by rinsing parts over the tank. This practice increases the heat loading. Gallons of water each hour (drag-in or add), times 8.33 (lb/gal), times the temperature rise (water temperature to tank operating temperature).

$$\text{gallons per hour} \times 8.33 \times \text{T rise}$$

Now determine total heating requirement by comparing initial heat-up requirements with the sum of the various losses. Assuming no additions or operating losses during the initial heatup, we can equate our heater size based on the initial heat-up requirement, plus the tank surface losses, plus the tank wall losses. This value must be compared with the operating requirements—tank surface losses, plus the tank wall losses, plus the rack (barrel) losses, plus the drag-in (make-up) losses. The larger value becomes the design basis for heater sizing.

Heater sizing can proceed based on the heating method employed. Electric immersion heaters are sized based on 3.412 BTUH per watt-hour (3,412 BTUH per kilowatt-hour). Divide the design heating requirement by 3,412 to find kilowatts of electric heat required.

$$\text{design heating requirements(BTUH)/3,412}$$

The immersion heater sheath temperature will be higher than the solution temperature. Consult your immersion heater supplier for its recommendations where solutions have high temperature limits. Electric heaters have the potential of achieving sheath temperatures, particularly in air, and are capable of igniting flammable materials; therefore, it is essential that liquid level switches and high sheath temperature cutoffs be employed. Look for (or ask about) Underwriters Laboratory or other independent agency listing labels on electric heaters for assurance that the product meets a recognized standard. Verify and install the sheath ground to minimize personnel shock hazard and, as with all heaters, use a quality temperature controller for economical operation.

Steam immersion heaters are sized based on steam pressure, overall transfer coefficients, area, and log mean temperature difference.

The overall transfer coefficient is a value determined by several basic values: the ability of the heater material to conduct heat, the ability of the two fluid films that form on the inside and outside of the heater to conduct heat, and the resistance to the flow of heat caused by fouling or buildup. You can significantly alter the performance of immersion heaters by the choice of materials and the supply or the lack of supply of tank agitation. By selecting proper materials the fouling caused by corrosion is either reduced or eliminated. Clean quality steam will reduce internal fouling while properly placed agitation can enhance overall thermal performance. The precise calculation of the overall transfer coefficient is detailed and will not be covered here, but is available from your heater supplier.

The following rule-of-thumb values can be used for estimating steam heater size. For metal coils, the range of values for the overall heat transfer coefficient is 100-200 BTU/hr/ft^2/$^\circ$F. For plastic coils, the overall heat transfer coefficient ranges from 20-50. Use 150 for metal and 40 for Teflon.

Now calculate the log mean temperature difference (LMTD) because the driving force for the heat exchange is a varying quantity that is expressed as this value.

$$\text{LMTD} = (\Delta T_1 - \Delta T_2)/[\ln(\Delta T_1/\Delta T_2)]$$

Steam pressure (psig)	5	10	15	20	25	30
Steam temperature (°F)	226	240	250	260	266	274
Heat of evaporation (BTU/lb)	960	950	945	940	935	930

Table IV: Steam Table

Nominal Pipe Size (in.)	*Steam Required (lb/hr)*
1	Up to 100
1½	100-300
2	300-500
3	300-1,000

Table V: Nominal Pipe Size for Various Steam Requirements

where ln = Naperian (natural) logarithms.

Steam pressure produces specific temperatures that will be used in the calculation of the LMTD. Typical values are given in Table IV.

As an example, assume 10 psig steam is to be used to heat a solution from 65°F (ambient shop temperature) to 140°F (solution operating temperature).

Steam temperature (from Table IV): 240°F

$$\Delta T_1 = 240 - 65 = 175^{\circ}F$$

$$\Delta T_2 = 240 - 140 = 100^{\circ}F$$

$$LMTD = (175 - 200)/[\ln(175/100)] = 75/0.55 = 134^{\circ}F$$

The heater area required to steam heat a process solution equals the design heating requirement, divided by the overall heat transfer coefficient, times the log mean temperature.

Design heating requirement (BTUH)/Overall heating requirement LMTD

As with any immersion heater, the heater surface temperature will be higher than the solution temperature. Obviously, it cannot exceed the steam temperature. If the solution has a high temperature limit below available steam temperatures, you may require a custom electric immersion heater or a hot water (or thermal fluid) heater with a lower heating temperature.

Although the heater temperature is limited to the steam temperature, damage to process tanks and accessories can result from overtemperature or low liquid levels. It is wise to equip your process tank with overtemperature and low liquid level cutoffs.

Once a coil size is selected, piping size should be investigated. The quantity of steam used for a specific coil size varies with the steam pressure (see Table V) and the heat released is the heat of evaporation (latent heat) only. The values in the table are in BTUs per pound of steam. So the quantity of steam required equals the design heating requirement, divided by the heat of evaporation of the steam.

Design heating requirement(BTUH)/Heat of evaporation (from Table IV)

The result, in pounds of steam per hour, can be equated to pipe size as shown in Table V. The condensate generated (condensed steam) must be "trapped," that is, equipped with a steam trap. Steam traps are sized based on pounds per hour times a safety factor. Since the amount of condensate varies with the temperature of the solution, it is wise to use a safety factor of four or better. Trap capacity equals the steam required times four.

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CV Factor	Diaphragm Valve Pipe Size (in.)	Steam Required (lb/hr)
4	½	120
5	¾	150
13.5	1	400
15	1¼	450
22.5	1½	675

Table VI: Recommended Valve Sizes

The condensate piping is smaller than the steam pipe since the condensate is liquid. Some of the condensate will convert back to steam because of condensate temperature and pressure. The use of piping smaller than in. nominal is not recommended since scale and buildup inside the pipe is a factor in all steam lines. We recommend using in. nominal pipe for condensate lines. This size will handle up to 1,920 lb/hr with a modest pressure drop.

Steam coil valve sizing is usually smaller than the pipe size since a pressure drop across the valve is required for proper operation. Some typical sizes for diaphragm solenoid valves are shown in Table VI.

Since the performance of the valve and trap can be affected by foreign matter in the steam, it is wise to place a 100-mesh strainer of the same pipe size as the steam pipe ahead of the valve.

Metal steam heaters, when suspended in electrified tanks, may conduct current through the steam lines to ground so it is a good practice to install nonconductive couplings between the heater and the pipe lines. This can be accomplished using a proprietary insulating coupling, dielectric union, or section of steam hose.

Finally, because some steam heaters may be buoyant (tend to float) when in service, it is necessary to secure these heaters through the use of ballasts or proprietary hold-down fixtures.

Hot water (thermal fluid) heating is similar to steam heating in the methods used for sizing. The basic differences involve the usually lower heating solution temperatures and the lower performance, overall heat transfer coefficient of the heater. As in the case of steam heating, the overall transfer coefficient is subject to varying performance and its precise computation is beyond the scope of this presentation. The following rule-of-thumb values can be used for estimating hot water heater sizes. For metal, the overall heat transfer coefficient is 70-100 BTU/hr/ft^2/^{O}F. For plastic, the range is 20-50. Use 95 for metal and 40 for Teflon.

The calculation of the LMTD uses the same equation but now the heating fluid temperature must change since it is yielding the fluid heat and not the evaporative heat available in steam. It is wise to limit the heat drop of the heating fluid to 10°F since greater drops may be impossible to achieve in a field-installed condition.

Nominal Pipe Size (in.)	Flow Rate (gal/min)
½	6
¾	10
1	20
1¼	30
1½	45

Table VII: Water Flow Rates for Various Nominal Pipe Sizes

CV Factor	Diaphragm Valve Pipe Size (in.)	Steam Required (lb/hr)
4.0	½	9
6.5	¾	14
13.5	1	30
22.5	1½	50

Table VIII: Typical Valve Sizes and Flow Rates for a Pressure Drop of 5 psig

Also, it is wise to design the exiting heating fluid temperature to be 15°F higher than the final solution temperature to ensure field reproduction of design performance. Consult your heater supplier for assistance if you experience any difficulty in sizing a heater.

As an example, heat a solution from 65°F (ambient shop temperature) to 140°F (operating temperature) using 195°F hot water. Limit the hot water temperature drop to 10°F or 185°F outlet. This temperature is more than 15°F above the final bath temperature.

$$\Delta T1=195 - 65=130^{\circ}F$$

$$\Delta T2=185 - 140=45^{\circ}F$$

$$LMTD=(130 - 45)/\ln(130/45)]=95/1.0607=80.56^{\circ}F$$

The heater area required to heat a process solution equals the design heating requirement divided by the overall heat transfer coefficient times the LMTD.

Design heating requirement/[Overall transfer coefficient LMTD]

With hot water heaters, it is a wise precaution to install high liquid level cutoffs that will shut off hot fluid flow in the event of a heater leak. If a high temperature heating fluid is used, solution temperature sensitivity must be evaluated and high temperature, low liquid level cutoffs may be in order.

Once the coil area has been selected, the hot water (thermal fluid) flow must be calculated. The flow is equal to the design heating requirement, divided by the temperature drop of the heating fluid, times the specific heat of the heating fluid, times the specific gravity of the heating fluid.

Design heating requirement/[Temperature drop × s.h.

× s.g.(all of the heating fluid)]

This results in the pounds per hour of heating fluid. To convert this into gallons per minute, divide the pounds per hour by the weight of fluid per gallon times 60 (water weighs 8.33 lb/gal). This value is used to evaluate pipe size (both inlet and outlet). Table VII gives a reasonable flow for water through various pipe sizes.

The control valve may be smaller than the pipe size. Some typical sizes for diaphragm valves with a water pressure drop of 5 psig are given in Table VIII.

As with steam heaters, it is a good practice to install a strainer to minimize foreign particles that may affect valve performance. A 60-mesh strainer is usually fine enough for hot fluid systems.

Metal heaters, when suspended in electrified tanks, may conduct current through supply lines to ground so it is a good practice to install nonconductive couplings between the heater and the pipe lines. A proprietary insulating coupling

or dielectric union can be used.

Plastic heaters and some empty metal heaters may be buoyant, so be sure to provide adequate anchoring if floating is suspected.

Thermal stratification is a fact of life in heated process tanks. To minimize this effect good agitation (mixing) is required. Classic air agitation is sized at one cfm per foot of length. When placed beneath a cathode (or anode) it provides sufficient agitation to that surface to enhance deposition rates. It does not, in this form, eliminate thermal stratification. Top-down mixing can be provided through recirculation pumping. Pumps sized for 10 turnovers or more per hour provide good mixing and uniform temperatures. Skimming style pump inlets with sparger bottom discharges are best since higher temperature solutions are forced to the cooler areas.

In tanks three feet deep and more, a vertical sump pump can be mounted on the tank flange with a length of discharge pipe anchored to the tank bottom. These can often be coupled to in-tank filters for removal of particulates while providing mixing. Air agitation, when properly placed, can "average" temperature in their zone of influence (usually 6-12 in.) and can be used to enhance response time for temperature controller sensors. As the air agitation is increased, heat losses also increase, making air agitation a less desirable means of dealing with thermal stratification.

Heat-sensitive solutions can be addressed by either electric or hot water (thermal fluid) heaters. Electric is the easiest to control since the heater surface temperature can be varied by varying the input voltage. A heater surface temperature controller can limit surface temperatures while still providing sufficient heat for the solution. Similarly, hot water systems can be sized for maximum hot water temperatures (and thus heater temperatures) but control and response are usually inferior to electric systems.

CONSIDERATIONS IN THE FINISHING EQUIPMENT SELECTION PROCESS

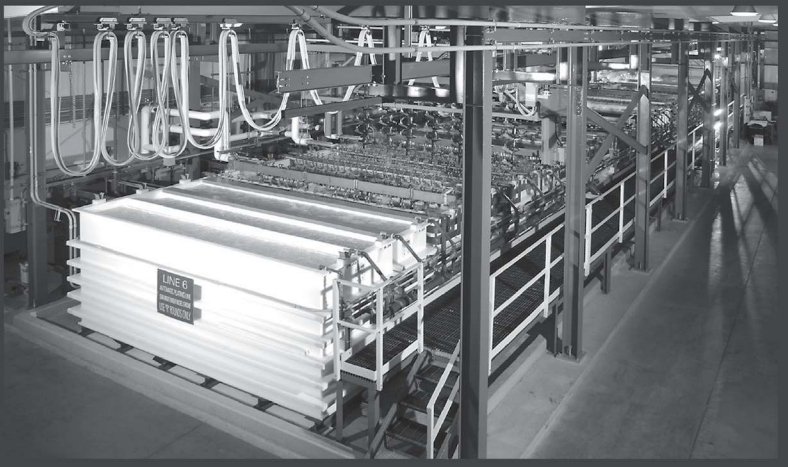
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When budgeting for new finishing equipment or upgrading an existing line, it is important to note that each requirement is unique and must be carefully considered before estimating a price. Otherwise, when the real purchase order materializes for the quoted system, all of the pre-engineering data must be available, as well as current costs, in order to build a particular line. This article will describe several key considerations in the selection process of a custom manual or automated plating, anodizing, or chemical process system.

Beyond the obvious—selecting floor coating, secondary containment trays, or berming, power, air, and exhaust requirements—the equipment selection process might proceed as follows:

- **The equipment estimator must first collect all the data.**
- **Then, a determination of how many parts are to be finished per year, month, week, day, must be broken down into hours per day, in order to size the process line.**
- **Pretreatment requirements, such as burnishing, tumbling, deburring, buffing, polishing, or degreasing, and selection of any specialized equipment, must be considered.**
- **Selection of the process, which will depend on whether the parts need to be barreled or racked, is yet another factor.**
- **Determine a plating or anodizing process cycle for the particular base material, as well as the configuration of the parts.**
- **Determine if the plating thickness requires electroplating, immersion, or autocatalytic (electroless) processing or Type I, II, or III anodizing, etc.**
- **Carefully calculate the surface area of a single part to determine how many parts may be loaded per barrel, rack, or fixture.**
- **If the parts are to be barrel plated, then determine if the parts will nest, or stick together; and, if so, what type of barrels will be used.**
- **If the parts are to be racked, then each part needs to have a special rack or fixture designed to accommodate that special part. If more than one rack per flight bar is required, determine just how many racks per load will achieve the best results.**
- **Masking considerations: Many parts will require masking with special tapes or waxes, as well as holes plugged with custom plugs.**
- **Reels of connector parts might require selective plating only in some areas, especially where precious metals are plated. Customized selective strip plating lines will be required for each special application.**

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Once the production quantities are determined, then the plating facility must be sized accordingly. The plating tanks must be laid out, and the footprint of all lines and systems measured, with optional floor coating, double containment of the tanks, with catwalk and grating provided. If a manual line is sufficient for the desired production volume, with one or more operators, then it must be determined if an overhead hoist will be needed—and if so, will it be a manual chain hoist, powered trolley with push button, or joy stick variable-speed motorized hoist.



Automatic solar panel plating line.
(All images courtesy of CJI Process Systems)



Phosphate line.

If an automatic hoist line is needed, then you'll need to determine precisely how many hoists will be required. Depending on the configuration of the line, there might be parallel lines, side by side, with load, unload at the same end, or load on one end, unload on the other end, and with either wet or dry shuttle transporting the barrels or racks from one side of the line to the other, or a U-shaped return line, and dryer.

The PC software must be programmable in order to allow control of all the process parameters, such as solution operating temperatures; low-level shut off, alarms, autofill of tanks; variable or constant current and voltage requirement of the rectifiers; cathodic or anodic; automatic ramp up of voltage for anodizing; historical process data recorded for future records; hoist location, position, and speeds; pumps and filtration operation; air blower pressure; and amp min/hr. Other parameters to consider are chemical dosing, and if any brightener feeders or chemical feeders are supplied with metering pumps, etc.

In order to design the plating line(s) correctly, key items must considered for every single tank in the line. The designer must go through each station or tank, one at a time, to decide which controls or accessories need to be installed on each tank. A manual line would need the same items as an automated line, except the automated line would have either single or multiple programmable hoists, which might be either a monorail type, sidearm, semi-bridge, bridge, or a "rail rider." The hoist positioning might be laser-controlled encoder or manual, with random loading scheduling—or it could be time-way based. The line might be totally enclosed because of either clean room or other environmental circumstances, with the operator working inside the enclosure.

All of the tanks must be sized to accommodate the barrels, or racks, with sufficient clearance for the heaters, sensors, coils, pumps, filters, spargers, level controls,



Rear view of large plating line.



Automatic electroless nickel plating line.

anode baskets, etc. The tank material must be chemically compatible—with the decision to either line the tank, or offer it without linings or inner coatings—for each solution, as well as each individual component. Each tank must be outfitted with a variety of components, based on just what the tank is supposed to accomplish.

The soak cleaner would need either electric heaters or heating coils, temperature controllers, sensors, hi/lo level sensors, individual solenoids for city water or deionized water feed, agitation sparger (with agitation either provided by low-pressure, oil-free filtered air), or eductor/pump agitation. Other necessities: oil skimmer, oil coalescer, pump and filter, and low-level shut off of the heater.

The rinse tanks might require auto-fill city or deionized water solenoids, air sparger manifolds, drain valves, overflow weirs, conductivity controllers, and possibly pump and filter, depending on particulate drug into them. Electro-cleaner tanks would also need a rectifier, anode/cathode bars, pump and filter, oil skimmer, heater or steam coil, solenoids for city and deionized water feed, etc.

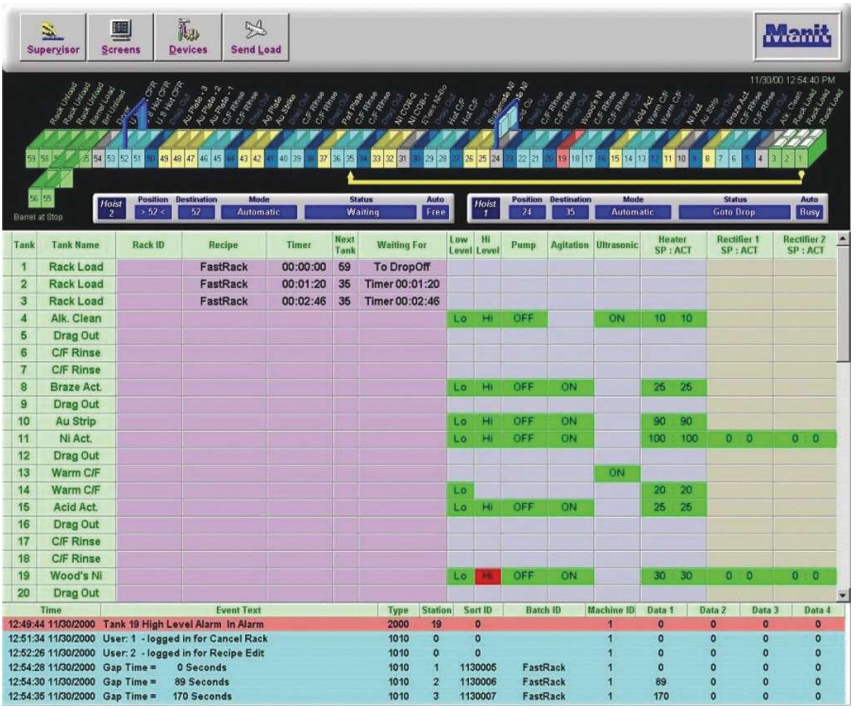
The process tanks would require similar components as the electro-cleaner, with an addition of rectifiers and other items, depending on the process. The rectifiers might be chosen to accommodate a variety of controls, such as constant current and/or constant voltage (pulsed, periodic reversed, or reverse pulsed; air, water, or convection cooled), and might include analog or digital amp/volt meters mounted remotely. The designer must decide just what type of heaters, agitation, cooling, filtration, circulation, rectification, and materials of construction, as well as what needs to be exhausted and which tanks need exhaust plenums. CFM requirements also need to be calculated for the entire line in order to size the air scrubber.

If the plating tank happens to be an electroless nickel process, then the decision must be made as to how to heat the tank. For example, would it be more practical to use heaters, steam, or hot water coils? Or does it make more sense to make the tank a double-boiler tank heated with coils in the lining of the tank?

CONSIDERATIONS WHEN DESIGNING A TANK

There are many considerations when building the tanks, including size, quantity, and spacing of the girths around each tanks, as well as factoring in the weight capacity of each solution. All of this depends on specific gravity, operating temperature, and geographical location. On the West Coast, for example, you might require seismic calculations on the larger tanks.

The plating lines might be either individual tanks sitting on a frame or mod-



Typical PLC screen on a CJI automatic hoist system.

ules. Either way, the lines should be plumbed with valves, solenoids, city and deionized water feeds, with separate drains to cyanide, acid/alkaline, and chrome lines to the wastewater treatment system. **Note**: every plating facility will need some type of treatment system, unless it's all hauled away and treated off site. The plating line should offer single-point connections after arriving for hook up of the utilities, air, water, or steam, and electricity. Most plating lines are wired "three-phase" wherever possible for energy efficiency savings.

Some plating lines are required to provide VFC (variable frequency controls) that vary the speed of the electric motors on the pumps, etc., depending on load requirements.

The wastewater treatment system must have many components to accommodate the plating line, and the plating line designer is usually asked to also quote the wastewater system supporting the plating or anodizing line. Aside from considerations regarding the wastewater treatment methodology of each plating line, the designer must determine just which type of system will be the most efficient system for that particular line while satisfying the local permitting laws.

CONCLUSIONS

The aforementioned factors should offer readers just a few examples of the magnitude of calculations, researching, sizing, etc., that might be required when estimating a new system. If the process line is designed properly to begin with, then the chemistry will have a much better opportunity of being successful.

FUNDAMENTALS OF PLATING RACK DESIGN

BY STEEN HEIMKE
BELKE MFG. CO., CHICAGO

The primary purpose of a plating rack is to hold a part in the most advantageous position for exposure to a plating current, which flows from an anode. Plating provides protective finishes to parts fabricated prior to plating so that the metal finish will not be damaged or ruptured during the fabrication process. Parts requiring a finish have an infinite variety of shapes and sizes, resulting in the need for fabrication of a custom plating rack. Before a plating rack can be fabricated, certain questions must be asked.

What kind of plating will be done?
What solutions will the rack be exposed to?
What rate of production is necessary to be cost effective?
Will the tips be stripped with a proprietary solution?
What portion of the part is to be plated?
How should the piece be held for proper density of the plating finish?
What sort of tip must be designed for proper positioning?
Will this design provide quick and easy racking and unracking?

For determining the answers to some of these questions, the basis for a good rack design will be developed. Proper rack design should be started with a description of the part, detailing any special surface problems, shading, and contact tip marking. Where can the piece be held? The number of pieces per rack will be determined by current per rack, weight of each part relating to total weight of the rack, and, most importantly, by the design of the rack.

RACK DIMENSIONS

The most important fundamental of plating rack design is determining the proper dimensions, making sure that each rack will fit with parts affixed into the smallest process tank in the plating line.

Dimension A—Overall Length

This is the distance from the cathode bar to the bottom of the rack, keeping in mind that each process tank has different space requirements relating to anodes, steam coils or immersion heaters, air agitation pipes, filters, overflow dams, and mechanical agitation. The rack should be several inches off the bottom of the tank, allowing for some accumulation of sludge. Also, improper anode length could result in a very uneven deposit.

Most parts should be positioned a minimum of 2 in. under the solution surface. It is important to check solution levels in all process tanks. Determine the dimension from the lowest level tank, thereby assuring complete immersion throughout the plating cycle.

Overall length is determined by Figure 1, dimension A, which is the distance between the cathode hook and the bottom of the rack.

Dimension B—Distance from Cathode Hook to Location of First Part

This dimension is very critical as it will determine the number of parts per rack.

Dimension C—Width

On return-type automatics, this width dimension is the direction of travel. Proper dimensions are extremely critical, as each manufacturer may have different width requirements. As in any automated system, this dimension might have some variables and the rack must be designed for the smallest cell. Improper width could result in damaged racks because of machine jam-ups.

This dimension on automated hoist lines or manual straight lines determines the number of racks on each work bar. Spacing between the racks is important, as this will ultimately determine production rates. How many racks will effectively fit on a work bar? Look at the design of the work bar to help with proper spacing, especially the location of the pick-up points.

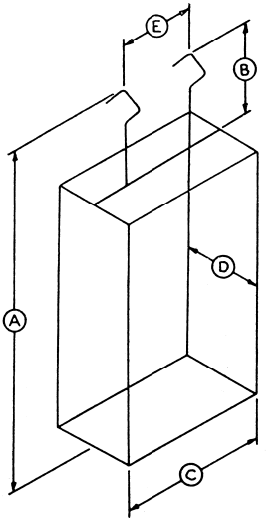


Fig. 1. Rack dimensions

Dimension D—Thickness

The thickness dimension is the direction of travel on an automated hoist line. Relating to plating rack design, this dimension is the most critical. The distance between the anodes and their relationship to the cathode bar will determine how wide the rack will be. The rack must fit between the anodes with ample room for holding the parts (usually 1-3 in.).

On a manual line it will be necessary to determine the smallest anode distance so that the rack will fit in all process tanks. Another factor on a hand line is making sure that the plater can easily put the rack in and out of each process tank without knocking parts off.

Dimension E

This is only for racks that have a double cathode hook and is usually for return-type automatics. This design is also used where additional stability is required or where weight might be a factor.

Having developed all the dimensions necessary for design of the spine, special attention must be focused on cathode hook design. What size of work bar will be used? It is important that the hook make clean contact with the bar so that current flows properly. This can be accomplished with the V-hook design, the most commonly used today. (See Fig. 2 for commonly used hook shapes.) Some manufacturers have developed their own hook design. Recent work bars have been rectangular for the primary reasons of stability in relationship to the speed of the machine and quick starts and stops.

CONSTRUCTION OF THE PLATING RACK SPINE

The plating rack spine (Fig. 3) is the backbone of a rack. It must be capable of carrying the necessary current to each tip, it must have adequate strength to support all the parts, plus be wear resistant, especially for use on an automatic machine. The plating bath in which the rack will be used has a known current density rat-

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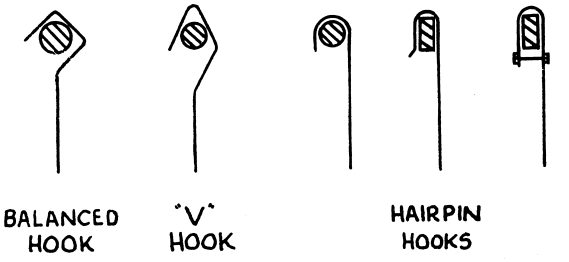


Fig. 2. Hook shapes.

ing in A/ft^2. Multiply this factor by square feet of parts on the rack to determine how much current the rack spine and hook must carry. (See Table I for plating solutions—cathode current densities.)

Generally, most single spines are fabricated with 1/4 × 3/4 in. or 1/4 × 1 in. copper, which will carry 200-250 A. (See Table II for a chart of relative conductivity.) Copper is the most commonly used material, as it has the highest conductivity in relationship to price.

Sometimes cathode hooks fabricated of copper and spines fabricated of steel, stainless steel, brass, or aluminum can be used if the connection is below solution level. Again, the main factor is conductivity. Steel, stainless steel, brass, and aluminum have lower conductivity than copper. The most common practice is to use steel for supporting members and not where conductivity is needed.

DESIGN OF PLATING RACK TIPS

Some practical objectives in the design of the tip are easy racking and unracking; adequate current flow (contact) to the part; tip designed to hold part in noncritical area; type of tip—gravity or spring type; and material.

Gravity Tip

A gravity tip is one that is styled for easy racking and unracking. The part to be plated usually has a hole for the tip to fit through. This style is most commonly used in zinc, electroless nickel, cadmium, or silver baths.

Spring-Type Tension Tip

A spring tension tip is used in baths, which require greater throwing power and positive contact such as chromium plating or anodizing. They are also needed whenever mechanical or air agitation is used.

Some principles of plating must be remembered in designing a plating tip.

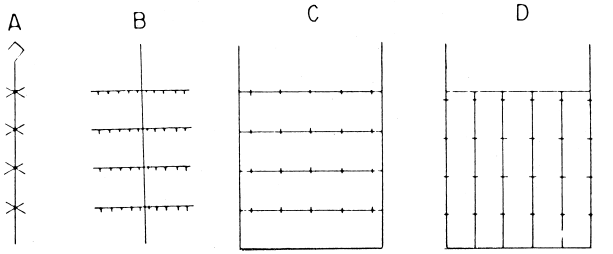


Fig. 3. Four basic types of plating rack construction; A — single spine; B — T type; C — box type; D — multiple spine.

Table I. Plating Solutions—Cathode Current Densities

Plating Bath	*A/ft²*	*Voltage*
Brass	5-20	2-5
Cadmium	5-50	2-5
Chromium (decorative)	100-200	4-6
Chromium (hard)	200-500	5-12
Copper (sulfate)	15-50	1-4
Copper (fluoborate)	15-50	1-4
Copper (cyanide)	20-60	2-5
Gold (acid)	10-30	5-6
Nickel	20-100	4-8
Silver	5-30	0.5-2
Tin (fluoborate)	25-150	1-3
Tin (stannate)	30-100	4-6
Tin (sulfate)	10-40	1-4
Zinc (cyanide)	10-90	1.5-6
Zinc (low cyanide)	20-80	1.5-6
Zinc (acid noncyanide)	20-80	1.5-6

Areas around the edge of large flat surfaces tend to plate more heavily than the center section. Edges will be exposed to higher current density. Parts with sharp points might require special care to prevent burning.

In some cases, auxiliary anodes are needed so that the plating deposit remains consistent and uniform within the plating specifications. Auxiliary anodes can reduce plating time by throwing a deposit into hard-to-reach areas requiring less plating time. Whenever an auxiliary anode is needed, special care should be taken in construction to make sure that it does not come in contact with the cathodic section of the rack. A nonconductive material is used to separate the anode and cathode sections. The material most commonly used is a fluorocarbon plastic because it can withstand the curing process. Polypropylene blocks can be used and added as a finishing operation.

Table II. Chart of Relative Conductivity

Size (in.)	*Copper*	*Aluminum*	*Brass*	*Steel*	*Phosphor Bronze*	*Stainless Steel (300 series)*	*Titanium*
1 1	1000	600	250	120	180	23	31
1	750	450	185	90	135	17	23
1	500	300	125	60	90	12	16
1	250	150	63	30	45	6	8
1 (dia.)	785	470	196	94	141	18	24
3/4	445	265	111	53	80	10	14
1/2	200	120	50	24	36	5	6
1/4	50	30	13	6	9	1	1
3/16	28	16	7	3 1/2	5	5/8	7/8
5/32	20	12	5	2 1/2	3 5/8	1/2	5/8
1/8	12	6	3	1 1/2	2	1/4	3/8
3/32	7	4	1	1 7/8	1 1/4	3/16	1/4
1/16	3	1 3/4	3/4	1/2	1/2	1/16	3/32

Design of the Spring Tension Tip

Questions to be considered in the design of a spring tension tip are:

What area of the part is most critical in the plating bath?
Where can a rack tip mark be permitted, as it is almost always present?
Of what kind of material is the tip fabricated?

Referring to the critical area to be plated, thought must be given to the part location relative to anode configuration, drainage of the part, high and low current density areas, and gassing around holes and openings.

A part should be held so that the rack mark is in the least critical area. Thought should be given as to what the end result will be with the finished plated part assembled and complete. After looking at this, a more objective rack mark area can be determined.

Special care must be taken to make sure that the contact is secure, will hold the part throughout the plating cycle, and will not scratch the part.

Materials Used for Tips

The two most common materials used in the fabrication of plating rack tips are phosphorus bronze and stainless steel in both gravity- and spring-type tips. Other metals commonly used with a gravity tip are Monel and titanium.

In the case of materials used for a spring-type tip, spring tempered or half-hard material is needed either in flat or round stock. Spring tempered is preferred because of the spring action present in the material, reducing metal fatigue. In the fabrication process sharp bends should be avoided as they create a fatigue factor and eventually the tip will break. In recent years, stainless steel has been widely used as a tip material because of the use of proprietary nitric or muriatic acid stripping solutions. Using phosphorus bronze with such strips would cause the tip to dissolve prematurely. It must be stated that phosphorus bronze has a greater current carrying capacity and should be used where current is a factor. Stainless steel tips do create some problems as their conductivity is so low that excess heat is created and could cause a premature breakdown of the plastisol rack coating.

Large parts are generally fabricated using flat stock, whereas smaller parts can use round stock.

FIXED VERSUS REPLACEABLE TIPS

There are two types of racks used in plating: fixed tip and replaceable tip. Each style has its own advantages. Fixed tip racks are generally less expensive on the original outlay, and usually require a very tough tip because of the weight of the part and/or rack.

The replaceable rack tip concept offers some advantages over a fixed tip rack:

1. Plating racks can be maintained at 100% capacity. When analyzing how many parts can be put on a rack and knowing what it takes to operate a plating line at a profit, each tip becomes a profit center with this concept. Whenever a tip breaks it can be replaced, thereby creating a consistent production output.
2. The replaceable tip allows many different and varied styles of tips to be used with the same spines, reducing the need to inventory racks for every style of part.
3. Cross bars can be made replaceable instead of every tip, creating some additional cost effectiveness.
4. The repair of the complete rack would be unnecessary as only the tips have to be replaced.

Connecting the Tips to the Spine

The most common method of attaching the tip to a spine is with a mechanical connection using a machine screw, lock washer, and nut. Materials vary with each manufacturer, but usually stainless steel, steel, or brass are used. Stainless steel connections are desirable because in the event of rack repair they suffer less corrosion attack than steel.

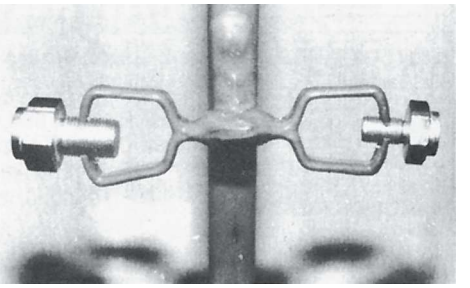


Fig. 4. Double tip connection.

Using copper or steel rivets is faster in assembling, but creates a problem when the rack has to be repaired and tips moved.

To connect a tip to a spine, a hole is drilled in the spine that will allow the screw to fit through, with a nut to attach to the screw for secure fastening. Using this type of connection, it might be desirable to solder the tip to maintain strength and corrosion resistance.

To maintain corrosion resistance, tip connections should be lead soldered. Silver solder can be used to increase conductivity in tip construction, but will increase the cost.

Most tips can be affixed to the spine with a single mechanical connection, but with large parts a double connection should be used. A double connection (Fig. 4) is desirable whenever the racking or unracking gives the operator an opportunity to give the tip a certain amount of torque by constant twisting, pulling, and adjusting, thereby loosening the connection at the spine. A double connection minimizes the chance of this happening.

Types of Replaceable Tip Connections

Type #1: This replaceable tip (Fig. 5) has a knurler, which bites into the copper spine with a stainless steel stud drawn tight with a plastic cap. This type of tip is normally lead soldered for corrosion resistance and strength.

Type #2: This replaceable tip uses a knurled section and threaded stud, which is drawn through a hole and then locked in place with a cap nut.

Type #3: This type represents a gravity-type replaceable tip either plain or plastic covered. This unit is threaded directly into the spine or cross bar.

COATING OF RACKS AND SPINES

The final process in fabricating a plating rack is the coating. This coating is commonly called plastisol or PVC (polyvinyl chloride) resin. Plastisol is 100% solid material and contains no solvents. Plastisol must be heated and cured at a temperature of 375-400°F. Prior to coating, the racks or tips are primed with an adhesive cement, which helps the plastisol adhere to the racks.

In the curing process, it is important that the oven maintain a consistent temperature for an even cure. The oven is vented to remove any curing smoke and plasticizers. Even before the rack or tip is cemented, it is necessary to rough up the surface for adequate adhesion. This process is called blasting—normally a procedure using some abrasive-type media such as aluminum grit, sand, or metal shot.

The plastisol's primary function is to provide a corrosion protective coat-

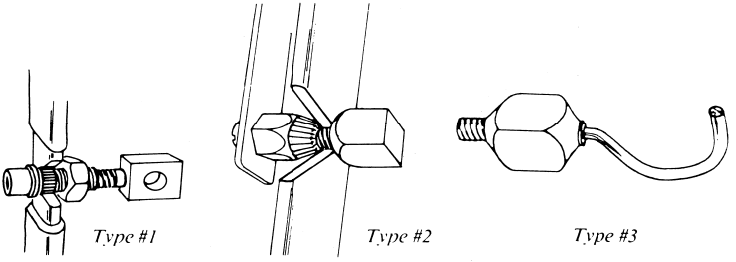


Fig. 5. Various types of replaceable tips.

ing, which is impervious to the acid or alkali attack that is prevalent in every plating line. Plastisol racks and tips can be trimmed easily, exposing only the contact area to grip the part to be plated.

Large racks will pick up more plastisol than small ones. It is important to try to maintain a consistent thickness, keeping in mind that small wire tips will retain very little heat and, therefore, pick up a lesser amount of coating. Replaceable tips have some advantage by being coated separately and retaining more heat, developing a thicker coating.

When plastisol is exposed to a trichloroethylene or perchloroethylene solvent, it will leach out the plasticizer and cause the coating to harden and crack.

SPECIAL APPLICATIONS

Anodizing Racks

Anodizing racks are presently constructed out of two kinds of materials: aluminum or titanium. Generally, anodizing racks are not coated. The main factor, as with copper racks, is that the contact with the anodized part must be positive. Titanium and aluminum do not lend themselves to spring-type tips as they are not spring-tempered materials. Aluminum is a much cheaper material, but it will be chemically attacked and also requires stripping of the anodic film after each cycle. Titanium has excellent corrosion resistance, long life, and maintenance-free operation. Titanium racks can be completely assembled with titanium nuts, bolts, and screws.

Printed Circuit Board Plating Racks

The requirements for printed circuit board (PCB) rack design for electronic plating of all types and sizes of boards are as complex as the microchip itself. The PCB rack must be designed to hold the board in a locked position with positive contact on the border of the board (see Fig. 6). The board must be held securely because of mechanical or air agitation in the various baths. The contact point should be T316 stainless steel with a thumb screw of T316 with a Teflon tip, thereby creating a positive contact with minimum plating buildup. The most commonly used thumb-screw size is 3/8-16. Some other sizes are 1/4-20, 5/16-18, 3/8-12.

The spine for PCB rack is fabricated out of copper with stainless steel reinforcement or bracing. Some PCB racks are fabricated entirely out of T316 stainless steel. All PCB racks have a top thumb screw, which securely fastens the rack to a work bar, this top thumb screw is stainless steel, plastisol coated, and is bigger than the screw that holds the board. The top thumb screw also is held

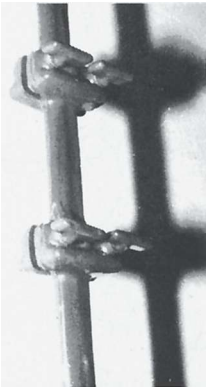


Fig. 6 Close up view of printed circuit board (PCB) tip showing only the stainless steel contact and plastisol trimmed away for a square fit for the PCB (two-point contact).

in place with the added support of a threaded top nut. This threaded top nut is needed to provide additional torque support for the top thumb screw when tightening the rack to the work bar.

PCB cleaning can be done in a slotted basket. The basket should have 1/4-in. spacing between slots, be fabricated out of stainless steel, or be plastisol- or Halar-coated steel.

Halar is a highly protective coating with high temperature characteristics, this coating is much more expensive than plastisol.

In the case of very flexible contacts, it is necessary to design racks for each individual operation depending on parameters that are specific to each PCB operation. Some PCB racks have been designed with adjustable spine or cross members to accommodate different size boards in each production process.

PCB racks after a period of time will accumulate plating buildup in the contact area and will need to be repaired to continue to be productive. The PCB racks are repaired by stripping off the metal buildup and plastisol, repairing and cleaning the contact area for corrosion, and fixing the spine. The rack is then plastisol coated and trimmed to customer specifications.

The contact area on a PCB rack is a slot with a contact point between the thumb screw and contact point. This slot is a specified width and the outside of the slot can be V-shaped to help with the racking of the board.

Electroless Nickel

Plating racks designed for electroless nickel can be as simple as using a strand of copper wire to hold the piece to be finished. Stainless steel contacts can also be utilized.

Electropolishing

Electropolishing racks can be grouped in the category of a rack that needs positive contact, usually a titanium tip, because of the need for chemical resistance. Copper spines are still used and the rack is plastisol coated. Racks should hold the work so that gas pockets will be eliminated.

FINISHING SYSTEM EFFICIENCY UPGRADES FOR A CAPITAL-CONSTRAINED MARKET

BY TIMOTHY KURCZ, DIRECTOR OF SALES, JESSUP ENGINEERING, ROCHESTER HILLS, MICH.

During this furtive economic recovery, captive and independent finishers face the need to increase capacity, improve quality, and reduce resource consumption as rising production volumes stretch a downsized industrial base. This challenge is the result of wholesale market consolidation and continued global competitive pressure. Unfortunately, recently imposed government banking controls limit capital availability and the option to purchase new machinery no matter how strong the business case.

With many new installations out of the picture for the short term, the too-often employed lowest cost solution is simply to increase demand on already stressed human/machine resources. This is risky given the operator-sensitive nature of the finishing business and finicky, well-worn machines. A better choice is targeted investment of carefully engineered upgrades designed to enhance existing plating, anodizing, coating, and other types of finishing systems.

Jessup Engineering,1 known as a leading manufacturer of programmable hoists and turnkey finishing systems, responded to customer demand for cost-effective, incremental machine improvements. Every customer installation requires careful analysis to fully understand, engineer, and prioritize improvement opportunity. Partnership work teams establish targets, and the customer selects the most cost-effective solution for each machine. Over the past year, the following upgrades achieved specific productivity goals for Jessup customers' existing plant and equipment.

1) An intuitive touch screen industrial personal computer/human machine interface (PC/HMI) is the heart of every Jessup controls upgrade (Figure 1). Available with single-touch toggled bilingual language format, it displays system overviews, recipe options, hoist programming, load/unload monitoring, process functions, load tracking, fault diagnostics, and pre-programmed maintenance schedules. For convenience, it also includes imbedded drawings, schematics, operations manuals, and spare parts lists. Control features include monitoring and control of hoist equipment, process tanks, and accessory equipment. Quick scan input devices may include bar code or radio frequency identification (RFID) technology. PC-controlled programmable logic controller (PC/PLC) systems provide load-by-load output data in a simple comma separated variable file (CSV) format for interface with customer quality and business management systems through Ethernet communications. Performance monitoring includes shift reports for total time and cycles, automatic vs. manual operation, load/unload delay, and fault data. To speed correction of unexpected stoppages, the control system provides automatic system diagnostics.

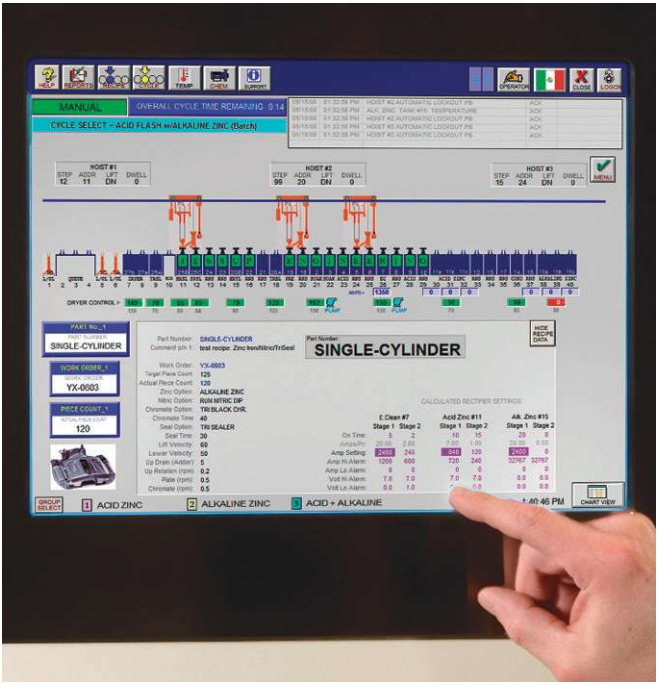


Figure 1. Jessup PC/HMI operator screen image

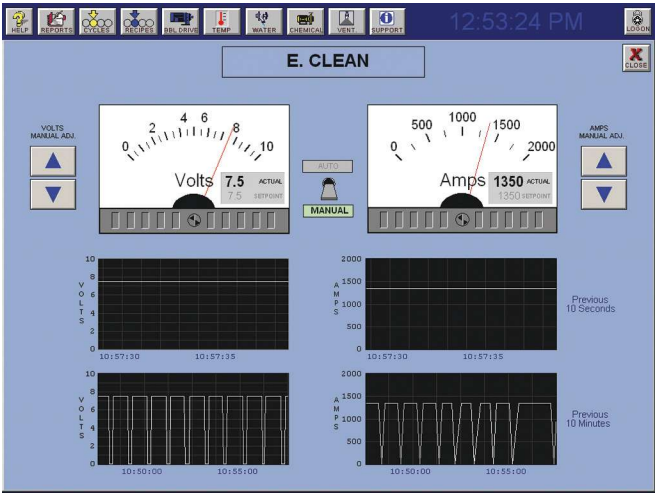


Figure 2. Jessup rectifier control screen.

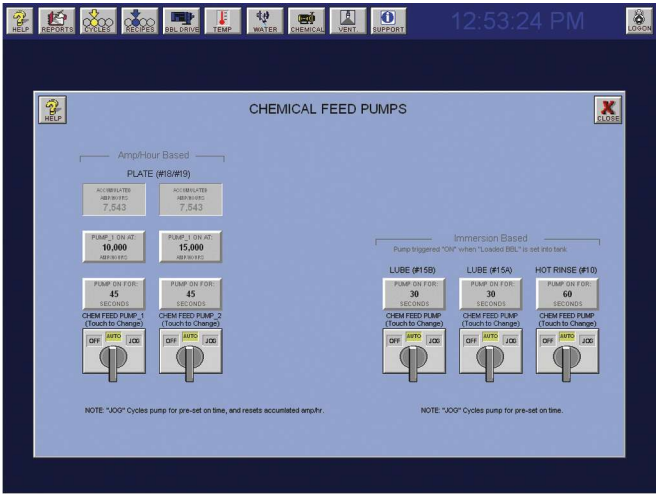


Figure 3. Jessup chemical feed control screen.



Figure 4. Jessup rinse water management screen.

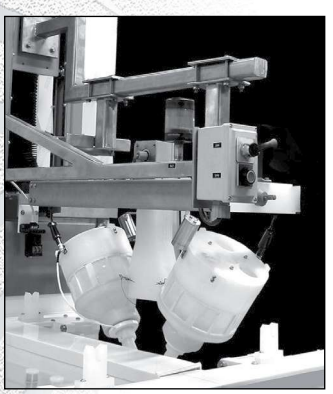
Detailed screens display fault location and actions needed to quickly restore production. Internet-based remote monitoring expedites troubleshooting and repairs.

Specific screen pages may include:

a) System overview, including hoists, tanks, carriers, etc.

b) Alarm history provides a view of recent alarm information.

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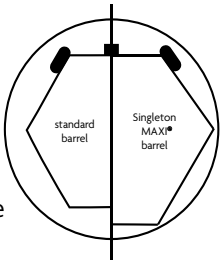


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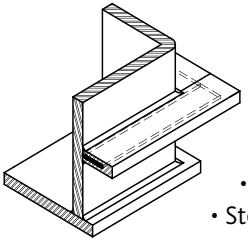
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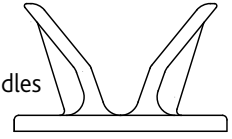


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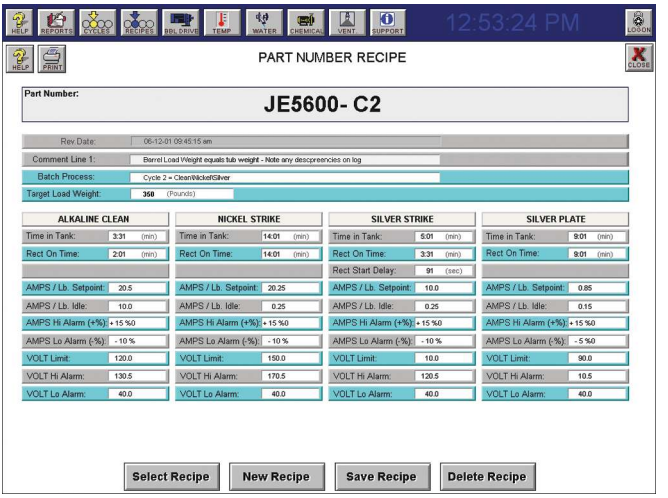


Figure 5. Jessup multi-process management screen.

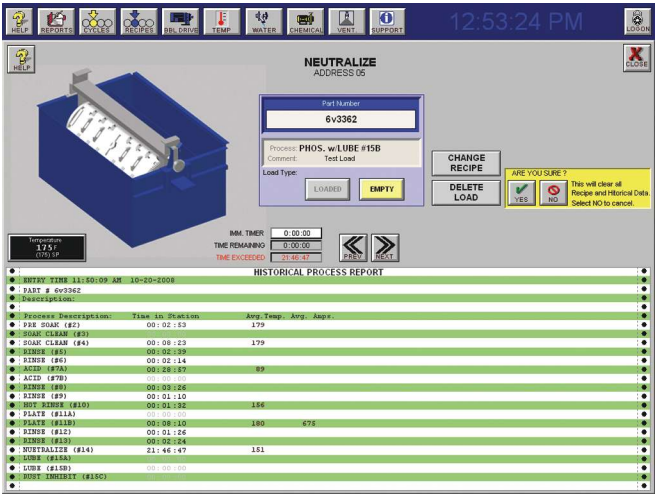


Figure 6. Jessup process history data screen.

c) Hoist programming requires no programmer or special devices.

d) Machine diagnostics provides detailed fault information.

e) Service reminder recommends maintenance procedures.

f) System security requires login and password for access.

g) Shift report provides machine performance data.

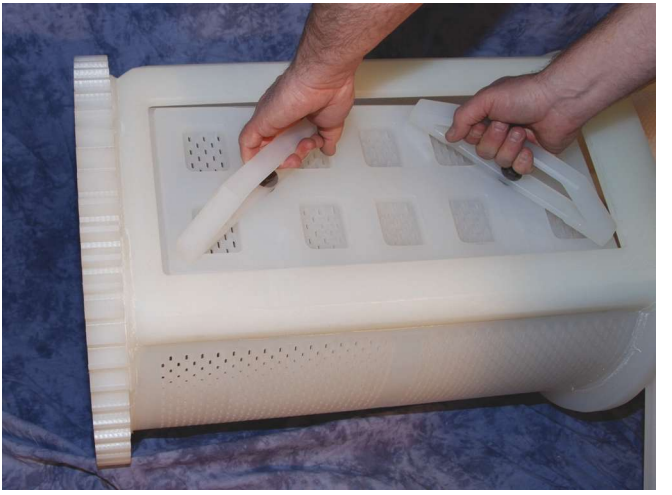


Figure 7. Jessup load-locker plating barrel

h) Tank detail includes time in tank and load identification.

i) Barrel drive controls rotation or oscillation profiles.

j) Recipe management allows 10,000 discreet processes.



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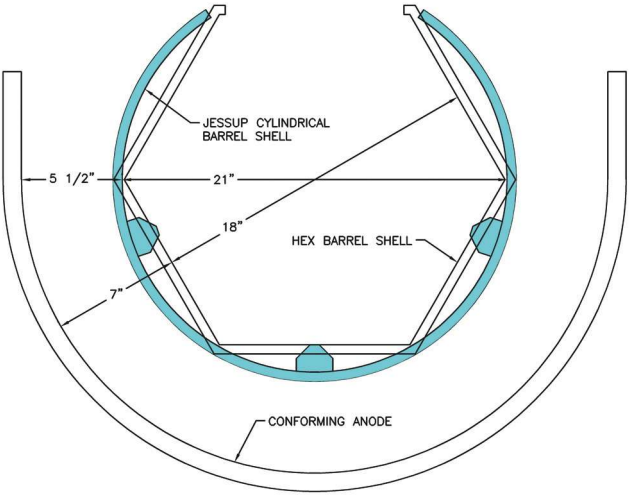


Figure 8. Jessup cylindrical vs. hex barrel comparison.

k) Bar code or keypad interface for recipe input.

l) Load-by-load data capture, storage, and export.

Except in cases where simple fixed process cycles run, or where machine management and data recording is unnecessary, PC/HMI operation of finishing systems is standard for all new machines. Retrofits are easily accomplished. They often include machine position sensors, rinse water control systems, and programmable chemical feed pumps. Machine monitoring, management, load-by-load data recording and paperless quality management features offer quick return of customer investment.

2) Programmable, recipe-based individual cell rectification enables precise, repeatable plating thickness for every load regardless of part

	Jessup barrel Cu. Ft.	Hex barrel Cu. Ft.	Difference Cu. Ft.	Difference %
Barrel fill @ 33%, cubic feet	4.0	3.32	.68	17%
	Constant	Average	Difference In.	Difference %
Anode-to-work spacing inches*	5.5	6.25	.75	12%

Table 1. Jessup barrel vs. hex barrel design. **The hex barrel anode-to-work spacing distance is the average of the nearest to the farthest spacing.*

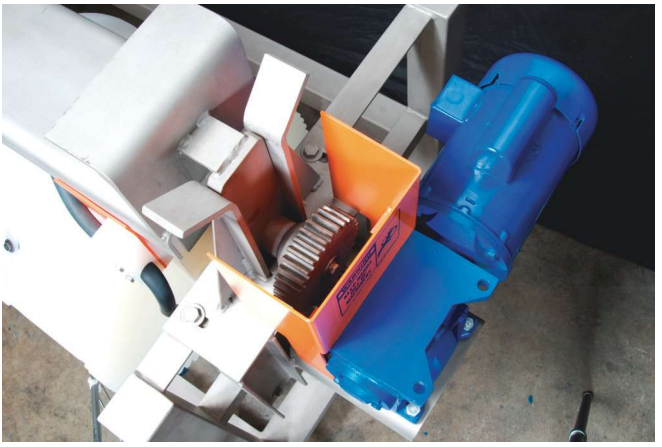


Figure 9. Jessup fixed engagement barrel drive.

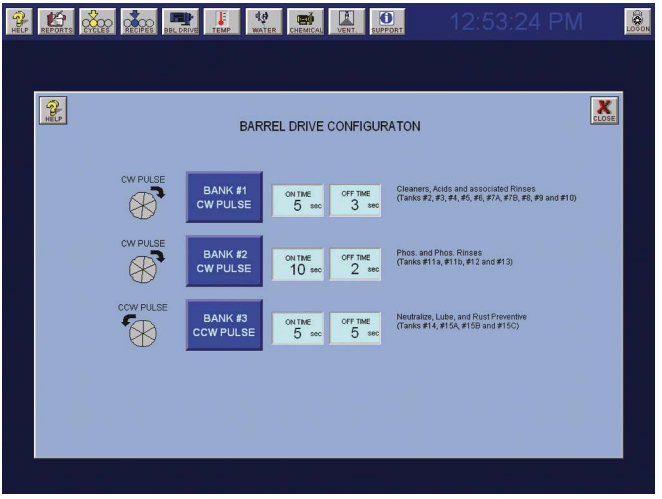


Figure 10. Jessup barrel drive control screen.

count for rack plating, or weight for barrel plating operations (Figure 2). This PC-driven feature derives and calculates surface area data from a customer-supplied lookup table on a discreet part number basis. Operator entered load data assures precise amp square foot (ASF) delivery for rack plating systems. Barrel weight is verified directly by load cells by either addition or subtraction methods. This assures correct ASF delivery for barrel plating systems. Installation of individual rectifiers integrated with a PC/HMI recipe-driven controls make over- and under-plating a distant memory.

3) Programmable chemistry replenishment reduces operator workload and improves quality by reducing fluctuations in process baths. This



Figure 11. Jessup programmable hoist with up barrel rotation.

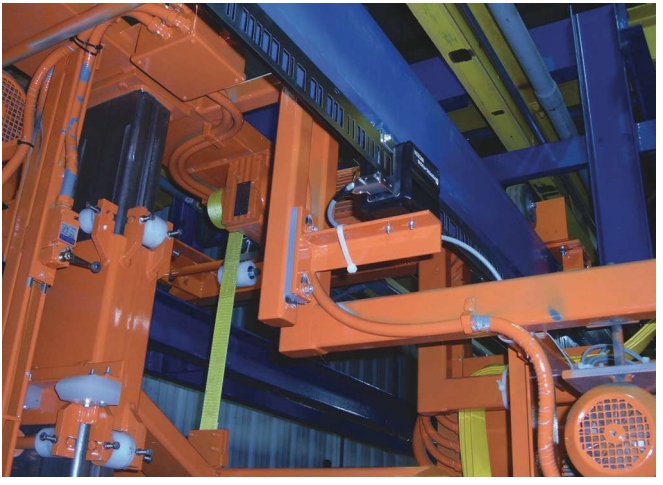


Figure 12. Jessup absolute linear encoder hoist positioning.

recipe-driven feature assures precise additions based on PC-tracked production information. The goal is to dampen the bath concentration saw-tooth effect common with manual addition practices. Precision control is available only by an integrated PC/HMI. The control screen allows external adjustment of replenishment volumes at any time during machine operation (Figure 3). Installation of PC/HMI-driven chemistry management controls will improve quality and reduce

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operator addition errors.

4) Programmable load-by-load rinse water replenishment allows optimization of water consumption on an individual part number basis. This feature enables experimentation with the minimum rinse water volume necessary to assure quality processing. The goal is to minimize total rinse water usage, thus reducing wastewater treatment volume and associated chemistry consumption. Precision control is available only by an integrated PC/HMI. The control screen allows separate replenishment volumes for full or empty loads, further minimizing rinse water usage (Figure 4). Installation of PC/HMI recipe-driven rinse water controls will immediately reduce rinse water consumption compared to constant flow rinse water replenishment systems.

5) Variable plate time programming for multi-process machines allows multiple immersion times and cycle options while maintaining repeatable process parameters. Production rate remains fixed to take best advantage of material handling equipment. The Jessup variable plating time process accepts work with differing plating tank immersion times while retaining predictable and repeatable process times in other areas of the machine (Figure 5). Immersion times are a multiple of the machine cycle time. This approach guarantees repeatable plating at a constant production rate. Load/unload operations and external logistics remain unaffected. Also available is process cycle re-engineering to speed changeover between processes. This becomes increasingly important as the industry shifts to smaller lots, which require more frequent break-in sequences. Retrofit hoists, controls, and variable plate time programming eliminate guesswork and operator sensitivity associated with older simple-cycle multi-process finishing systems.

6) NADCAP & ISO quality system capable automation is assured with PC/HMI over-the-top and appropriate sensor technology monitors, controls, and records critical quality control information. Data such as tank temperatures, immersion times, rectification, pH, conductivity, barrel rotation or oscillation speed and/or duration, chemistry additions, and rinse water usage is collected and stored on a load-by-load basis. Further, data is exported to the customer data highway for upload into quality management database. This system creates truly paperless quality control. The Jessup PC/HMI system captures more data than end-user customers require. The finisher's quality control department will have access to current and historical trend data never before available.

7) Jessup cylindrical barrels can offer 17% increased capacity and 12% better work-to-anode relationship compared to hex barrels for more productive plating. More consistent anode-to-work relationship improves plating efficiency (Table 1). The drawing and comparison chart clearly illustrate capacity and work-to-anode differences. Jessup plating barrel design features include: a one-piece cylindrical shell;

tongue-and-groove, double-welded construction; integrated, heat-fused tumbling ribs; CNC drilled or slotted perforation patterns for shorter drain dwells; and knob or quick-change inside-out style load-locker covers (Figures 7 & 8). A machine specific tab-lock design is also available for Jessup robotic cover handling systems used for fully automated bulk load/unload systems.

Jessup cylindrical barrels retrofitted to your plating line can deliver 17% more production with no other machine changes compared to hex barrels. The example 60-inch-wide barrels fit an identical workspace anode. Run at 12 loads per hour (LPH), the Jessup barrel delivers 8.16 more cubic feet. At 20 hours per day, this equates to 163.2 more cubic feet. If this machine runs 240 days per year, the difference is an incredible 39,168 cubic feet more production delivered on an annual basis by installing Jessup barrels!

Jessup barrels are also available with center partitions, enabling large machines to process smaller lot sizes. This feature assures optimum machine utilization and maintains critical workload separation when combined with divided load/unload systems. PC over-the-top controls

FINISHING EQUIPMENT SYSTEMS



Finishing Equipment Systems
- Hoist systems for Barrel or Rack
- Batch and/or random processing capabilities
- Split Rail machine, single or double file
- Full customization to meet customer needs



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- Cyclic Corrosion Chambers
- Salt Fog & Humdity Chambers
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track, record, and export separate data for part numbers run simultaneously to a customer data highway for paperless quality control management and reporting. Partitioned barrels add small lot flexibility to large capacity machines.

8) The Jessup single-point set-down superstructure design incorporates fixed drive gear engagement (Figure 9). This eliminates ratcheting associated with designs using adjustable gear mesh. It also reduces wear and tear on motors, drives, and associated components by eliminating superstructure rock common to multi-point set-down designs.

Delicate parts suffer from one-process-fits-all rotation management. Recipe-driven control of barrel rotation and/or oscillation with a PC/HMI enables gentler treatment of sensitive parts (Figure 10). If new barrels and superstructures are part of a customer upgrade plan, the single-point set-down design and individual barrel control is a welcome improvement when integrated along with new drives and saddles.

9) Hoist-mounted barrel drives engage in the up position, allowing barrel rotation during the process cycle (Figure 11). Programmable speed and duration dramatically reduce drag-out induced carry over by draining work directly over the process tank. This feature is especially important for parts known to cup solution. PC/HMI controlled up rotation combined with rinse water management reduces water consumption, waste treatment, and chemistry usage. Up-barrel rotation is mandatory for critical resource reduction needed in today's highly competitive finishing environment.

10) Hoist and motion control upgrades such as high efficiency VFD controlled Energy Star-rated Eurodrive motor/drive combinations for electrical energy savings. Smooth-operating, corrosion-proof belt lift conversions replace older wound wire cables. This dramatically extends hoist lift maintenance intervals. Full-length, non-contact absolute linear encoders allow faster hoist operation with smoother motion profiles eliminating rack or barrel shake (Figure 12). Together they improve machine productivity and operator safety. Finally, extremely durable overhead cat-track wire ways eliminate the more sensitive exposed festooning umbilical cables. Multiple hoist improvements reduce energy consumption and create faster, smoother motions, thereby reducing wear and improving safety for finishing systems.

CONCLUSION

If your company is capital constrained for any reason, the best option to remain competitive is to improve existing equipment incrementally until the economy supports a new machine purchase. Clearly, there are many options available for older finishing systems. Whether load/unload equipment, new controls, or hoist automation, Jessup offers productivity improvements priced to fit any budget.

REFERENCES

1. Jessup Engineering formed in 1971 to manufacture automated hoist systems for the metal finishing industry. Over the past 39 years, customer demand drove Jessup to become a turnkey finishing system provider, delivering hoist automation, system components, and peripheral accessories. With more than 630 systems incorporating 1,250 hoists and countless conversions installed, the Jessup team has the experience needed to integrate an ever-increasing array of mechanical, hydraulic, electric, and electronic upgrade components. We believe in a long-term customer focus and support, exacting quality, and on time start-up. In-house mechanical, electrical, controls, parts and service support originates from our Rochester Hills, Mich., location. To learn more about Jessup Engineering products and services, go to www.jessupengineering.com or call to schedule a visit.

ABOUT THE AUTHOR

Timothy J. Kurcz, director of sales for Jessup Engineering, is also responsible for market and product development. A member of the surface engineering community for more than 33 years, his experience includes process automation for adhesives, sealants, coatings, electrolytic and electroless plating, fluorescent penetrant inspection, cleaning, passivation, dip-spin, electrocoat, and autophoretic paint coatings. Kurcz can be reached at (248) 853-5600 or via e-mail at tkurcz@jessupengineering.com.

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RECTIFIER OVERVIEW

Rectifiers were introduced to the surface-finishing industry over a half century ago to replace rotating DC generators. Rectifiers have a major advantage in that they have few, if any, moving parts, which results in significant decreases in maintenance and downtime. Today, rectifiers are one of the most reliable and efficient means of power conversion, and nearly all surface-finishing rotating generators have been replaced.

A rectifier can be divided into three major components: a main power transformer, a regulating device to control the DC output, and a rectifying element to convert the incoming AC to output DC. A rectifier also contains auxiliary components, such as control electronics and cooling.

Main Power Transformer

The main power transformer receives line voltage and steps it down to a suitable but unregulated AC voltage. To produce a transformer of the highest efficiency and reliability, three major design factors must be considered. First, all conductors must consist of electrolytically pure copper. Second, the core laminates must be made from low-loss, high-quality transformer steel. Third, extremely high-quality, high-temperature insulating material must be utilized. If the quality of any of these areas is compromised, transformer efficiency and longevity will be sacrificed.

In a high-quality transformer, electrolytically pure copper is used to wind the transformer coils, with insulating material located between each conductor. Once wound, the coils are vacuum impregnated with a high-temperature varnish, and all terminals are then silver brazed. The coils are then placed onto the core.

The transformer core is constructed from low-loss, grain-oriented silicon transformer steel. The steel is cut into the proper lengths and single stack laminated to form the core structure. If a great deal of attention has not been paid to the construction of the core, there will be air gaps between the laminations. This will decrease the transformer's ability to handle magnetic flux, resulting in a transformer with less efficiency.

The majority of transformer power losses is the result of excessive temperatures. The only way to avoid this condition is through proper engineering. This includes designing for low-current densities in the windings, low-flux density in the transformer core, and of course, ensuring proper transformer assembly.

Quality transformers are manufactured in this manner. Unfortunately, improper transformer design or construction is not always visible to the naked eye. A conservatively designed quality transformer will look physically similar to a lesser quality transformer. Because the differences lie in the design and materials, the effect will only become apparent during operation. A higher quality transformer will run 10 to 15% cooler. A transformer operating at lower temperatures will have a much higher efficiency and greater longevity. Although the manufacturing cost is higher on the more efficient unit, the payback for the additional

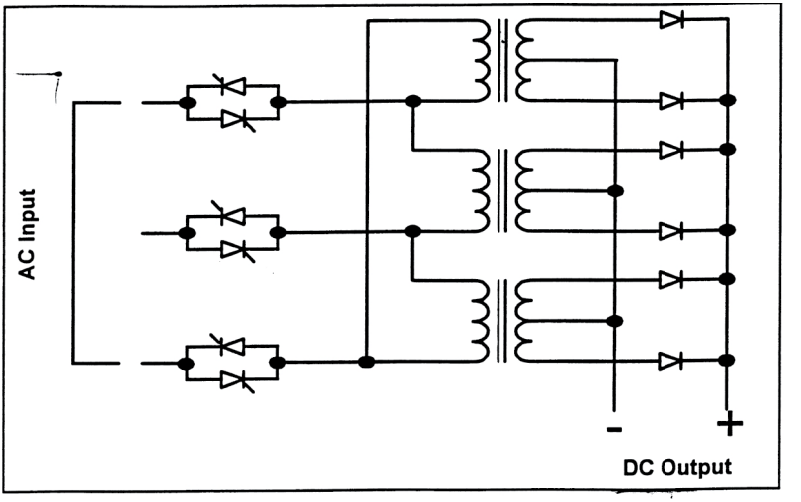


Fig. 1. Primary thyristor.

expense is relatively short. Most manufacturers will guarantee a well-designed transformer for 5 years; however, such well designed transformers will typically operate for a minimum of 15 years without problems.

Rectification and Regulation

The silicon diodes used in rectifiers are the simplest and most reliable rectifying devices available. Silicon, when properly treated with certain elements, allows current to flow in one direction only. When a silicon diode is hermetically sealed, it becomes completely impervious to external conditions, making it capable of withstanding the harsh environments commonly found in metal-finishing facilities.

Another silicon device that is instrumental of today's rectifiers is the silicon-controlled rectifier, commonly known as a thyristor or silicon-controlled rectifier (SCR). The thyristor is basically a silicon diode that will conduct only in one direction and only when a signal is applied to a terminal on the thyristor known as a "gate." In some instances,

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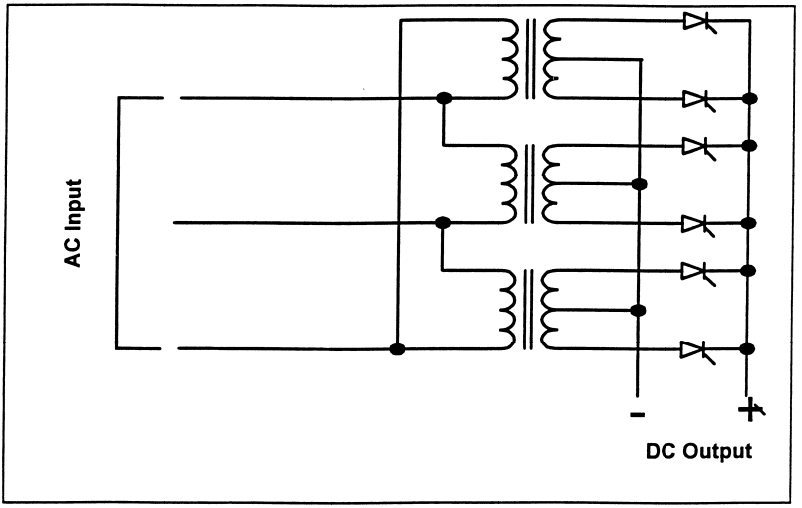


Fig. 2. Secondary thyristor.

the thyristor functions as a regulating element, whereas in others, it acts as both a rectifying and a regulating device.

In the primary thyristor configuration, illustrated in Fig. 1, thyristors are connected between the incoming voltage source and the transformer. In this design, a thyristor operates at a relatively high voltage and low current. Generally, all thyristors have a fixed forward voltage drop across them. This drop ranges from 1 to 1.5 V. When the highest quality thyristors are used as primary elements, with an input of 230 or 460 V, the efficiency of the thyristor network is greater than 99%.

In the primary thyristor configuration, the thyristor is solely used to vary the AC supply voltage from zero through maximum. In order to make a fully regulated controller, each phase of the three-phase input must have two thyristors connected back to back, as shown, and their gates must be symmetrically triggered.

The regulated voltage is then fed from the thyristors to the isolation transformer, which converts the incoming high voltage/low current to a lower voltage and a higher current. From the transformer, you now have the desired output voltage and current, but it is still in an AC form. It is here that the silicon diodes are utilized. The function of the diodes, as stated earlier, is to allow conduction of current in only one direction. When the diodes are used, as shown in Fig. 1, they will rectify the transformer output and provide DC.

Another method is to place the thyristors on the secondary side of the transformer, as shown in Fig. 2. This is known as a secondary thyristor design. In this configuration, the thyristors perform both the regulation and rectification operations, and no diodes are required. Either design can provide the desired DC output, and although each method has its advantages and disadvantages, the cost is usually the determining factor.

The advantages of the primary method are as follows:

Soft start—Because the controlling element is in the primary side of the transformer, it can control the inrush current to the transformer.

Efficiency—It is slightly more efficient than some secondary designs.

The advantages of the secondary method are as follows:

Reliability—Fewer components mean greater reliability. It has greater voltage safety margin on SCRs. It is less susceptible to line voltage transients.

Reversing—It is able to achieve solid-state reversing.

PLATING

Direct Current Plating

Direct current electroplating covers a broad range of processes. These include, but are not limited to, chromium, nickel, copper, zinc, cadmium, silver, and gold. Whereas each of these processes vary somewhat in their particular voltage and current requirements, they all require some form of DC power to deposit the metal out of solution onto the part being plated.

A typical DC plating power supply will have a three-phase input of either 230 or 460 V AC. The output will be somewhere in the range of 6 to 18 V and between 50 and 10,000 A. These values will vary depending on whether still- or barrel-plating methods are employed, the type of finish required, and the size of the parts being plated.

Direct current plating power supplies are relatively straightforward. The incoming AC is converted to DC by means of the main power transformer and either a primary thyristor/secondary diode or secondary thyristor rectification system. In modern systems, the output voltage and current are controlled by the phase angle of the thyristors. Most rectifiers today are equipped with both automatic voltage control (AVC) and automatic current control (ACC) as standard equipment. In many cases, a variable ramp system is also provided to regulate automatically the rate at which the output is increased from minimum to the desired level.

The ripple component of the output at full-rated power is nominally 5% rms of nameplate rating. This will increase as the thyristor's phase angles are changed to reduce the output. If particular processes demand continuous use of a system phased back, either a properly sized unit should be utilized, or a ripple filter should be installed to bring the ripple component to an acceptable level.

Cooling can be by a number of different methods. Forced air and direct water are the most common. Forced air is acceptable when the surrounding environment is relatively clean and free of contaminants. In a forced-air system, air is drawn in through a series of filtered openings in the rectifier enclosure, forced past the internal power-supply components, and exited through an opening, typically in the top of the supply. Air that contains corrosive materials can cause accelerated deterioration inside the power supply, resulting in reduced life and efficiency.

If a plating rectifier is situated in an aggressive atmosphere, direct water cooling should be considered. Direct water-cooling systems pass water through a series of cooling passages in the main power transformer and semiconductor heat sinks. Water-cooled systems are more compact than air-cooled designs, and multiple rectifier systems can be placed closer to each other than air-cooled power supplies; however, water-cooled systems are sensitive to contamination and minerals in the supply water, and in these cases, the power supplies may require periodic maintenance to clean the water passages and filters.

Pulse Plating

Direct current plating deposits metal utilizing a continuous application of ener-

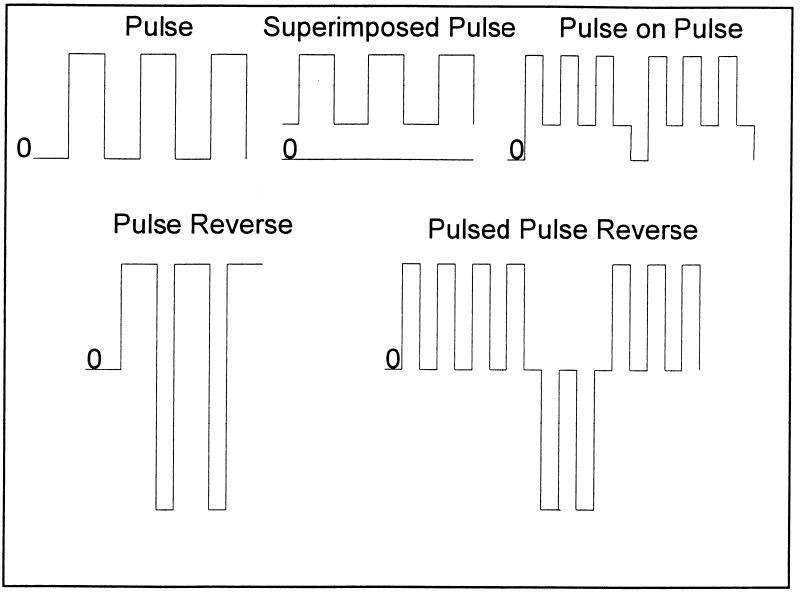


Fig. 3. Common pulse waveforms.

gy, pulse-plating systems provide the opportunity to modulate the voltage or current to achieve different results. The application of gold, silver, and copper with pulse plating results in finer grain structures, higher surface densities, and lower electrical resistance. Additionally, plating times can be reduced by up to 50%. These characteristics make pulse plating attractive, if not mandatory, in the electronics industry.

From an industrial standpoint, pulse plating has found a number of important applications. For example, when used in chromium plating, pulse plating will result in a harder, more wear-resistant surface. In a nickel plating application, using pulse plating may eliminate the need to add organic compounds to control stress and will result in a brighter finish with better thickness control and reduced plating times.

Many plating profiles are available, including standard pulse, superimposed pulse, duplex pulse, pulsed pulse, and pulse on pulse. These waveforms can be obtained from a unipolar power supply. Other variations, possible when using a bipolar pulsing rectifier, include pulse reverse, pulse reverse with off time, pulsed pulse reverse, and pulse-on-pulse reverse. Fig. 3 illustrates a few of the many different pulse waveforms available. The pulsing profile you use will be determined by the type of plating finish desired, the makeup of the plating bath, and the type of power supply available.

There are three basic types of power supply technologies employed to achieve pulsed outputs. The most common design consists of a standard SCR phase-controlled rectifier with a semiconductor switch on the output. Although this system can be successfully employed in almost all pulsing applications, there are some drawbacks, mainly the inherent limitations associated with pulse rise and fall times.

Table I. Pulse Technology Comparison

Type of Power Supply	Ripple	Efficiency	Bandwidth	Size	Cost
SCR	High	Highest	Low	Mid	Lowest
SCR with filter	Low	High	Lowest	Largest	Low
Linear	Lowest	Lowest	Highest	Largest	Highest
Switcher	Highest	High	Mid	Lowest	Mid
Switcher with filter	Low	High	Mid	Small	Mid

SCR, silicon-controlled rectifier.

When faster pulsing speeds or square waves are required, linear power supplies are a viable technology. A linear design consists of a fixed output power supply, followed by a parallel combination of field-effect transistor (FET) or bipolar transistors, with the exact configuration determined by the output voltage levels required. This bank of transistors determines the final output by pulsing the fixed DC supplied to it.

The efficiency of a linear supply is generally less than that of a SCR phase-control design, due to the fact that the rectification section always provides full power to the regulator, which must then dissipate the energy difference between full power and the desired output voltage.

On the other hand, linear designs are capable of providing virtually perfect square wave pulses, due to the ability of the transistors to cycle on and off rapidly. A reversing linear system can also provide transition through zero output with no dead time.

A relatively new configuration, when compared with SCR and linear designs, is the switch mode power supply, more commonly known as a switcher. Although an SCR phase-controlled power supply technically is a switcher, practical considerations usually limit pulse repetition rates to 12 times line frequency.

Functionally, a switcher will typically start by rectifying the incoming line directly. This raw DC will then be chopped by a variable pulse width modulator, feeding the primary of a high-frequency transformer. The high-frequency transformer performs the desired voltage/current transformation. The output from the secondary of the transformer is then rectified and filtered.

Switchers have a number of advantages over the other designs. Because of the higher frequencies, both transformer and filter inductor sizes and weights can be reduced, resulting in a more compact unit.

Additionally, switchers have efficiencies comparable to that of phase-control systems. This is due to the fact that the semiconductors are either fully on (saturated) or off, as opposed to the linear supplies, where the semiconductors are biased in the active region.

Table I illustrates the relative merits of each design when considering ripple efficiency, bandwidth, physical size, and initial cost. The configuration that is most suited to your application will depend on factors such as those. Contact your power-supply manufacturer for additional information.

ANODIZING

Direct Current Anodizing

As in the case of electroplating, there is a wide variety of anodizing processes currently in use. Electroplating deposits a metal layer onto a substrate, which may be a metal itself or some nonmetallic material such as plastic. Anodizing, on the

other hand, is the conversion of the surface layer of a metal to an oxide. The metal most commonly anodized is aluminum, but other metals, such as magnesium and titanium, can also be successfully anodized.

Aluminum will naturally form an oxide layer when exposed to oxygen, but this is a relatively thin layer. Anodizing provides a much thicker coating. Anodized finishes exhibit a number of desirable properties. They are capable of being processed further to modify the appearance of the aluminum. For example, colored finishes are easily obtained by such techniques as dyeing or color anodizing. Anodizing also improves the wearability of aluminum. An anodized finish is much more resistant to abrasion than the base metal. Anodizing is also extensively used in environments where corrosion is a problem.

A number of anodizing processes are employed for aluminum. The most common is the sulfuric acid anodizing process. This provides a coating typically 0.1 to 1.0 mil. thick and lends itself to further color processing. Other conventional aluminum anodizing processes are those utilizing chromic acid (found in marine and aircraft applications) and phosphoric acid (used as a surface preparation for adhesive bonding and as a base for electroplating).

These conventional anodizing processes require a DC power supply similar in nature to those found in electroplating, except that the voltages typically used in conventional anodizing (18-50 V) are higher than those commonly found in plating (6-18 V). Otherwise, the design of the rectifiers for DC electroplating and DC anodizing is basically the same.

Hard-coat anodizing is often employed in applications where a more abrasive or corrosion-resistant oxide layer than that obtained with conventional anodizing is desired. Hard-coat anodizing processes typically demand voltages between 50 and 150 V, and in many cases, pulse power supplies are utilized to obtain specific results. As in electroplating, the pulse rectifiers are very similar in design, options, and usage.

Color Anodizing

Many architectural aluminum anodizing applications require that color be applied to the finished product. Colored finishes are obtained through the use of dyeing, integral, or electrolytic color processes.

Dyeing is a simple process. A dye bath is composed of water and dyeing material, and the anodized aluminum is placed in the dye bath for some minutes. After removal from the dye bath, the aluminum is then rinsed and sealed in a normal manner.

Integral color is a process by which the color is produced during the conventional anodizing process. Organic acids are added to the anodizing bath, and these acids produce a color, ranging from amber through black, in the aluminum oxide. Standard DC rectifiers are used, though at a voltage approximately three times that found in sulfuric acid anodizing.

The electrolytic or two-step process begins by conventional sulfuric acid anodizing using DC power. The parts are then placed into a coloring solution consisting of salts of various metals such as tin, nickel, and cobalt, and AC power is applied. The AC current causes the deposition of metallic particles in the pores of the anodic coating. By varying the relative amplitudes and times of the positive and negative half cycles of the AC output, numerous colors and finish characteristics can be obtained. The electrolytic coloring processes have become popular as they require less energy than competing methods.

An ideal power supply for the two-step process will provide the opportunity

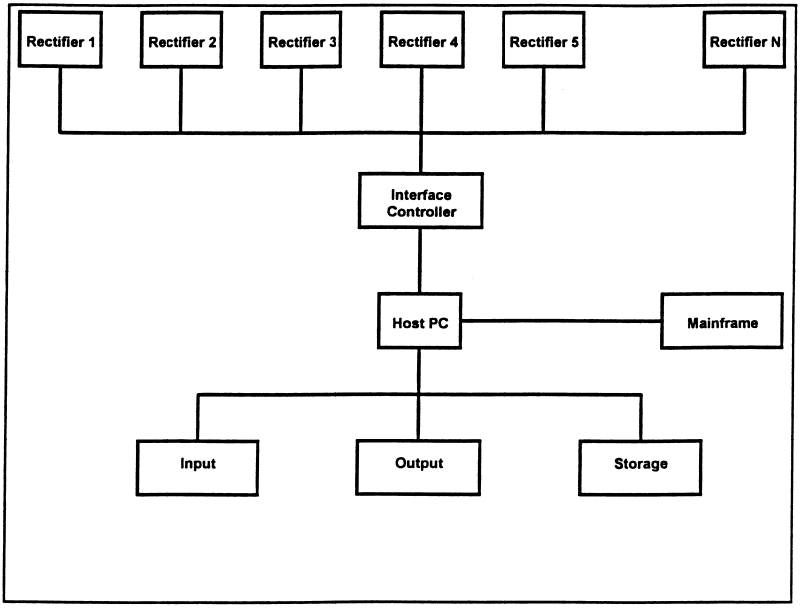


Fig. 4. Multirectifier computer-controlled system.

to adjust the voltage and on-and-off times of the positive and negative portions of the output independently. This provides the maximum amount of flexibility to generate the broad range of colors available through electrolytic coloring.

COMPUTERIZATION

In the 1970s many metal finishers investigated modifications that would be required to upgrade their rectifiers to computer control. At that time, however, the price and risk of automation was too high for most companies, forcing them to continue using manual control.

Today, the importance of incorporating some degree of automation into the metal-finishing processes is becoming more evident. For example, smaller firms find themselves at a disadvantage when competing against larger, more automated companies, especially for jobs where the finished parts require precise coating thickness and consistent finish qualities. Additionally, certain plating applications require multiple layer applications to achieve the desired coating thickness and surface quality. These multilayer processes demand extremely accurate and repeatable coatings.

The major advantage of computer over manual control of a rectifier is the computer's ability to repeat a particular operation or procedure time after time. Computers can perform a variety of different functions when integrated with rectifiers. The computer can simultaneously monitor a number of output currents and voltages, detailing them on a video-display terminal. It can also maintain those voltages and currents within designated parameters, thereby compensating for varying input voltage or load changes. The computer can easily regulate pulsing and reversing power supplies. The computer replaces

the switches, meters, and potentiometers typically required for manual operation; yet a manual override is included in case of malfunction.

The advantages of a simple computer package are easily seen. The first major improvement is in the consistency of a finished product. Due to the precise application of power, the coating is exact from piece to piece, and this can significantly reduce rework and reject rates. Furthermore, a computer's precision control of cycle times and rectifier operation can reduce power consumption, resulting in lower electricity bills. Finally, the computer can calculate and transfer exact amounts of chemicals to finishing tanks, minimizing associated material costs and reducing waste and sludge-disposal expenditures.

A computerized system should be custom designed for the specific application, regardless of the size of the finishing operation or the degree of automation desired. Customization is the key to successful systems integration. The system should, however, be designed and constructed using standard components. This procedure provides a system that exactly matches the needs of the user while minimizing the initial cost.

A computer control system typically consists of a number of basic component groups. The illustration in Fig. 4 shows the structure of a multiple rectifier computer control system. A review of each of the basic groups provides a better understanding of how the system works as a whole.

The Rectifier

For a rectifier to be controlled by a computer, there must be a means for the computer to communicate with the rectifier. The rectifier must then be capable of modifying its operation to satisfy the requests of the computer. Typical commands sent from the computer to the rectifier include output voltage, output current, ramp timer, ramp rate, power on/off, and cycle start/stop.

Additionally, information might be sent from the rectifier to the computer, for example, power status, output voltage, output current, interlock status, and cooling system operation.

In some instances these signals will be transferred directly between the computer and the rectifier. In other cases there may be an intermediary computer that processes some or all of the information. A third situation may arise in which there is a single board computer located in the rectifier itself that has the singular role of operating the rectifier based on data from the control computer. Virtually any rectifier utilizing solid-state electronics to control the output can be adapted to computer automation.

The Host Personal Computer

The host personal computer (PC) is the center of the automated system. It is typically configured around a PC compatible and can be enhanced by a wide variety of peripherals. The host computer is the "brains" of the system, providing the input/output, storage, and communications capabilities needed for optimum operation.

Input Devices

In most cases a keyboard is used to enter information into the computer. It allows an operator to change process data, load parameter profiles, or commence or terminate plating cycles, along with other functions determined by the user.

Most host PCs will include a floppy disk drive. Floppy disks may contain data such as profile information, system software updates, and security codes. The floppy disk can be programmed by a supervisor on a PC in his/her office, and the disk

can then be taken to the host PC and the data transferred.

Another type of input device is a bar-code reader. A bar code consists of a series of alternating black and white vertical bars that contain information defined by the user. A bar-code scanner is passed across the bar code to read it. The spacing and width of the bars determine the data contained therein. Information such as part number, process identification, vendor, and customer are typical examples of data that can be contained in a bar-code format.

Output Devices

A monitor to verify data being entered from one of the input devices is necessary with any computerized system. Once a process is running, the monitor can display a number of different screens. These screens can include process status, alarm conditions, rectifier operation, and virtually any other information desired by the user. It is quite possible for the computer to monitor, display, and control nonrectifier operations, such as bath heaters/coolers, bath agitators, and chemical feeders.

A printer may be desired to obtain a hard copy of any of the data recorded or operations performed by the computer. This information can be used in a number of different ways, from statistical process control to process tracking.

Data Storage

A means to store the operating system, control programming, process profiles, and operating data must be provided. The most economical data storage device is a hard disk, which should be located in the host computer. By using a hard disk a process profile can be retrieved almost instantaneously simply by calling up a code number or name. By using profiles from the computer to control the metal-finishing operation, as opposed to setting parameters manually by turning knobs and pushing buttons, consistency is maintained.

Some method of backing up the data on the hard disk is mandatory. If, for example, there is a power disruption or a failure of the computer, information will most likely be lost. If a regular backup is performed many hours of reprogramming may be avoided by simply restoring the data from the backup device to the computer. Although floppy disks are commonly used for backup, a streaming tape system, which utilizes a removable tape cassette, is a much better alternative, as all the data from a hard disk can usually be stored on one tape.

The Interface Controller

The interface controller acts as the translator between the computer and the rectifier. It receives commands from the computer and converts those commands to a language the rectifier can understand. The rectifier transmits information to the interface controller, which sends it to the computer. Both inputs to, and outputs from, the interface controller come in digital signals over interface cables. The interface controller may be situated in the computer itself, or it may be a separate system located adjacent to the computer.

The Interface

To keep the equipment as standard as possible, the popular choices for interfaces are the RS-232 and RS-422. Each requires only a pair of shielded, twisted wires to transmit information. This significantly reduces the number of wires needed for a multiple-rectifier system, as the twisted pair simply connects from the interface controller to each rectifier in a sequential fashion. In other words, the same pair of wires goes to the first rectifier to the second to the third, and so on.

This eliminates the many wires that are commonly found connecting remotely located control panels to rectifiers.

The Software

The software should consist of standard control packages modified to meet the user's specific requirements. A language such as Quick Basic, used on the host computer, will provide the necessary operating speed for the host, along with the ability to modify or upgrade the program easily at any point. Faster languages, such as assembly code, may be required for a microcomputer located on the rectifier to control output waveforms adequately.

A Main Frame

A link between a main frame and the host computer is always a possibility, increasing the overall capability of the system. Such a link might be the first step toward complete factory automation. Use of a main frame provides a means for data from all parts of the finishing operation to be accumulated, correlated, and disseminated to various departments.

For many smaller and middle-sized operations, computer automation is becoming financially feasible. Benefits include reductions in rework and reject rates, in downtime, and in chemical costs. Additional savings could be realized by the reduced power usage of a computer-controlled operation. In the near future computer automation may very well be the key factor in whether certain metal-finishing operations are profitable.

RECOMMENDED TEST EQUIPMENT

Aside from the usual hand tools usually found in a well-equipped industrial tool box, the following are recommended tools for power supply troubleshooting:

1. A clamp-on AC ammeter
2. A digital volt-ohm meter (DVM)
3. A battery-operated oscilloscope

There are several options to consider when purchasing these instruments for testing in an industrial environment. The clamp-on ammeter should be an AC device, as it will be used at currents up to 1,000 A AC. All exposed metal parts must be sufficiently insulated to ensure safe use around 600 V AC equipment. An analog-type clamp-on ammeter is preferred over most digital ammeter types, unless the digital unit is sufficiently filtered to prevent display jitter when measuring incoming line AC. When buying a digital ammeter, one should test the instrument on an operating power supply before making the final purchase decision.

The digital volt-ohm meter best suited for power-supply testing is battery operated and durably packaged so that it will stand up in an industrial environment. A heavy-duty rubber-covered case is best. To be the most useful, the DVM should have "true rms reading" capabilities. Make sure that the test leads are equipped with heavy plastic leads and rated for 5,000 V DC service. The DVM should have at least the following ranges: voltage of 10 mV to 1,000 V AC and DC, current of 1 to 10 mA AC and DC, and resistance of 0.1 ohm to 10 megohm. Some additional features to look for are autoranging and/or a diode testing range, which measures the forward voltage of a diode rectifier. An alarm on some DVM instruments is a convenient means to measure continuity in cables and wire harnesses.

The oscilloscope should be a high-quality, battery-operated portable instru-

ment. Some models incorporate a built-in digital display, which allows one to observe the power-supply output waveform while reading the DC operating point and the AC ripple content at the output bus. Although an oscilloscope is not always necessary, you will find it a convenient tool when making a quick check on an operating power supply to see if any further testing is necessary.

Of these three electronic tools, the clamp-on ammeter is the first one you will most likely use to measure the three-phase line current. The measurement point should be just after the main contactor, near the transformer input terminals. This measurement can be performed at no load to determine the magnetizing current of the main transformer, which should be about 5% of full load rated line current. With a load on the DC output bus of the rectifier, the balance of the AC line current can be measured, and the three line currents should be within 10% of each other.

The next instrument you may use is the DVM. It will allow you to verify the three-phase, line-to-line input voltages at the thyristor regulator section just ahead of the main transformer. If you then measure the line-to-line voltages on the transformer side of the thyristors, you can determine if the thyristor regulator part of the system is feeding balanced voltages to the main transformer.

The oscilloscope is valuable when performing fast maintenance checks on a number of power supplies. The scope should be connected to the back of the output DC panel voltmeter. As the voltage control on the panel is increased, a waveform will appear that has six peaks and valleys for each cycle of the line frequency. Each period is 16.6 milliseconds long. If any of the six major peaks is missing or the valleys are too wide, there is a serious problem in the power circuit that must be investigated further.

BASIC TROUBLESHOOTING

This section briefly describes some basic diagnostics to determine why a power supply is not operating properly. Before starting any diagnostic test on a power supply, you should obtain a copy of the electrical schematic drawings for the particular equipment you are working on. On these drawings, you should be able to identify the basic functional areas that make up virtually any rectifier. The four basic building blocks of a power supply are the following:

1. Electrical controls
2. AC power circuits
3. DC power circuits
4. Electronic controls

CAUTION: Only qualified personnel should attempt to service power supply equipment. Dangerous and lethal voltages may be present.

The electrical controls provide simple low-power functions for the power supply. You will notice such items as push buttons (stop, start), pilot lights, relays, timers, limit switches, flow switches, thermal switches, thermal overlay relays (heaters), and other 120 V AC protective devices. These items are typically drawn in the familiar ladder diagram format. Diagnostics in this area will usually require the DVM to measure continuity or the presence of control voltages at various components.

To check for proper voltages at the low-power components, find the common on the ladder diagram and attach the voltmeter to it in the actual circuit. With the control power energized, you will be able to check the AC controls on the ladder diagram

and measure for the presence of an AC voltage at the corresponding point in the actual circuit. This method is most useful when there is a loss of control circuit voltage that prevents a portion of the controls from working properly. When the missing voltage returns at a particular point in the circuit, this indicates you have just moved past the defective component, such as a contact, a terminal, an interlock, or a thermal switch. The faulty component can then be repaired or replaced. You may find there is more than one bad part; so be sure to test all of the low-power components.

The AC power circuit is the portion of the power supply located between the AC input power terminals and the regulation thyristors at the primary of the three-phase power

transformer (assuming a primary thyristor/secondary diode configuration). The components representing this AC power section are usually found near the center of the electrical schematic.

The clamp-on ammeter is the diagnostic tool used in the AC power circuit. Place the ammeter around one of the incoming AC conductors. Operate the power supply with no load and check that the magnetizing current of the main transformer is no more than 5% of the full load rated line current, which is usually indicated on the electrical schematic. If this reading is correct, the next step is to measure the line current with a load of parts in the process tank that will require full output of the power supply. Measure all three incoming lines and verify that the currents are balanced to within 10% from one phase to the next. If an imbalance is detected, there could be a fuse blown or a thyristor shorted, or the gate signal to some of the thyristors may be improper.

To determine which of the above is the problem, use the DVM on a high AC voltage range and measure the line-to-line AC voltages. Extreme care should be exercised when making line voltage measurements to prevent any metal parts from coming in contact with the live conductors. At the same time, protective eye wear should be used. Measure the line-to-line voltages at each of the thyristors, after the thyristor fuses. If all voltages are okay, no fuses are blown, and all contactors and safety switches are working, next measure the line-to-line voltage at the output of the thyristors near the connection to the primary of the main power transformer. If these voltages are relatively balanced but reduced in value, the thyristor regulator is in proper working condition.

If after testing both the electrical controls and the AC power sections you find that everything is normal (i.e., no defective fuses or thyristors, all electrical controls functioning) except for unbalanced line currents, there may be a problem with the main power transformer or the diode section on the low-voltage secondary side of the transformer.

The DC power section typically consists of diodes, output bus connections, and metering for output voltage and current (in a secondary thyristor configuration, you would find thyristors in place of diodes). Testing in this section of the power supply consists of locating shorted or open diodes and verifying metering calibrations. Because of the high currents that flow in the low-voltage diode busing, a loose connection will cause a great deal of heat to be generated, which will cause a discoloration of the copper bus bars. By physically inspecting the DC power section in detail, some of these connection problems may be located and repaired simply by cleaning. The clamp-on ammeter may be useful for moderate-sized diodes that are supplied with a flexible cable connection from one side of the case.

Diodes that are supplied with a flexible connection at one end of the case can be checked with the clamp-on ammeter. Measure the current at each diode by plac-

ing the clamp-on ammeter around the flexible lead. A diode that is open will draw no current, whereas a diode that is shorted will draw excessive current. In either case, the diode should be replaced. As these diodes are removed, the DVM may be used on the diode range to verify that the diode being removed is, in fact, bad. A defective diode will read either open or shorted in both directions.

The DVM may be also used to determine possible metering circuit defects. To check the power-supply voltmeter, measure the voltage across the output terminals of the rectifier and the terminals at the back of the panel voltmeter. Compare these readings with that of the panel voltmeter. They should all agree.

Current is typically determined by measuring the voltage drop across a precision resistor placed at the output terminals known as a shunt. This voltage drop at full output will typically be 50 mV. This low-level voltage signal has to be multiplied by a factor before comparing it to the actual meter reading.

The oscilloscope is useful in locating problems where complete diode circuit branches have burned open and left a missing section in the wave shape; however, this may also be a symptom of thyristor problems on the primary of the main transformer. If the AC ripple component of the output is important to the process, then an oscilloscope with a built-in true rms feature can be used to view the ripple waveform, as well as determine the AC to DC ratio of the ripple using the AC and DC coupling of the scope.

The electronics are the most complex part of the power supply. Electronic circuits are usually indicated on schematics by boxes with terminal numbers and functions labeled along the edges. The DVM is commonly used in the testing of these electronic circuits to measure signal and control voltages. Although there are many different types of electronic circuits, two are found in every power supply and must function correctly for proper power supply operation. These are the drive circuit and the firing circuit. In some cases, these will be on one circuit board, whereas at other times, they will be on separate boards.

The drive circuit is an analog amplifier circuit. It receives current and voltage reference signals from the operators ACC and AVC potentiometers. These control signals will typically range between 0 and 2.5 V DC, depending on the position of the operator controls. To check a typical drive circuit initially, verify that there is 120 V AC on the power terminals and that there are reference voltages on the ACC and AVC input terminals. You should then have a voltage at the output terminals. If no signal is available at these output terminals, the drive circuit may be defective or seriously out of adjustment. Remove and further test the drive circuit using the test procedures found in your operators manual.

The firing circuit accepts the output signals of the drive circuit and produces synchronized gate pulses that fire the thyristors in the AC power circuit, which in turn regulates the voltage to the primary of the main power transformer. To test this circuit, ensure there is a signal of more than 2V DC at the input from the firing circuit. Then measure the signals at the gate outputs to the thyristors with the DVM. They should typically be about 1 V DC. Perform these measurements with great care against shorting any of the leads to ground or to another pair of terminals, as there may be line voltages of up to 600 V AC between these terminals and ground. As with the drive circuit, if any signals are missing or incorrect, remove the board and bench repair using the procedures outlined in the operators handbook.

BASIC REPAIRS

Once a defective component has been located, it should be replaced with a part of comparable quality and ratings. It is especially important when replacing temperature sensors that the replacement have the same temperature rating as the original.

Caution: Before attempting replacement of any component, ensure that the power is removed from the rectifier and that the capacitors are discharged.

Electrical and Electronics Components

Replacement of electrical components, such as push buttons, thermal switches, relays, and switches, as well as electronic PC boards, is relatively straightforward. Carefully mark all connections to the defective device before removal, replace with the correct item, and reattach the wires. It is also advisable to check the rest of the rectifier for clean and correct connections at this time.

Thyristors and Diodes

Thyristors are typically found in modular, stud-mount, and flat-pack configurations, whereas diodes are usually the stud-mount or flat-pack style. The replacement procedures for stud-mount and flat-pack thyristors and diodes are virtually identical, with the difference being that thyristors will have two additional small leads to be attached.

The modular thyristor is the smallest of the three types and is typically found in lower power systems. The module contains two thyristors and has terminals for connecting gate and input/output leads. Mounting holes in the base allow attachment to the bus bar. To replace a modular thyristor, perform the following steps:

1. Note where the gate and input/output leads are attached.
2. Mark the leads and remove the thyristor.
3. Clean the bus bar surface and the new thyristor surface.
4. Apply heat sink compound sparingly to both surfaces.
5. Fasten the new thyristor to the bus bar.
6. Reattach the leads. Replacement is now complete.

Stud-mount thyristors and diodes are no more difficult to replace. Stud-mount devices can be mounted on either air- or water-cooled heat sinks and are typically found with or in. diameter studs. Replacement of stud-mount devices is the same for both air- and water-cooled systems, following the steps below:

1. Mark and remove the two signal leads from the terminal blocks (thyristor). One of these is the gate lead, and the other is the cathode signal lead.
2. Remove the large braided cable.
3. Remove the nut and washers, and remove the device from the heat sink.
4. Clean the bus bar and new thyristor surfaces.
5. Spread a small amount of thermal compound on the new thyristor, taking care not to get any compound on the thyristor threads.
6. Insert the stud in the heat sink, reassemble the flat washer and the star washer, and then tighten the retaining nut.
7. Attach all leads to the proper locations, being sure that all connections are clean and tight.

Flat-pack thyristors and diodes, sometimes referred to as “hockey pucks,” are used in higher power rectifiers. They range from 2 through 4 in. in diameter.

As with the stud-mount devices, the only difference between a flat-pack thyristor and diode is the presence of gate and cathode leads on the device.

A flat-pack device is secured between two current-carrying bus bars by a clamping mechanism. Some clamps have indicators built in, whereas others do not. When replacing a device secured with a gauged clamp, note the reading before removing the device.

The other type of clamps used are either 5,000- or 10,000-lb clamps. These systems consist of a pair of clamping bars, connected by two studs, between which is sandwiched the bus bars, a Belville washer system, and the semiconductor device. Replacement of thyristors or diodes utilizing these types of clamps requires the use of measuring devices. The following steps should be taken to replace a flat-pack thyristor or diode (refer to Fig. 8).

1. Note the clamping arrangement being used. If a gauge is present on the lamp, record the indication. Mark and remove the gauge and cathode leads if replacing a thyristor.
2. Uniformly and slowly loosen the nuts on the clamp studs. Remove the Belville washer assembly and the device. Note that the Belville washer is made up of four parts: a centering section, a flat washer, and two concave washers.
3. Clean the surfaces of both bus bars and the new thyristor or diode. Clean both clamping bars, and check that the insulated surfaces of the clamp have not been damaged.
4. Apply heat sink compound sparingly to both surfaces of the device and to the bus bars.
5. Place the new flat pack in the clamping mechanism, ensuring that the device is oriented properly. Check the other devices to verify this. There are typically roll pins in the bus bars that align with depressions in the device. Make sure the roll pins do not damage the flat-pack surfaces.
6. Reassemble the Belville washers as shown, making sure the two concave washers are back to back. Now place the washers in the clamp.
7. Finger tighten the clamp nuts, ensuring all parts are situated properly, and tighten the nuts with a wrench one-quarter additional turn. Check that approximately the same number of threads are visible beyond the nuts on each stud.
8. Using a depth gauge, measure through the center of the hole in the bus bar and Belville washer system. Note this reading.
9. Tighten each nut one-half turn, and recheck with the depth gauge. Continue this tightening procedure until the difference from the original reading is 0.048 ± 0.004 in. for a 10,000 lb clamp, and 0.026 ± 0.002 in. for a 5,000 lb clamp.
10. Reattach the gate and cathode thyristor leads.

PREVENTIVE MAINTENANCE

Nothing is more important to rectifier reliability and longevity than a consistent program of preventive maintenance. The efforts expended in taking periodic care of any equipment, especially those operated in the aggressive environments typically found in metal-finishing processes, will be returned many times over.

The following provides a brief outline of the minimum maintenance that should be performed every month and every 6 months. The program you implement should take into consideration the number of rectifiers, how many shifts,

what type of processes, and the duty cycles of your particular operation.

Monthly

1. Ensure that all doors and panels are on the rectifiers and that the area around the rectifier is free and clear of items that would hinder proper airflow or operation.
2. On air-cooled systems, wash or replace the air filters. Refrain from using inexpensive cardboard framed filters, as the thin metal facing can quickly deteriorate and be drawn into the rectifier. Also, check that the fan blades are secured to the fan motor shafts and that they run without vibration.
3. On water-cooled systems, remove and clean or replace the inlet water strainer. Check all water lines for signs of leaks or contamination accumulations. If contamination is evident, determine the source and correct if possible.
4. Check panel gaskets and repair or replace as necessary.
5. Check components such as pilot lights, switches, push buttons, etc., for proper operation and replace as required.

EVERY 6 MONTHS

1. Check writing and bus connections for tightness and cleanliness. Repair as required.
2. Clean semiconductors and heat sinks. Dirty and corroded heat sinks can significantly increase the operating temperatures of the semiconductors and reduce the life of the rectifier.

SELECTION AND CARE OF PUMPS

BY JACK H. BERG
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Since the pump is the heart of the filtration system, it must have the ability to deliver and maintain the desired flow rate and pressure as the dirt builds up on the filter medium. Proper pump and seal selection is critical and requires the following considerations:

1. Flow rate required (tank turnovers per hour in gph)
2. Location (in or out-of-tank)
3. Discharge head and distance
4. Filter medium and pressure drop
5. Solution corrosivity
6. Solution temperature

All construction materials must be compatible with the solution being pumped. In some cases, it is advisable to specify a construction material that will corrode slowly within tolerable limits if the material of ideal chemical resistance is too costly. In addition to the initial investment, careful consideration must be paid to the costs of pump operation, down time, parts, and labor. One should also consider, for each application, the relative advantages and disadvantages of the various styles.

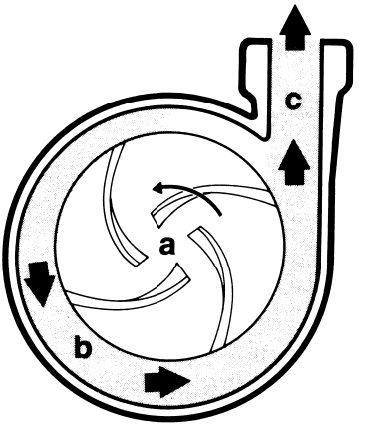


Fig. 1. Horizontal centrifugal pump. The rotation of the impeller imparts velocity to the liquid. Centrifugal force moves the liquid to the periphery of the casing and toward the discharge port. When the liquid in the impeller is forced away from the center of the liquid, a reduced pressure is produced and consequently more liquid flows forward.

PUMP TYPES

Horizontal centrifugal pumps (Fig. 1) are the most common pumps used in the plating industry. Usually, the only part that wears is the seal. Flow rates are high, and pressure is moderate; thus, this pump is suitable for most filtration requirements. Care must be taken when pumping liquids with a specific gravity higher than 1.0 to ensure that the motor is not overloaded. A valve on the discharge adjusts the flow and thus the required power when the centrifugal pump is working against virtually no restriction, such as when operating with a clean filter. Care is usually taken by the manufacturer to supply a sufficient amount of horsepower to prevent this overloading, and also protection is provided in the motor starter. Some users de-rate the system by using a motor of lower horsepower to save on operating cost. To guard against overload, the discharge valve must be employed.

Close-coupled, horizontal pump-motor units are available in all price ranges and sizes and offer the greatest advantage in

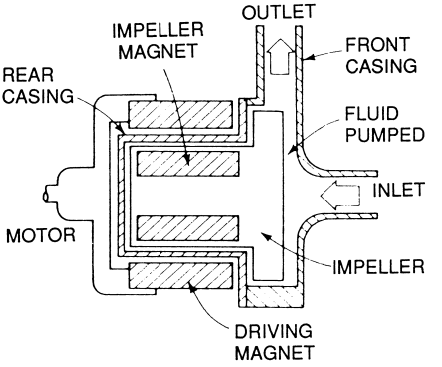


Fig. 2. Magnetic-coupled pumps can be of any hydraulic design, but they always use magnets to transmit the required driving torque.

always assuring proper alignment between the pump and the motor. They are compact and, therefore, require less floor space. Long-coupled pump-motor units use standard motors and usually require an additional mounting plate to assure proper alignment. Improper alignment causes vibration of the pump and motor assembly, which, in turn, causes failure at the motor and pump bearing; it also has an adverse effect on the pump seal.

Turbine pumps are similar to centrifugal pumps in basic design. These pumps provide high-discharge head at lower flow rates than do centrifugal pumps. However, they should only handle clean, low-viscosity liquids.

Vertical sump pumps are usually of the centrifugal type and, depending upon design, may have no bearings at all. This first type is referred to as a cantilever or bearingless vertical pump. They are capable of running dry at high speed but are limited to a length of 1 ft. If pumping is initiated only after the pump casing is immersed, a suction extension will allow up to 10 ft of deep drainage from a 1-ft long cantilevered pump. Cantilever-type pumps can also be mounted external to the tank.

The short plastic cantilever pump is well suited to mixing, agitating, or transferring many types of solutions. The performance is like that of their horizontal counterpart; however, there are no wearable parts. The short cantilever shaft requires no support and has neither seals nor bearings. A double impeller prevents the solution from being pumped up the column, even at no flow and maximum head. Since these pumps are sealless and have generous clearances, they are suitable for electroless nickel and can even run dry. These pumps are said to be maintenance free.

Longer pumps require one or more bearings, which may also act as seals. Vertical pumps with sleeve bearings should be specified with as short a column length as is practical. They should be driven by 1,725 rpm motors where possible to reduce the load and subsequent wear on the bearings; however, loss of performance should be expected at 1,725 versus 3,450. For the best results, bearings should receive fresh water rather than product flush. Long pump columns with multiple bearing sets demand perfect motor-bearing-pump alignment.

Magnetic-coupled pumps (Fig. 2) are unique because they require no direct mechanical coupling of the motor to the pump impeller or shaft, and therefore no seals are needed, making them truly leakproof. The pump body is generally constructed of various plastics, and the impeller magnets are encapsulated in plastic to eliminate any metal contact with the solution. Those without internal carbon bearings are used for electroless solutions. Magnetic pumps are also available with encapsulated motors, so that the entire unit may be submerged in the liquid. This is an extremely desirable feature for use in precious metal plating, to avoid loss of expensive plating solutions.

To efficiently provide a self-priming feature, close tolerances or actual rubbing must occur on both impeller and/or moving parts on the body of the pump. Most note-

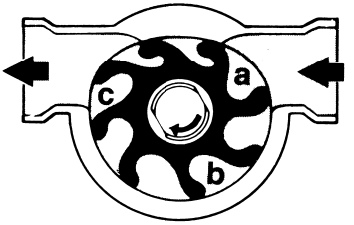


Fig. 3. Flexible impeller pumps utilize an elastomeric impeller that pushes the liquid from the inlet to the outlet port.

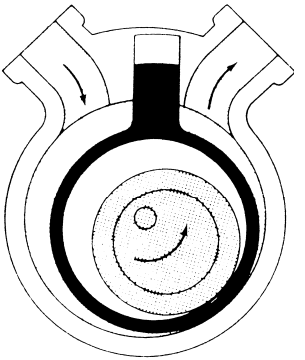


Fig. 4. Flexible linear pumps utilize an elastomeric liner that has an eccentric cam turning within it. As this rotates, it pushes the liquid from the inlet to the outlet port.

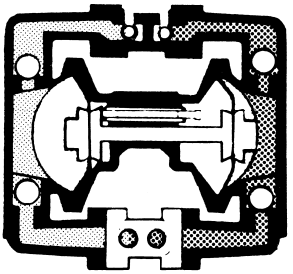


Fig. 5. Air-operated diaphragm pumps utilize air pressure acting on a manifold valve to provide alternate reciprocating motion to opposed diaphragms. When one diaphragm is pushing liquid out, the opposite diaphragm is pulling liquid in.

worthy is the fact that the greatest amount of wear occurs when the pump is developing its greatest amount of pressure as the plating filter is approaching maximum reduction of flow due to dirt pickup. Therefore, oversizing the filter will reduce the frequency of this occurrence. The flexible impeller (Fig. 3) and the liner impeller (Fig. 4) are both self-priming. They develop pressures up to 20 psi but require relatively frequent impeller or liner replacement when used continuously. Also, they cannot be used on abrasive solutions or where dry-running capability is required.

Air-operated diaphragm pumps (Fig. 5) do not have rotating seals, impellers, or other internal parts. They depend on a pulsing, intermittent reciprocating motion acting on an elastomeric membrane to form a liquid chamber between two check valves and thus produce low flow rates at high pressure. The air supply can be regulated to produce certain performance requirements. Because of their self-priming feature, capability to run dry, and ability to handle extremely viscous liquids or materials with a high solids content, they are widely used in waste treatment and in other industrial applications. However, since these pumps pulsate, the filter and piping require pulsation dampening.

Another common self-priming pump design is the progressive cavity design (Fig. 6). This design uses a rotor, which has a helix turning inside a stator with a similar helix at a set pitch. Liquid is passed from one chamber to another along the length

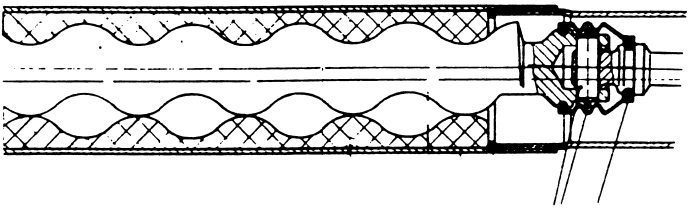


Fig. 6. Progressive cavity pumps. As one cavity formed by the offset helix diminishes, the opposite cavity increases. The result is constant, uniform flow over the length and out the discharge port.

of the rotor. These pumps are well suited for high-pressure, low-flow conditions on either low- or high-viscosity liquids.

Horizontal centrifugal pumps not normally thought of as self-priming can be made self-priming by the addition of a priming chamber to the suction or discharge sides (or both) of the pump. Once the chamber is filled with liquid and the fill port securely sealed, suction lifts of up to 25 ft (depending on individual pump characteristics) may be achieved. Some pumps are capable of only a few feet of suction lift when a priming chamber is used. Basket strainers are available for priming chambers to prevent large solids from damaging pump internals.

CENTRIFUGAL PUMP PRIMING

Priming of centrifugal pumps can be made easier if the following precautions are taken. Avoid all sharp bends or crimps in the suction hose. Prevent small parts from entering or restricting flow to the suction hose. Prevent air from getting into the pump by checking for poorly connected hose or flanged fittings, which may have vibrated loose. The slightest amount of air coming from an insufficiently tight threaded fitting or a loose flanged fitting prevents successful priming. Fittings with an "O" ring provide for a positive seal. As the pump packing wears, it will also suck air and, depending on usage, must be adjusted as required. (See tips on pump packing and the use of water lubrication to prevent sucking air.)

If frequent venting of the filter chamber is necessary when the filter is running, it is likely that an air leak has developed some place at the previously described two locations, and sooner or later priming will become more difficult. Air in the filter chamber is also an indication that the suction from the tank may be too close to an air outlet being used for solution agitation. A pump discharge fitted with a set of eductors could eliminate the problems associated with air agitation. Remember, the larger the pump, the more velocity is created and the more tendency to pull air into the suction opening. Priming is made easier with a slurry tank or priming chamber above the pump, making it possible to always have a flooded suction. Recirculating through the pump, filter, and slurry tank and then slowly opening the line to the plating tank gradually purges the system of air. The suction valve from the plating tank should initially be opened only a crack, so that the pump does not get a slug of air at one time. This air also collects in the filter chamber and must be released by venting. In a precoated filter, any constant collection and venting of air soon results in ineffective filtration. As air collects, the cake falls away and is redeposited elsewhere. Subsequent venting returns solution to the unprecoated surface, where there is no filtering action, and the contaminated solution passes through.

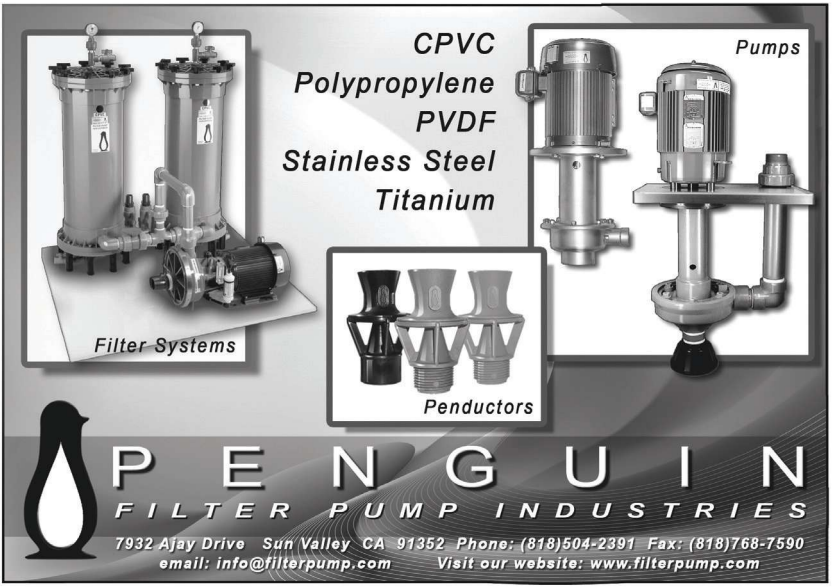
To prime a centrifugal pump, if a hose is used on the suction side of the pump (without a slurry tank), liquid may be introduced through the hose and pump

into the filter chamber. The filter need not be filled completely, but most contain a sufficient volume of liquid so that, as the hose is lowered to approximately the same height as liquid in the chamber, the hose will gradually fill with solution. Shake the hose to make certain any air trapped in the top of the pump or in other high points is completely expelled. When the liquid level completely fills the hose, keep the tip of the hose at the same position, but close the valve between the pump and the filter chamber. Now insert the hose in the tank (since the valve is closed, virtually no liquid will run out of the hose if a gloved hand is cupped over the end). Start the motor and wait until the motor has reached its proper speed; then slowly open the valve to the filter. This is a further precaution, which will enable the pump to create enough suction to handle the small amount of air that may still be in the line.

When transfer pumping out a tank, it is advisable to connect a 90° hose barb or a strainer to the suction end of the hose so that it may be lowered as solution level drops. This prevents cavitating the pump, which could occur if the end of the hose rested flat on the bottom or against the side of the tank. If the hose has a tendency to curl, insert a length of straight, corrosion-resistant pipe into the end to accomplish the preceding purpose. Since the most difficult time to prime a pump is after most of the solution has been removed from the tank, operators often dump this remaining heel, which is a needless waste of solution. Plating tanks with sumps at one end minimize this loss when solution transfer is necessary. Small self-priming pumps, such as drum pumps, may be used to salvage the heel left in the plating or treatment tank.

PUMP SEALS

The available types of pump seals vary from no seal at all to lip type, packed stuffing box, and mechanical. Since conventional pumps have an interconnecting shaft



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between the pump impeller and the motor, a suitable seal is necessary to prevent leakage during the rotation of this shaft. A magnetically driven impeller or vertical cantilever are perhaps the only truly seal-less pumps. Other pumps, which use a liner, or section of hose, are seal-less; but, since these components may fail through usage, fatigue, and abrasive wear, the system, like any other, is subject to eventual leakage. It is always desirable to replace seal components before leakage occurs. Unfortunately, one never knows just how much longer a seal will last before replacement is necessary. They may operate from a few minutes to a more realistic several years.

A lip-type seal consists of a molded, rubberlike material, which has a squeegee action in snugging itself around the shaft. A mechanical seal consists of two mirrorlike lapped surfaces, one rotating with the shaft, the other stationary in the pump, which are held together by a light spring pressure, preventing leakage. The preferred arrangement is an outboard mounted seal, so that exotic or nonmetallic seals are eliminated. A packing stuffing box consists of a suitable cavity, with the rotating shaft in the center, around which a compressible-type material may be inserted in alternating rings and held in place and adjusted by tightening the packing gland. Both the mechanical seal and the stuffing box seal are available with provision for water lubrication or recirculation of the solution being pumped. Usually, water from an external pressure water line is desirable, because it assures cooling and lubrication of the seal components. It reduces wear by keeping filter aid and dirt out of the seal area. The water also prevents the solution from crystallizing on the seal faces during shutdown periods. Even while the pump is running, crystals may form as plate-out might occur with electroless solutions.

On double-seal pumps, care must be taken through the use of a check valve, or siphon breaker, so that no solution is pumped into the water system during an unexpected failure. Also, a regulator should be installed in the water line to control the pressure, because it will vary from low when the plating room is in operation to high during the weekend when no other water is being used. If the water pressure and flow to the seal are not regulated, it is possible to actually draw water through the packing into the plating tank, especially when the filter is clean, because a negative pressure exists at this point. This could cause chemical imbalance and even overflow of the plating tank. Solutions requiring deionized water for the seal use a double-seal arrangement, with an additional small pump recirculating the deionized water in the seal area.

When selecting the type of seal to use, consider the fact that a stuffing box seal or lip-type seal wears slowly, giving warning that replacement will be necessary by gradually increasing constant leakage. A mechanical seal is more trouble-free on a day-to-day basis and yet may fail without warning; thus, there is a need for preventive maintenance. (See piping instructions to minimize solution loss.)

Certain types of packing are more suitable for acid, and others are more suitable for alkaline solutions. The construction materials in a mechanical seal, such as the type of carbon and ceramic, along with what type of elastomer, also vary. Therefore, it is important to give the type of service to the manufacturer to assure suitable materials of construction. Some seal wear has to be expected, and periodic replacement of components is necessary. Whenever replacing the seal or packing, the pump shaft should be inspected. If worn or scored, it must be replaced.

CHEMICAL-RESISTANT TANKS AND LININGS

BY C. E. ZARNITZ
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The dominant and most economical construction materials used in the metal-finishing industry are steel and concrete. Unfortunately, both of these materials are highly susceptible to corrosive attack from many of the chemicals used in the metal-finishing industry. Pickling and plating chemicals are highly corrosive and, without proper protection, the life span of steel and concrete is limited. Tanks and tank linings must be capable of:

1. resisting attack from organic and inorganic, oxidizing and nonoxidizing chemicals at varying concentrations, as well as from various solvents;
2. resisting broad thermal variances including thermal shock;
3. resisting weather extremes because economics dictate that very large storage and waste treatment vessels be located outdoors;
4. resisting physical abuse that accompanies processing strip, heavy parts, shapes and castings; and
5. maximizing performance, value, and ease of maintenance.

TANKS AND LININGS

The type of tanks that have excelled in the metal-finishing industries include lined carbon steel; lined, precast, or poured-in-place concrete; precast or poured-in-place polymer concrete; self-supporting plastics, i.e., thermosets and thermoplastics; and alloys.

The success of steel or concrete-lined tanks is predicated on good engineering design of the structural shell. The ultimate success of the lining, besides good engineering design, is predicated on the finish and structural integrity of the substrate, as well as on the skills and proficiency of the applicator. If the structure cannot sustain the stress imposed by the process, lining failure is imminent. Similarly, plastic or alloy tanks will fail if good design engineering has been compromised.

Carbon Steel Tanks

When fabricating carbon steel tanks for subsequent lining, the following are important:

1. Minimum number of pieces and sufficient reinforcement must be used to prevent bulging when subjected to optimum process stress.
2. Vertical reinforcing is preferred to horizontal. Ledges are eliminated, thus minimizing potential for drag-out to hang, concentrate, and corrode the vessel from the "outside-in."
3. Welds to receive lining are to be solid and continuous.
4. All corners are to be ground to a minimum radius of in.; no sharp right angles.
5. Exterior reinforcing members may be skip welded.
6. All body seams must be butt welded true and flat with variation on alignment not to exceed 25% of plate thickness and in no case more than in.
7. All outlets to be flanged.
8. Interior of vessel must be free of weld splatter, pits, deep gouges, and all welds

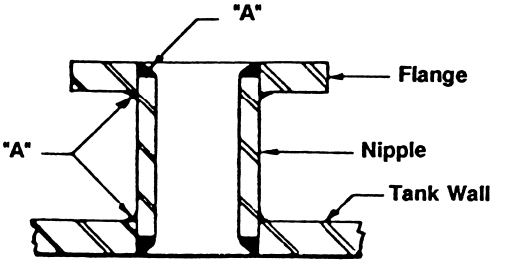


Fig. 1. Flanged nipple outlets in tanks and covers. Welds "A" should be burned into plate so welds meet from opposite sides, thereby excluding air pocket. Welds must be peened and ground smooth.

ground smooth.

The following typical outlet and weld details are suggested when fabricating carbon steel that will be lined with various types of linings (see Figs. 1 and 2).

Stainless Steel Tanks

Stainless steel tanks can be compared to plastic tanks in the respect that they are solid steel, thus eliminating the need to protect a vulnerable exterior from fumes and splash. Stainless steels generally are classified as straight iron-chromium alloys and iron-chromium-nickel alloys. In the metal-finishing industry, the iron-chromium-nickel alloys, i.e., the 300 series appear to be the most popular. Types 302, 304, 321, and 347 are considered to be generally equivalent in chemical resistance.

The stainless steel alloys exhibit excellent resistance to such oxidizing acids as nitric and chromic. They have virtually no resistance to hydrochloric and hydrofluoric acids.

The vulnerability of stainless steels to halogenated acids is easy to understand when you recognize that pickling solutions for stainless steel are acids such as hydrochloric and hydrofluoric and various combinations of nitric and hydrofluoric. Figs. 3-5 provide typical outlet and weld details for the fabrication of tanks.

Portland Cement Concrete Tanks

Concrete tanks are acceptable so long as good design engineering is practiced and includes: sufficient reinforcement to prevent buckling and cracking; minimum 3,000 psi compressive strength after 28 days; smooth, monolithic interior free of ridges, depressions, honeycomb, form marks, etc.; freedom from contaminants and additives, i.e., form release agents, air entraining agents, etc.; and hydrostatically tight and waterproofed on the exterior if located below grade.

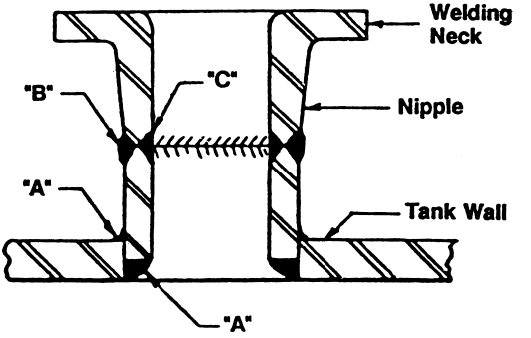


Fig. 2. Flanged nipple outlets when welding neck is specified. Weld "B" to be laid in V in beads not to exceed 1/8-in. deep. After "B" is built up above plate outside, the inner surface must be routed out sufficiently to remove all scale and slag. Weld "C" is to be built up above the surface of plate, peened, and ground flush.

Self-supporting plastic and stainless steel tanks must comply with similar structural mandates as those enumerated for carbon steel and Portland cement concrete.

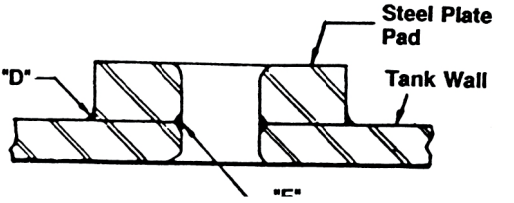


Fig. 3. Pad outlets. Weld "D" is the same as "A," except penetration is not required. Drill two -in. diameter holes, 180° apart, through weld for vent. Weld "E" plate must be bevelled distance equal to thickness of tank wall. Weld is to be built up above the surface of plate, peened and ground smooth and flush with plate.

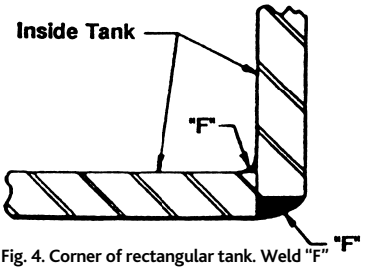


Fig. 4. Corner of rectangular tank. Weld "F" should be burned into plate so welds meet from opposite sides, thereby excluding air pockets. Welds must be peened and ground flush.

Polymer Concretes

Polymer concretes are a generation of materials that have rapidly matured because of their outstanding chemical resistance and physical properties. They are not to be confused with Portland cement concrete or polymer-modified Portland cement concrete. The only similarity to Portland cement concrete or polymer-modified Portland cement concrete is the use of properly graded and sized aggregate in order to optimize workability and physical properties of the composition. Polymer concretes utilize inert siliceous aggregates with binding systems based on such resins as furan, epoxy, polyester, vinyl ester, and acrylic. (See Table I for typical physical properties of polymer concretes.)

The advantages to be derived from polymer-modified Portland cement concrete when compared with Portland cement concrete are:

1. Permits placement of concrete in thinner cross-sections.
2. Excellent bonding to existing concrete substrates.
3. Increased impact resistance.
4. Reduced porosity.
5. Faster set and cure.
6. Improved resistance to salt. It does not improve resistance to chemicals.

Polymer modifiers are generally based on various resins and latexes, such as natural rubber, styrene-butadiene, acrylic, polyvinyl acetate, epoxy, and urethane.

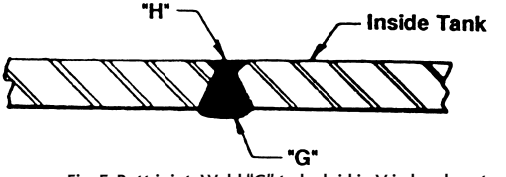


Fig. 5. Butt joint. Weld "G" to be laid in V in beads not exceeding -in. deep. After "G" is built up above plate on outside, the inner surface must be gouged out sufficiently to remove all scale and slag. Weld "H" is to be built up above the surface of plate, peened and ground flush.

LININGS

There are a host of lining

Table I. Typical Physical Properties of Polymer Concretes

Property	*Test Method*	*Typical Value*
Tensile strength, psi (MPa)	ASTM C 307	1,000-2,000 (7-14)
Compressive strength, psi (MPa)	ASTM C 039	10,000-12,000 (70-82)
Flexural strength, psi (MPa)	ASTM C 580	2,000-4,000 (14-28)
Linear shrinkage, %	ASTM C 531	< 0.1
Density, lb/ft3	ASTM D 792	130-145 (2.1-2.3)
Water absorption, %	ASTM C 413	< 0.1
Maximum use temperature, °F(°C)		
Continuous	—	150 (66)
Intermittent	—	200 (93)
Thickness, in. (mm)	—	0.5 (13)

The chemical resistance of polymer concretes is similar to their synthetic resin lining system counterparts as indicated in Table VII.

materials available for protecting concrete and steel. The three basic types are glass-fiber-reinforced sheet and molten asphaltics; sheet rubber, plastics, and elastomers; and reinforced and nonreinforced ambient-cured synthetic resin systems.

Conspicuous by its absence from this list is protective coatings. This is not to say they can't be used; however, 60 mils is usually considered to be a minimum acceptable thickness for a material to be considered a tank lining. If a coating can be economically applied (initial cost and longevity) to a minimum thickness of 60 mils, free of pinholes and holidays, and can resist the process chemicals and temperatures as well as physical abuse, consideration should be given to their use. Generally speaking, coatings are used for fume and splash protection and not necessarily for total immersion process applications.

Asphaltic linings are equally appropriate for application to concrete and steel. The hot-applied, molten materials, as well as sheet stock can be used on concrete tanks. For steel tanks, glass-fiber-reinforced sheet is the most desirable. Both types of asphaltic linings, sheet and molten, are seldom, if ever, used without being further protected with a chemical-resistant brick lining. Without further protection from a brick sheathing, these linings can cold flow and be easily damaged from impact, abrasion, and thermal excursions. Masonry sheathings provide a rugged, chemical-resistant insulating barrier for protection of asphaltic as well as other types of linings. The physical properties and the chemical resistance of asphaltic linings are shown in Tables II and III, respectively.

Adhesive-bonded sheet linings, such as various plasticized plastics, rubbers and elastomers are most commonly used for steel tanks. Successful applications have been made on concrete; however, it is not the most desirable substrate on which to bond and cure many of these systems. The physical properties and the chemical resistance of sheet linings are shown in Tables IV and V, respectively.

Mechanically bonded rigid plastic linings for precast and poured-in-place concrete tanks are a relatively new concept. Instead of bonding with adhesives, this system utilizes anchor studs sonically welded to the back of the sheet for locking or mechanically bonding the sheet to the concrete.

Ambient temperature-cured, spray- and trowel-applied synthetic resin lining systems are based on the following resins: furan, epoxy, polyester, vinyl ester, and urethane.

These systems are entirely appropriate for application to steel and concrete. They have also been successfully applied to wood, certain plastics, and various

Table II. Physical Properties of Asphaltic Linings

	Value	
Property	*Type A*	*Type B*
Softening point, °F (°C)	200-225 (93-107)	250-275 (121-135)
Ash, max., %	0.5	0.5
Penetration		
77°F (25°C), 100 g—5sec.	38	18
115°F (46°C), 50 g—5sec.	75	27
Chemical resistance	Very good	Very good

metallic substrates. These lining systems utilize such filler reinforcements as flake glass and mica. Fabric reinforcements such as fiberglass are the most common; however, synthetic fabrics are used where fluorides are present.

These linings are extremely versatile and can be applied by maintenance personnel with skills in the painting and masonry trades. Most manufacturers of these lining systems provide training programs for plant maintenance personnel. The physical properties and the chemical resistance of ambient-cured synthetic resin lining systems are shown in Tables VI and VII, respectively.

The tables shown above all provide the design and corrosion engineer with basic information on the various lining systems discussed. They identify specific corrosives encountered in various metal-finishing operations. Enumerated are each of the various types of linings and a general recommendation for its use in the par-

Table III. Chemical Resistance of Asphaltic Linings

Medium	*Type A*	*Type B*
Aluminum salts	R	R
Cadmium salts	R	R
Chromic acid, to 10%	R	R
Copper salts	R	R
Gold cyanide	R	R
Hydrochloric acid	R	R
Hydrofluoric acid	C	C
Iron salts	R	R
Magnesium salts	R	R
Nickel salts	R	R
Nitric acid, to 20%	C	C
Perchloric acid	NR	NR
Phosphoric acid	R	R
Sodium chloride	R	R
Sodium cyanide	R	R
Sodium hydroxide, to 30%	R	R
Sodium salts	R	R
Sulfuric acid, to 50%	R	R
Trichloroethylene	NR	NR
Trisodium phosphate	C	C
Zinc salts	R	R

C, conditional; R, recommended; NR, not recommended.

Table IV. Physical Properties of Sheet Linings

	Temperature Resistance	
Type	*Max., °F (°C)*	*Chemical Resistance*
Natural rubber		
Soft	150 (66)	Very good
Semihard	180 (82)	Very good
Hard	180 (82)	Very good
Neoprene	180 (82)	Very good
Butyl rubber	185 (85)	Very good
Chlorobutyl rubber	185 (85)	Very good
Polyvinyl chloridE		
Plasticized	150 (66)	Excellent
Plasticized rigid (2 ply)	150 (66)	Excellent
Chlorosulfonated polyethylene	275 (135)	Very good
Fluorocarbons	450 (232)	Excellent

ticular medium. It is recommended that the acceptability of specific linings, in specific media, be verified with the manufacturer.

Chemical-Resistant Brick and Tile Linings

Historically, chemical-resistant brick and tile linings go back approximately 100 years, paralleling the development of sulfuric acid, various dyestuffs, and explosives.

The use of masonry construction has grown in the basic steel, metal-working, and metal-finishing industries. Chemical-resistant masonry sheathings are not to be con-

Table V. Chemical Resistance of Sheet Linings

Medium	*1*[a]	*2*	*3*	*4*	*5*	*6*
Aluminum salts	R	R	R	R	R	R
Cadmium salts	R	R	R	R	R	R
Chromic acid, to 10%	NR	NR	NR	R	R	R
Copper salts	R	R	R	R	R	R
Gold cyanide	R	R	R	R	R	R
Hydrochloric acid	R	NR	R	R	R	R
Hydrofluoric acid	R	NR	R	R	NR	R
Iron salts	R	R	R	R	R	R
Magnesium salts	R	R	R	R	R	R
Nickel salts	R	R	R	R	R	R
Nitric acid, to 20%	NR	NR	R	R	C	R
Perchloric acid	NR	NR	NR	C	NR	R
Phosphoric acid	R	R	R	R	R	R
Sodium chloride	R	R	R	R	R	R
Sodium cyanide	R	R	R	R	R	R
Sodium hydroxide, to 30%	R	R	R	R	R	R
Sodium salts	R	R	R	R	R	R
Sulfuric acid, to 20%	R	R	R	R	R	R
Trichloroethylene	NR	NR	NR	NR	NR	R
Trisodium phosphate	R	R	R	R	R	R
Zinc salts	R	R	R	R	R	R

R, recommended; C, conditional; NR, not recommended.
[a]1 = natural rubber—all grades; 2 = Neoprene; 3 = Butyl and chlorobutyl; 4 = polyvinyl chloride; 5 = chlorosulfonated polyethylene; 6 = fluorocarbons.

Table VI. Physical Properties of Ambient-Cured Synthetic Lining Resin Systems

	Temperature Resistance[a]	
Type	Max., °F (°C)	Chemical Resistance
Furan	125 (52)	Excellent
Epoxy	160 (71)	Very good
Polyester	180 (82)	Very good
Vinyl ester	160 (71)	Very good
Urethane	150 (65)	Good

[a]Suggested limit without a masonry sheathing.

strued as hydrostatically tight tank linings. They are, in fact, porous, and consequently must be considered as chemical, physical, and thermal barriers for protecting membranes installed behind these sheathings. Brick sheathings contribute to the longevity of tank linings by offering additional chemical, thermal, and physical protection. They are excellent insulating barriers and, consequently, can be considered as energy savers.

PLASTIC TANKS AND LININGS

There are a multitude of plastics available for solving corrosion problems in the metal-finishing industry. The more popular and cost effective are polyvinyl chloride (PVC), Type I; polypropylene (PP); linear polyethylene (PE); and fiberglass-reinforced plastics (FRP).

Table VII. Chemical Resistance of Ambient-Cured Synthetic Resin Lining Systems

Medium	1[a]	2	3	4	5
Aluminum salts	R	R	R	R	R
Cadmium salts	R	R	R	R	R
Chromic acids, to 10%	NR	NR	R	R	C
Copper salts	R	R	R	R	R
Gold cyanide	R	R	R	R	R
Hydrochloric acid	R	R	R	R	R
Hydrofluoric acid	Rb	R	R	R	C
Iron salts	R	R	R	R	R
Magnesium salts	R	R	R	R	R
Nickel salts	R	R	R	R	R
Nitric acid, to 20%	NR	NR	R	R	R
Perchloric acid	NR	NR	C	NR	NR
Phosphoric acid	R	R	R	R	R
Sodium chloride	R	R	R	R	R
Sodium cyanide	R	R	R	R	R
Sodium hydroxide, to 30%	R	R	Bis A Type	R	R
Sodium salts	R	R	R	R	R
Sulfuric acid, to 50%	R	C	R	R	R
Trichloroethylene	R	NR	C	NR	NR
Trisodium phosphate	R	R	Bis A Type	R	R
Zinc salts	R	R	R	R	R

R, recommended; C, conditional; NR, not recommended.
[a]1 = furan; 2 = epoxy; 3 = polyester; 4 = vinyl ester; 5 = urethane.
[b]Carbon filled materials and/or final application with synthetic fabrics.

Table VIII. Chemical Resistance of Structural Plastics

Medium	*Polyvinyl Chloride*	*Polyethylene*	*Polypropylene*
Aluminum salts	R	R	R
Cadmium salts	R	R	R
Chromic acid, to 10%	R	R	R
Copper salts	R	R	R
Gold cyanide	R	R	R
Hydrochloric acid	R	R	R
Hydrofluoric acid	R	R	R
Iron salts	R	R	R
Magnesium salts	R	R	R
Nickel salts	R	R	R
Nitric acid, to 20%	R	R	R
Perchloric acid	R	C	C
Phosphoric acid	R	R	R
Sodium chloride	R	R	R
Sodium cyanide	R	R	R
Sodium hydroxide, to 30%	R	R	R
Sodium salts	R	R	R
Sulfuric acid, to 50%	R	R	R
Trichloroethylene	NR	NR	NR
Trisodium phosphate	R	R	R
Zinc salts	R	R	R

C, conditional; R, recommended; NR, not recommended.

All of these plastics have been successfully used as self-supporting tanks and "drop-in" tank liners for process and storage applications. The thermoplastics (PVC, PP, and PE) are being used for mechanical bonding to concrete for similar applications.

Polyvinyl chloride is one of the oldest proven plastics for fabricating highly chemical-resistant structures. (See Table VIII for the chemical resistance of structural plastics.) Type I PVC is one of the best plastics available for resistance to a multitude of strong oxidizing environments up to its thermal limitation of approximately 150°F (66°C).

Type I PVC has outstanding structural integrity attributable to its high tensile, compressive, and flexural properties. It is one of the easiest plastics from which to construct tanks, tank liners, dipping baskets,

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and other storage and process equipment. PVC is easily thermoformed, cut, drilled, tapped, machined, and welded, consequently, making it an excellent, versatile, and cost-effective material from which to fabricate corrosion-resistant equipment.

Polypropylene has arrived. Its popularity is attributable to its excellent chemical resistance and surpasses PVC because of its superior physical and thermal resistance. It is available as flame and nonflame retardant homopolymer and copolymer sheet stock. Polypropylene utilizes fabricating techniques similar to those used for PVC. Small tanks for pickling and plating, large tanks for continuous strip pickling lines, and pickling line covers have been fabricated of polypropylene. These and similar fabrications are enjoying an enviable record of success in challenging chemical and physical applications.

Linear polyethylene fabrications have performed well in the small-parts metal-finishing industry because of their low absorption, high chemical resistance, and outstanding resistance to impact. They do not possess the rigidity and flexural capabilities of PVC or PP and, consequently, the fabrications are significantly smaller. A new generation of PE is making significant inroads into the finishing industry. Crosslinkable, high-density PE for rotational molding is being used for tanks of 5-10,000-gal capacity. These new resins exhibit excellent physical properties and good resistance to weathering. Applications for the most part have been indoor and outdoor storage tanks and portable receiver tanks.

Fiberglass-reinforced plastics have been successfully used for a multitude of applications for many years. The earliest fabrications utilized furan and phenolic resin binder systems. The more popular resin binder systems in use today are polyester, epoxy, and vinyl ester.

The success of FRP structures is substantially predicated on the proper choice of resin and hardener system most inert to the environment to which the fabrication will be subjected. It is not enough to request an FRP tank, any more than it is to request a flake-glass-reinforced polyester tank. It is important to either provide the fabricator with all chemical, thermal, and physical information pertinent to the process in order that the proper resin and hardener system might be selected, or to have in-house technical competency capable of making the proper selection of the resin-hardener system from which the manufacturer can fabricate the desired equipment.

There are numerous polyester resins available; however, for aggressive corrosion environments, such as high concentrations of alkalies and a broad range of acids, the bisphenol-A fumarate resin is the best recommendation.

Vinyl esters are epoxy-resin-based, thermosetting resins that provide chemical resistance similar to that of bisphenol A polyesters. They are considered to be slightly better in high concentrations of alkaline hypochlorites than the bisphenol A polyester. Vinyl esters exhibit outstanding physical properties, i.e., tensile, flexural, and elongation that are normally associated with epoxies.

The chemical resistance and physical properties of epoxy resins are functions of the resins, but equally important, they are very much functions of the curing systems employed.

Aliphatic and aromatic amine curing systems impart better chemical resistance to epoxy resins than do polyamide curing agents. Polyamides, however, impart better impact resistance to epoxies than do aliphatic or aromatic curing systems.

The intention of these three examples of the resin systems utilized for constructing fiberglass-reinforced tanks and tank linings is to point out the neces-

sity of knowing the chemistry of the system, or relying on reputable manufacturers to provide the technology required to make the best selection to fulfill end use requirements.

Where the chemistry of these various systems contributes substantially to the physical properties of the structure, the most profound influence on physical properties is derived from the proper design and use of various reinforcing mediums, i.e., glass fibers, glass cloth, roving, mat, veil, etc. Consult reputable manufacturers for proper design consistent with the end-use mandates for chemical, thermal, and physical properties.

The chemical resistance of FRP is comparable to the chemical resistance data shown in Table VII. Table VIII summarizes the chemical resistance of PVC, PE, and PP.

The mechanically bonded thermoplastic lining system previously described circumvents many of the limitations inherent in some plastics, as well as coating, and many other elastomeric and resin lining systems. The sonically welded anchor studs are of the same plastic as the sheet and are placed at approximately 2-3 in. on centers. Sheet thickness and anchor stud density provide the rigidity necessary for a successful thermoplastic lining application. The studs, being of the same plastic as the sheet, ensure thermal and physical property similarity. The lining system is equally appropriate for new and existing concrete, as well as for salvaging used steel tanks. Upon removal of the concrete forms and the welding of all joints, utilizing thermoplastic welding techniques, spark testing is used for quality assurance of the lining.

The system is available in a single- or double-wall system to ensure compliance with the most rigid of environmental mandates. Leak detection systems are available and are integral with the lining system.

SELECTING CARTRIDGE FILTERS FOR POWDER COATING OPERATIONS

BY JOHN WALZ, CHEMCO MANUFACTURING CO., NORTHBROOK, ILL.

As air emission standards have become more and more stringent over the last 20 years, the trend toward powder coating—which typically eliminates the VOCs and hazardous waste generated by more traditional painting methods—continues to grow as we move forward into the 21st century. Contributing greatly to this growth was the early 1980's advent of the cartridge filter recovery system, which enabled metal finishers to utilize as much as 99% of the powder paint purchased. This advancement in powder recovery technology dramatically enhanced powder coating productivity and allowed finishers to realize significant cost savings by switching from liquid to powder.

Today, the cartridge filter collector is the most popular type of powder separation and recovery system in the marketplace. The focus of this article will be on the most critical aspect of this system—the cartridge filter. We will discuss the range of products available, the effect different conditions and circumstances can have on filter performance, and what types of cartridges should be selected for these various situations. In doing so, we hope to show why cartridge filters used in powder coating equipment should be viewed as something more than just a commodity.

Cartridge filter replacement can be one of the larger operating expenses in a powder booth system. So to adopt an "I'll buy what came with the system" mentality, or to choose a filter solely based on price, can be a costly mistake. Buying the lowest priced option can actually be more expensive in the long run, since there are usually some undesirable reasons why it is the cheapest item. While the service life and price of the filter determine the cartridge replacement cost, improved filter performance (i.e., higher efficiency, lower pressure drop, reduced downtime for maintenance, better quality reclaim, etc.) can have an even larger impact on the total cost of operating a powder system. Consistent airflow, for instance, is a critical factor necessary for efficient booth operation. Air velocity through the application booth should be between 100–120 fpm to ensure good transfer efficiency and to contain the powder overspray from drifting outside the booth. Selecting the wrong cartridge filter is one way to compromise consistent air flow through a system.



Figure 1: Various types of cartridge filters.

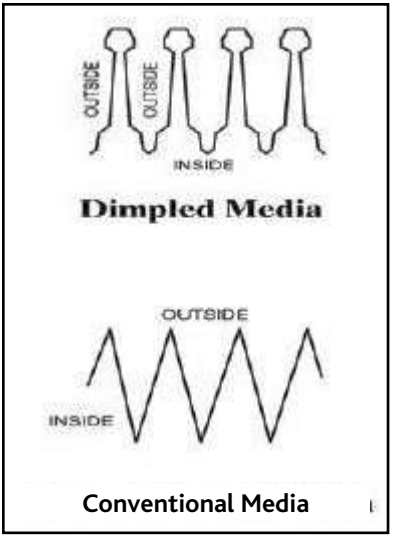


Figure 2: Comparing cartridge filters without airflow.

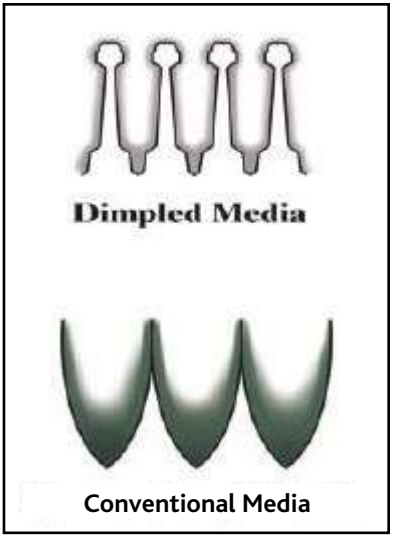


Figure 3: Comparing cartridge filters with airflow and loaded with powder.

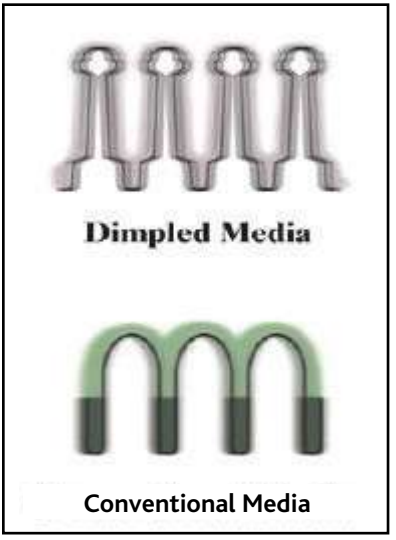


Figure 4: Comparing cartridge filters during pulsing.

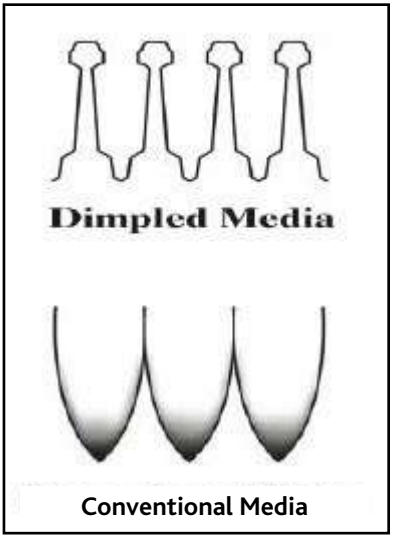


Figure 5: Comparing cartridge filters immediately after pulsing.

There are a wide range of powder cartridge filter products available today—different media, various treatments, as well as customized manufacturing technologies (i.e., special gasketing, variation in pleat count, design, depth and spacing, etc.). To ensure optimum performance and value, one must consider the design capabilities and limitations of the filter, in addition to the application factors that might have an impact on a filter's performance.

There are three media styles typically used in powder cartridges: cellulose, spun bond polyester and expanded polytetraflouroethylene (ePTFE) membrane; 100% cellulose and 80/20 blend (80% cellulose – 20% polyester) are "depth-loading" media constructed with tightly packed pleats and an outer wire mesh screen for support. This is the least expensive media style available, offers only moderate efficiency, and is best suited for low- to mid-volume, spray-to- waste powder operations. Pulse cleaning cellulose cartridges can be difficult at times because the powder has a tendency to become trapped between the pleats, resulting in very high powder retention within the filter (20–45 lbs.) and more rapid pressure drop. Cellulose-style cartridges would not be appropriate for high-moisture conditions or high-volume reclaim operations, as they tend to plug up much quicker.

One-hundred percent spun bond polyester is a continuous strand, "surface-loading" media that is tougher and slicker than cellulose and does not require outer screen support to maintain pleat rigidity and strength. Spun bond polyester cartridges also require 50–70% less surface area than cellulose filters to handle a given air volume. This allows for a wider pleat spacing and fuller utilization of filter media, and together with the higher efficiency that polyester provides, results in the following benefits in relation to cellulose:

- **Lower pressure drop and longer service life**
- **Higher recovery rate of reclaim powder**
- **Less powder retention within cartridge (80–90% less)**
- **Less compressed air needed to pulse clean filters (40–60psi)**
- **Less downstream contamination of system and plant air**
- **No linting contamination of reclaimed powder or paint finish**
  Better resistance to aggressive and abrasive powder (i.e., frit or porcelain)
- **Superior moisture resistance**
- **Ability to wash and reuse filters**

Spunbond polyester media also offers several specialty treatments and membrane selections to enhance filter performance in more challenging conditions:

Aluminized polyester (anti-static). This treatment coats the face of the media with a thin layer of aluminum, which dissipates the electrical charge of the filtered powder. This makes it an ideal filter for effective pulse cleaning when static electricity buildup is a concern.

Hydro-oleophobic polyester (moisture-resistant). This type of cartridge is treated with a fluorocarbon or teflon bath that provides an oil and water repel-

lant to both sides of the media to ensure effective pulse cleaning ability in both humid and oily conditions.

ePTFE laminated polyester (membrane). Another type of spunbound polyester, this consists of a thin membrane of expanded PTFE laminated over a polyester substrate that results in a slick and microporous surface providing 100% efficiency at 1 micron and above. Expanded PTFE membrane cartridges offer the highest efficiency and best powder release properties of any media choice in the powder cartridge market, making it the ideal filter choice for users needing to maximize the amount & quality of their reclaimed powder. PTFE cartridges also do not require seasoning, and are an effective filter option when ultra-fines or high-moisture conditions exist.

Another new technology, which is available only on spunbond polyester and treated polyester cartridges, is the "dual dimple" pleat design, which imparts opposing dimples along the entire length of each individual pleat. This dimpling technology significantly optimizes the efficiency of pulse cleaning and the capacity of the filter by preventing the pleats from pinching together regardless of the conditions or dust load. (See Figures 2 through 5.)

Once product options are reviewed, consideration must be given to the conditions or circumstances that make a given operation unique, since they, too, can affect the performance of cartridge filters.

Possibly the biggest factor in cartridge filter selection is whether an operation is reclaiming its powder or spraying to waste. One of the biggest advantages of switching from liquid to powder is the ability to reclaim and reuse the powder once it is sprayed. This benefit is lost, however, when using cellulose cartridges since they typically retain between 20–45 lbs. of powder over its useful life that cannot be extracted or reused. Polyester cartridges, on the other hand, only retain 4–8 lbs. of powder over the life of the filter, while ePTFE membrane filters retain only 1–2 lbs! (By simply multiplying the dollar cost per pound of powder by the weight gain in each cartridge, one can estimate the potential cost savings to be realized by using polyester or membrane cartridges.)

Another primary concern for powder reclaim systems is reclaim powder contamination and "linting," which is the breaking off of fibers from cellulose-style cartridges during pulse cleaning. Lint and other sources of dirt that enter the booth air stream will not only contaminate the reclaim powder, but can also bounce back onto the parts being sprayed, causing rejects. Companies typically upgrade to spunbond polyester or membrane-style cartridges to eliminate contamination or linting issues.

Some of the other key factors that should influence decision-makers to select polyester and membrane filters over cellulose style include:

- **Humidity or oil/moisture in compressed air**
  "Fines" or small micron size powder (1-3 micron) common in reclaim systems and combination cyclone/cartridge collectors
- **Aggressive or abrasive powders, such as frit or porcelain**
- **Heated powder, which tends to stick to filter media (i.e., pyrolytic powder)**
- **Polyester powder, which tends to retain electrostatic charge more than other powder types**

- **Wasted powder during cartridge seasoning process**
- **Excessive noise from having to pulse clean cellulose cartridges at 80-90 PSI**

CONCLUSION

Choosing the most suitable cartridge filter for your powder coating system need not be a confusing or time-consuming task. We have tried to show why this process should not be a simple search for the lowest price or quickest delivery, but rather viewed as an opportunity to reduce operational costs and substantially improve the efficiency of the powder application system. By analyzing the facts, it is clear that choosing the better quality filter will guarantee increased productivity and your peace of mind.

BIO

John Walz is the manager of the powder coating and dust collection division at Chemco Manufacturing Co. in Northbrook, Ill., a major filter manufacturer in the finishing and dust collection industries. For more information on the new "dual dimple" polyester powder cartridges, call (800) 323-0431, ext 199.

PRETREATMENT SYSTEM DESIGN FOR OPTIMUM END-USE PERFORMANCE

CINCINNATI INDUSTRIAL MACHINERY, DIV. OF EAGLE PICHER, CINCINNATI

A finishing system may have many possible arrangements, but only one is best suited to the user's plant conditions and needs. Only after working closely with the user and suppliers are you able to determine the system best suited to your requirements.

Finishing systems are comprised of washers, dry-off ovens, incinerators, pretreatment, electrocoating, spray booths, flowcoaters, dip tanks, cure ovens, conveyors, waste treatment, and air makeup. A complete paint finishing system consists of an integrally designed combination of equipment (or single compact machine) that conveys parts through the cleaning, pretreatment, paint application, and baking steps to deliver a finished part — often without labor between loading and unloading. Systems can include makeup air equipment to replace exhausted air, loading and unloading devices, and other related equipment. A typical schematic is pictured in Fig.1.

DEFINING PARAMETERS

Pretreatment can be accomplished in many different ways involving several technologies (see Table I). The optimum design for a family of parts evolves from understanding the following parameters and applying them with consistent design integrity: (1) quantity and configuration of parts; (2) material composition of parts; (3) desired material handling methods; (4) understanding soils and cleanliness desired; (5) facilities and utilities available; and (6) environmental considerations.

Each of these parameters will influence the design of the system. Early involvement of competent representatives from chemical suppliers, equipment manufacturing companies, and paint companies will improve the design phase and enhance your objective. Once the parameters have been defined the design can begin.

Quantity and Configuration of Parts

The production rate obviously determines the level of automation, capacity of the equipment, energy consumption, chemical usage, etc. Selection for today's requirements may be inadequate for tomorrow's needs and sizing the system too large can waste money. Long-term planning will help determine production rate, future designs, and available financial resources.

The proper analysis is essential. List all parts, their sizes, and annual production rate that you plan to process with the system. This will give you the yearly production requirements. Then, based on one, two, or three shifts, determine production time available. When comparing production requirements with production time available you can establish rate in feet per minute.

The smallest, the largest, and the average part size must be defined in terms of dimensions. This allows equipment manufacturers to size the openings for washers (to minimize overspray), determine optimum drain length (minimize solution carryover), and size heaters, pumps, and fans.

The overall weight of the part or batch of parts being conveyed must be known to calculate heat loss through the washer and ovens.

Unusual shapes must be identified for early consideration. For example small, blind holes on surfaces could negate the power wash approach, whereas large, open or flat surfaces that can drain are ideal. Small parts that can withstand tum-

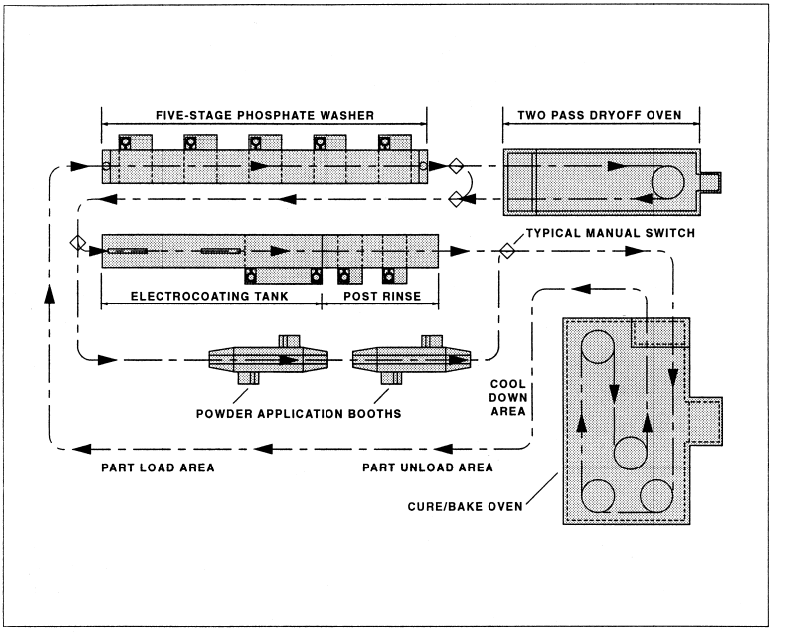


Figure 1. Schematic for finishing system with four-stage washer and choice of electrocoating or powder application.

Table I. Comparison of Iron, Zinc, and Manganese Phosphating

Phosphating Material	*Benefits*	*Drawbacks*	*Typical Applications*
Iron	Lowest chemical costs, lowest equipment investment, good paint adhesion, easiest to control, gives higher gloss with less paint, can be applied in thinner coatings, minimum sludge formation, lowest heating requirements, adequate corrosion protection for most indoor and some outdoor applications.	Not as corrosion resistant as zinc phosphating, shorter chemical life.	Metal cabinets, furniture, electrical and electronic enclosures, and toys and other novelties.
Zinc	Excellent paint adhesion, excellent corrosion resistance in all environments, better chemical life than three-stage iron, moderate heating requirements.	Higher chemical costs than iron, more sludge formation, higher maintenance costs than iron, more difficult to control than iron.	Water heaters, refrigerators, air conditioners, outdoor furniture, washing machine parts.
Manganese	Heaviest coatings, good tank life, excellent rust preventive, best for retention of oils and drawing compounds.	Not used as a paint base, higher temperature requirements, greatest sludge formation.	Heavy gears, engine parts, parts to be deep drawn.

bling can be ideal for a drum washer; baskets of parts that cannot be tumbled can be immersed and agitated. The same situation is true with paint application. Smooth, flat parts can be easily automated, while complex shapes may require additional, manual reinforcement for complete coverage.

Material Composition of Parts

Knowing the base materials will allow compatibility with selected cleaners, subsequent waste treatment requirements, operating temperature, method of handling, and process specifications.

Desired Material Handling Methods

Selecting the appropriate material handling method should be done based on the principles of increasing productivity. The method selected must incorporate reliability, economy, flexibility, and ease of installation. For example an overhead monorail-type conveyor system is relatively low in cost but not very flexible, while a power-and-free system is very flexible but higher in cost.

Understanding Soils and Cleanliness

Contaminants determine chemical selection and spray or immersion selection, and ancillary equipment for handling the effluent (chips, oil, or heavy metals) will impact the waste treatment stream. If the cleaning process is not defined it is important to get contaminated parts to the chemical and equipment suppliers and have the parts tested in a laboratory. While in the laboratory your suppliers can simulate conditions and test the different variables.

Minimizing or avoiding contamination is the key to keeping your factory and parts clean. Know where your soils are coming from and why. This allows you to take steps to contain soils in the area where they occur.

Effective and inexpensive means to check for clean parts are the "water-break-free surface test" and "white towel test." If organic soil has been effectively removed a uniform sheeting of the rinsewater will occur as parts exit the last pretreatment stage. If the surface has beaded water standing you have not adequately removed organic soils. Inorganic soils can be checked by using a white towel after they have passed through the dry-off oven. If the towel is dirty you have not adequately removed the inorganic soils.

More sophisticated is the millipore test. This test requires a vacuum pump, flask, funnel, filter papers, isopropyl alcohol, oven, and scale. This test can detect micron particle size and weight in milligrams.

Facilities and Utilities Available

A floor layout with height clearance is important for design considerations. Often, space constraints dictate process times. Although it may not be the optimum process it may achieve acceptable results.

Availability of electrical service, heating preference, and plant conditions (such as availability of truck dock, building door size,floor and roof construction, distance from unloading site to erection site, and whether there is a clear path) must also be considered.

Environmental Considerations

Local, regional, and federal regulations are continually being added and changed. The recent Clean Air Act Amendments of 1990 established procedures for a national permit system for air pollutante missions, as well as establishing a basis for more stringent controls on emissions from all manufacturing operations. Waste stream com-

pliance is forcing many manufacturing companies to invest in waste treatment plants. Understanding your local laws and knowing your process will determine your direction. If you are not familiar with either, outside help must be sought.

COMPONENT DESIGN

Material Handling

Selection of the material handling method varies directly with production volume and desired cleanliness. In general the monorail is the most economical, flexible, and reliable method of handling product,but it is not the ideal solution for all cases.

If you handle product in batches/baskets a belt internal to the machine can provide an excellent and consistent means of transporting product through the washer. If your product can tolerate "bumping," such as nuts or bolts, a drum machine is a cost-effective means of conveying high volumes with excellent results.

There are also situations where combinations of belt and monorail are appropriate. Rather than having two machines you can easily assimilate dual lines into one washer.

Conveyor systems are discussed in further detail in a separate section of this Guidebook. System size is a function of conveyor speed, which is actually based on part density rather than raw production rate. As an example, to determine the line speed for a given production shift divide the number of parts desired by the number of parts per rack times the rack spacing divided by the number of minutes available per shift.

Washers/Pretreatment

The choice of a spray wand, three-stage, or five-stage machine is based on a number of variables: incoming soil loads, space available, results required, energy consumption, total initial cost, estimated total operating cost, production volume, size of part, etc. The initial cost of a five-stage machine (clean, rinse, phosphate, rinse, rinse) is somewhat higher than a three-stage type but operating economies and higher quality quickly offset the investment. The five-stage machine ensures longer chemical life.

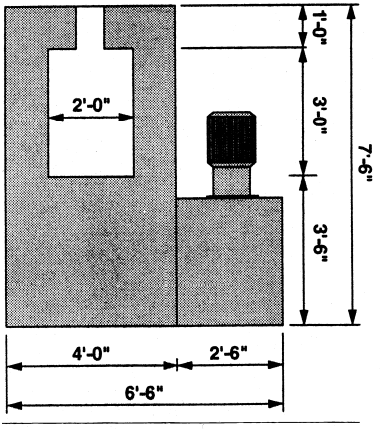


Figure 2. Entrance profile for sample monorail conveyor washer design.

The high-pressure heated spray wand is an excellent choice for low-volume, hard-to-handle parts. This approach is a cost-effective technology with a great deal of flexibility and versatility.

From experience and the recommendation of various chemical companies, to remove shop dirt and light machine oil a three-stage machine is adequate. The typical process would be a one-minute wash stage (heated), 30-second rinse (ambient), and a 30-second rinse/inhibit (ambient or heated).

If you have a more critical cleaning specification or phosphating requirement a five-stage washer with one-minute wash (heated),30-second rinse (ambient), one-minute phosphate (heated), 30-second rinse (ambient),

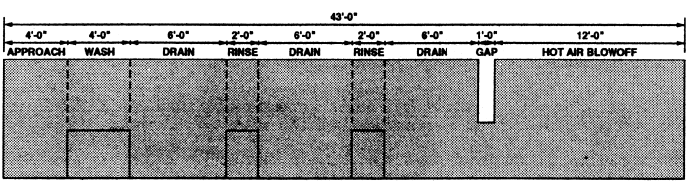


Fig. 3. Machine length for sample design of three-stage washer and dryer.

and 30-second rinse/inhibit (ambient) will be required

Spray versus Immersion

In general, spray processing provides the most effective cleaning and rinsing capabilities owing to increased mechanical action, liquid impingement, and natural draining; however, for impingement of recessed or hidden surfaces of complex parts and assemblies, immersion processing is more appropriate. The addition of ultrasonics or agitation can enhance the impingement capability, but it is costly. When processing complex parts or heavily loaded baskets of parts a combination of immersion and spray stages is often required. Testing dirty parts in a laboratory will provide proper selection.

Sample Three-Stage Washer

The first step in the design is to lay out the system (using a conveyor speed of 4 fpm and a largest part size of 2½ ft x 18 in. x 18 in.). The entrance profile should include a 3-in. clearance around the part. This will provide flexibility to process larger parts if required (see Fig. 2).

A housing space of 1 ft on each side of tunnel openings allows for spray risers and piping. The cleanout section can be 2 to 2½; 3½ ft from the floor to the bottom of the tunnel opening will provide enough space to have the tank capacity to keep the pump-to-tank ratio around 3:1. The overall height of the machine is 7½ft, but we need to allow another 3 ft minimum for ventilating ductwork.

The machine length for a three-stage washer, allowing three minutes of drying, is shown in Fig. 3. You know that one minute in the wash stage is required and that the conveyor is traveling at 4 fpm, so you can size the wash stage at 4 ft. Similarly, rinse stages are 30 seconds; thus, they are each sized at 2 ft in length.

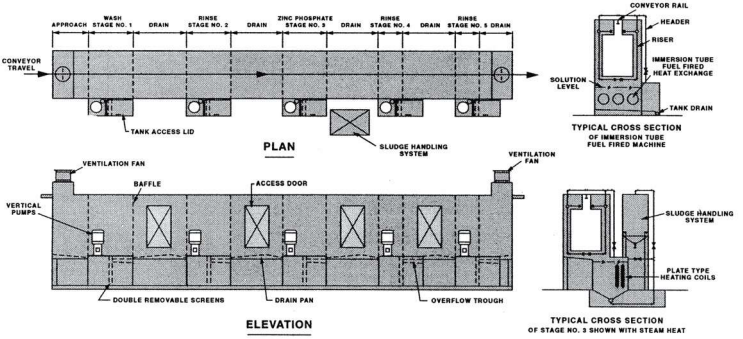


Fig. 4. Five-stage monorail-type zinc phosphating machine (see Table I for details).

Table II. Typical Monorail-Type Construction for Five-Stage Iron, Zinc, or Manganese Phosphate Washer

	Stage No. 1 *Wash*	*Stage No. 2* *Rinse*	*Stage No. 3* *Phosphate*	*Stage No. 4* *Rinse*	*Stage No. 5* *Acidified Rinse*
Design temperature	145°F	Room	160°F	Room	145°F to assist drying
Time cycle (seconds)	60	30	60	30	30
Type nozzle	VeeJet	VeeJet	Whirl-Jet	VeeJet	VeeJet
Nozzle pressure (psi)	15	15	10	10	10
Materials for construction:					
Tank	1/4-in. mild steel	1/4-in. mild steel	11-gauge stainless steel or mild steel	1/4-in. mild steel	1/4-in. mild steel
Housing	1/8-in. mild steel	1/8-in. mild steel	14-gauge stainless steel or 3/16 mild steel	1/8-in. mild steel	1/8-in. mild steel
Nozzles	Mild or stainless steel	Mild or stainless steel	Stainless steel	Mild or stainless steel	Mild or stainless steel
Piping	Steel	Steel	Stainless steel or extra heavy steel	Steel	Steel
Pump	Standard cast iron	Standard cast iron	Stainless steel	Standard cast iron	Standard cast iron
Immersed heating equipment	Mild steel	Mild steel	Stainless steel or extra heavy steel		Mild steel
Settling tank			Mild steel		

Considering both energy and pollution problems, new processes allow lower processing temperatures in some cases.

Table III. Typical Belt-Type Construction for Five-Stage Iron Phosphate Machine

	Stage No. 1 *Wash*	*Stage No. 2* *Rinse*	*Stage No. 3* *Phosphate*	*Stage No. 4* *Rinse*	*Stage No. 5* *Acidified Rinse*
Design temperature	145°F	Room	160°F	Room	145°F to assist drying
Time cycle (seconds)	60	30	60	30	30
Type nozzle	VeeJet	VeeJet	Whirl-Jet	VeeJet	VeeJet
Nozzle pressure (psi)	15	15	10	10	10
Materials for construction:					
Tank	1/4-in. mild steel	1/4-in. mild steel	1/4-in. mild steel	1/4-in. mild steel	1/4-in. mild steel
Housing	1/8-in. mild steel	1/8-in. mild steel	1/8-in. mild steel	1/8-in. mild steel	1/8-in. mild steel
Nozzles	Mild or stainless steel	Mild or stainless steel	Mild or stainless steel	Mild or stainless steel	Mild or stainless steel
Piping	Steel	Steel	Steel	Steel	Steel
Pump	Iron	Iron	Iron	Iron	Iron
Immersed heating equipment	Mild steel	Mild steel	Mild steel	Mild steel	Mild steel

Considering both energy and pollution problems, new processes allow lower processing temperatures in some cases.

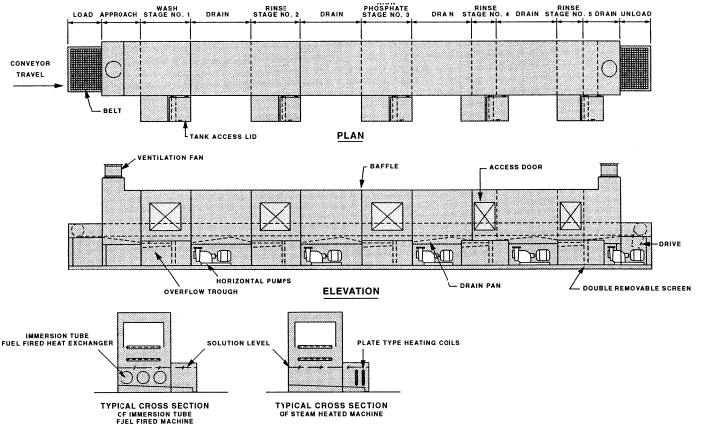


Fig. 5. Five-stage belt-type iron phosphating machine (see Table III for details).

Good design practice dictates that the approaches and exits should be two times the tunnel width; therefore, they should be 4 ft long. The drains should be three times the tunnel width, minimizing spraying and carryover contamination; therefore, they are 6 ft in length. Special consideration for drain lengths may be necessary for long parts or slow line speeds.

The hot air blow-off will require three minutes of drying time, so size that at 12 ft. You also must have 1 ft between washer and hot air blow-off fan for ventilating.

ENVIRONMENTAL CONCERNS

Most washer systems require waste treatment of the effluent from the system prior to disposal to the sewer. In some cases, where the potential discharge of cleaners and phosphates to the sewer are significant, a self-contained treatment system is required. Most municipal waste treatment authorities have a list of chemicals they can accept and in what concentrations. Check with the local authorities for additional information, or consultants are available to assist in your decision-making process.

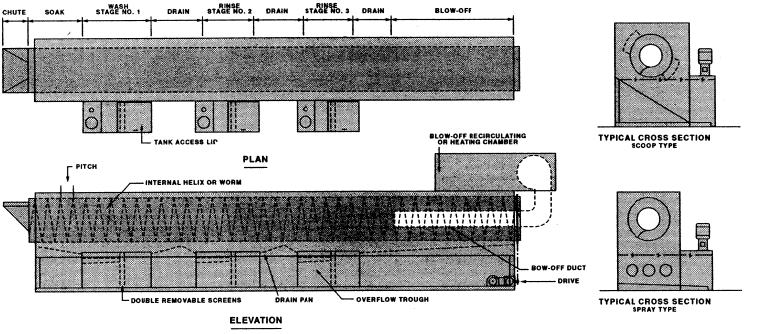


Fig. 6. Three-stage drum-type washer with blow-off (see Table IV for details).

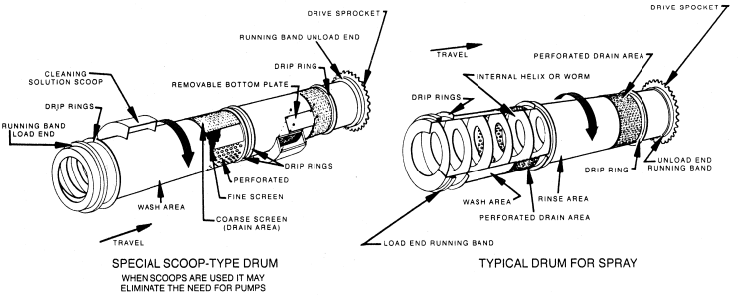


Fig. 7. Drum washer construction details.

FIVE-STAGE WASHERS

A five-stage monorail-type zinc phosphating machine is shown in Fig. 4. Table II provides details for each stage.Table III provides similar information for the five-stage iron phosphating system pictured in Fig. 5.

DRUM-TYPE WASHERS

Figure 6 depicts a typical three-stage drum-type washer. Concentration details are shown in Fig.7. Table III gives further details on drum-type systems.

OVENS

In former years there was a tendency to over simplify oven problems. There was a widely held idea that an oven was "just a heated box" through which parts were passed to dry or bake a finish or to evaporate and remove moisture or otherwise

Table IV. Typical Drum-Type Construction for Three-Stage Washer with Blow-Off

	Stage No. 1 Wash	*Stage No. 2 Rinse*	*Stage No. 3 Rinse*	*Blow-off/Dryer*
Design temperature	145°F	Room	160°F to assist drying	220°F
Time cycle (seconds)	60	30	30	180
Type nozzle	VeeJet	VeeJet	VeeJet	
Nozzle pressure (psi)	10	10	10	
Materials for construction:				
Tank	1/4-in. mild steel	1/4-in. mild steel	1/4-in. mild steel	
Housing	1/8-in. mild steel	1/8-in. mild steel	1/8-in. mild steel	1/8-in. mild steel
Nozzles	Mild or stainless steel	Mild or stainless steel	Mild or stainless steel	
Piping	Steel	Steel	Steel	
Pump	Iron	Iron	Iron	
Immersed heating equipment	Mild steel	Mild steel	Mild steel	
Air heating equipment				Mild steel

Considering both energy and pollution problems, new processes allow lower processing temperatures in some cases.

process by heat application. In more recent years the scientific aspects of heat engineering have come to be appreciated. True economy in operation matched by superior results can only be obtained by expert design based on sound engineering followed by quality manufacturing and conscientious installation.

The ovens may be on the plant floor or elevated overhead, either inside the plant or outside, on the ground or on the roof. With the ovens elevated the factory floor may be used for manufacturing or storage. The oven panels should be tongue-and-groove, all-welded construction, fabricated of heavy-gauge sheet steel, with a minimum of through metal, which reduces the transmission of heat by conductance. To avoid "insulation sag," which would leave an open space at the top of the wall panels, oven panels should be insulated with mineral wool batts ¼ in. greater in thickness than the oven panels. Access doors should be fully insulated or of nonsagging construction and equipped with explosion latches. These doors should allow opening from inside or outside the oven.

The relatively few ovens shown here are merely examples of the many types being built, each representing dozens and even hundreds of similar installations. Many special types are not shown because of limited use. For standard ovens, custom designs, and even economical prefabricated components it pays to consult true experts in heat engineering.

Direct versus Indirect Heating Systems

In a direct fuel-fired system the products of combustion are allowed to come into contact with the work; the combustion equipment can be located inside or outside the oven. Although gas is generally used with a direct fuel-fired system, modern processing of fuel oils, along with improved handling and firing equipment, has increased their use in this area. An indirect-fired system does not allow products of combustion to come into contact with the work. Electric and steam heating are common choices and fuel-fired equipment may be used in conjunction with a heat exchanger to separate the products of combustion from the oven atmosphere.

Fuels

The brief outline that follows describes the most popular fuels being used today. You may want to investigate the possibility of using one as an alternative to back up your present system or as a supplement.

Gas: This is generally considered a clean, convenient, and easy-to-use fuel. Work loads are commonly heated by the direct-fired method with no adverse effect from the products of combustion; however, because the availability and overall costs have changed it may be to your advantage to check the alternative fuels in your area.

Oil: Many of the problems that once plagued the use of oil with direct-fired oven equipment have been eliminated, and indirect-fired systems are easily designed and installed when needed.In either case plan for a safe, convenient storage space.

Steam: A very clean source that is simple, easy to control, and reliable for low-to-medium temperature operations, steam can be produced in a number of ways that are most economical.

Electricity: This is a clean, simple, and efficient source of heat. High temperatures are easily obtained and heat recovery systems are available to economically reduce operating cost.

Combination: Combination fuel systems are very popular with people who have been plagued by fuel price increases and shortages because they allow the ability to switch from one fuel to another without stopping production or adversely affecting the product.

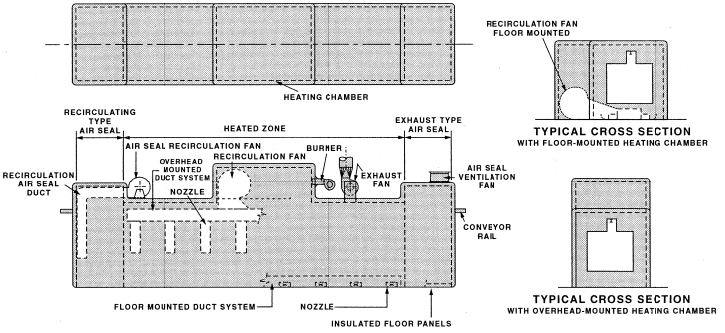


Fig. 8. Monorail dry-off oven features.

Recovery: Recovery systems have recently become very important to all users of energy. As fuel costs increase heat recovery systems become more practical.

Radiant: This is particularly applicable to flat parts and batches processed on the basis of part shape and size. It is a clean, high-energy source of heat where high surface temperatures are easily obtained in short periods of time. Although expensive to control it can provide shorter cure times and minimal floor space.

Features

Knowledgeable plant operators want panels and the general construction to provide maximum strength and rigidity, minimum heat transfer or loss, and an attractive appearance. The panels should be filled with insulation of full thickness, formed in batts to resist sagging and settling that can leave uninsulated areas. Tongue-and-groove construction mates into a strong, neat joint. Ovens should be able to be readily disassembled and moved if necessary. A typical oven system is shown in Fig. 8.

Air seals: Ovens can be provided with a variety of seals to prevent escape of heated air and fumes. The bottom entry oven, which must be elevated, has a natural type of seal because the heated air rises into the upper, sealed portion of the oven. Exhaust-type seals,where conveyor openings into the oven are enclosed by a hood with an exhaust fan, are also available.

In theory the most practical type of seal is the recirculating seal, which has been far from perfect in the past. Companies have invested considerable time and money in this seal and they are now producing recirculating seals that allow adjustment to compensate for various oven temperature losses. By providing a recirculating fan with adjustable vents at least 80% of the normally escaping heat can be retained.

Ovens can be designed as a high-velocity type or low-velocity type depending on the application. In most cases ovens are designed with both types in special zones to control paint popping, blistering, or in the case of a powder oven, dry powder blow-off.

Low-velocity or "quiet" zones allow the coating to cure slowly, allowing solvents to evaporate before the surface film is set, which minimizes pops and blisters. Radiant and infrared ovens can fit into this category.

High-velocity zones allow direct impingement of the air to the work,which allows for quicker curing of the coating or evaporation of water. This air movement helps to obtain even temperatures throughout the oven as well. The air movement is induced by high-velocity nozzles designed to improve direct impingement of heated air on the work surface. Attempting to dry or cure a painted part too quickly is a notable cause of paint "skinning," resulting in bubbles, blemishes, and powder blow-off.

Rolling air or high turnover rates: This induces an air movement that helps to obtain re-

markably even temperatures. The air movement is induced by high-velocity nozzles that also prevent direct impingement of heated air on the work surface, a notable cause of "skin-drying," resultant bubbles and blemishes, and powder blow-off.

Burner size: When selecting burners for an oven concentrate on the total needs of the job at hand; then allow for a reserve capacity to handle higher work loads without expensive alterations. This provides the greatest overall economy and equipment flexibility because the burners are efficient throughout their operating ranges.

Combustion chambers: Ovens are usually designed with the combustion chamber as an integral part of the unit, streamlining the appearance and eliminating the need for exterior ductwork. This compact arrangement also reduces power requirements connected with excessive ductwork, saving floor space as well.

Disposable filters: Intake air filters can minimize the intake of dust, which can cause finish flaws. The filters should be arranged for quick and easy changing without use of tools. The best disposable filters to use are frameless, eliminating the usual cardboard frame as a possible fire hazard.

Simple erection: Ovens should be constructed of prefabricated panels for easy erection. All components—panels, structurals, ductwork, wiring, and piping—should be keyed to assembly drawings and manufactured to fit easily, quickly, and precisely in the field. The purchaser can in many cases erect the oven with existing plant person-

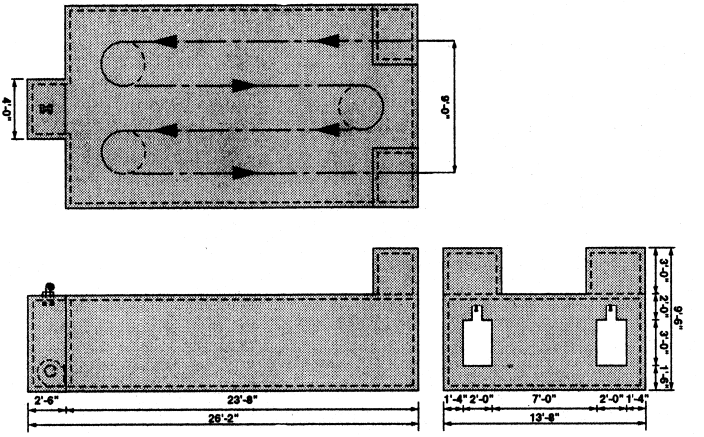


Fig. 9. Layout for cure/bake oven sample design.

nel under supervision for significant savings. For more complex ovens suppliers provide a complete service ranging from basic erection to complete turn-key jobs.

Dry-Off Ovens

The dry-off oven is usually a continuation of the washer. Drying metal pans with no "puddling" of water requires three to five minutes, depending on temperature. At 4 fpm you will need 12 to 20 ft of dry-off oven, excluding air seals. The next unit requiring the largest amount of floor space is the cure oven. Assume for design purposes that the paint you are using requires a 20-minute cure at 350°F. Again, conveyor speed is 4 fpm so you have to be in the oven at temperature for 80 ft of conveyor travel.

The oven can be fabricated in practically any configuration, depending on the floor space available. It could be a single-pass oven (80 ft long) or a two-pass oven

(40 ft long) or a four-pass oven (20 ft long).This you can determine from the floor space available. If floor space is a premium and the building height will allow it the oven can be hung from cross-beams supported from the floor or mounted on the roof. Available space usually dictates the position of the oven.

The tunnel opening of the oven is normally the same dimensions as the washer except that usually 18 in. to 2 ft from the bottom of the tunnel opening to the floor is ample for ductwork.

To sketch the oven layout you know that the maximum part width is 1½ ft and that they are spaced on 24-in. centers. This indicates that a 3-ft-diameter wheel turn will permit clearance of parts on a turn, so the proposed oven is outlined as shown in Fig. 9.

PAINTING SYSTEMS

The major types of paint systems fall into five categories: conventional solvent systems, water-reducible systems, high-solids systems, powder systems, and electrodeposition systems. Defining your criteria relative to operational characteristics, coating properties, initial capital expenditure, and operational costs will determine the paint system. A powder system and electrodeposition system have been included to demonstrate layout. The following are component design considerations for an electrodeposition system.

ELECTROCOAT (ELECTRODEPOSITION) PAINTING

Coating Thickness Control

The main factors controlling film thickness are the applied voltage and the film resistance. Increasing the coating voltage or lowering the specific film resistance causes an increase in film thickness. You simply dial the desired coating thickness.

The electrocoating process will continue until the organic film deposited provides an electrical insulating resistance, which prevents further current flow.

When the coated parts are removed from the bath they are rinsed in permeate and deionized water to remove nondeposited paint particles.

Tank Design

Electrocoat tanks are designed for an immersion time of 1½ to 2 minutes. It is possible to deposit approximately 1.0 mil organic coating in the first 15 seconds; however, for heavier film deposits a longer time is required.

Tank equipment includes dual pumps with each pump able to maintain the bath and prevent the setting of paint solids. Plate-and-frame heat exchangers are used with chiller units to maintain proper tank temperature.

Tank Design is Vital

In the design of the electrocoat tanks some of the most important items are circulation rate, circulation flow, and density of the paint. With the paint solids normally at 8 to 10% density a flow rate and pattern is determined to prevent settling.

The flow rate in the average tank is accomplished by the use of headers with eductors. The flow pattern in the bottom of the tank is opposite that of the conveyor movement and with the conveyor at the top of the tank. The exit end of the tank is equipped with an overflow weir tank designed to prevent foaming without dropping or aerating the paint. The recirculating pump suctions are also connected to this tank.

Filter Systems

Conventional filter systems are provided with approximately 50 micron filter media to remove foreign debris that may enter the bath.

An ultrafiltration system will be used to remove soluble salt and water carried into the bath from the cleaning process by the parts being coated.

Ultrafiltration may also be used to recover paint solids from the postrinse so they may be returned to the bath. A virtually closed system exists when ultrafiltration is used to provide rinse water in the place of deionized water. This arrangement will aid considerably in the prevention of water pollution.

SUMMARY

Getting value from your finishing system involves a comprehensive review of your requirements and, as necessary, applying some or all of the many technologies available into your system design. Normally, one person or one company does not possess all resources to do this task. A good approach is to consult reputable suppliers and follow their recommendations. The best solution to your system design is one in which every selected supplier works as part of your team toward the common goal of a successful system installation, start-up, and operation.

SPRAY BOOTHS

GLOBAL FINISHING SOLUTIONS, DALLAS, TEXAS

Before learning the features, benefits, and uses for spray booths, it is important to know the basics that apply to all spray booths: the reasons for using a spray booth, what a spray booth can and cannot do, the various federal, state, and local agencies that give approval to a new spray booth installation, National Fire Protection Association Bulletin 33 (NFPA-33) as it relates to spray booth design and booth classifications, the difference between code compliance and environmental compliance, how to determine booth efficiency, and the most common types of spray booths and how they are used.

The various codes and agencies that govern spray booth classification, installation and operation can be very confusing. Understanding the codes and how they apply to spray booths allows for identifying the most appropriate booth.

The purpose of a spray booth is to confine the application of a hazardous material to a restricted controlled environment. Spray booths prevent hazardous overspray and volatiles from escaping confinement and causing fire or explosion hazard to nearby operations. They control the air-fuel mixture so that a combustible combination cannot occur. In addition, spray booths provide a clean environment in which to paint.

REGULATION OF SPRAY BOOTHS

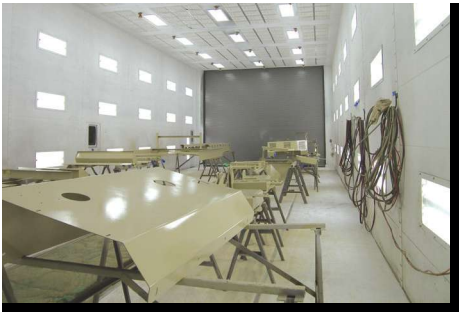
The primary function of a paint spray booth is to reduce the likelihood of fires and explosions. A secondary consideration is protecting the operator from toxic materials. This protection is best done with respirators, protective clothing, and hoods. Spray booths cannot be designed to adequately protect the operator from overspray contamination. It is not unusual for part geometry to require the spray gun to be directed near the operator.

A spray booth is not an emission control device even though some end users assume that a spray booth is an emission control device that must comply with Environmental Protection Agency (EPA) standards. EPA standards place limitations only on the amount of toxic material in the form of solvent vapor, known as volatile organic compounds (VOCs), entering the environment through the booth exhaust stack.

A spray booth is designed to collect solid particulates only, not solvent vapors. To comply with EPA requirements, exhaust air may need to be treated with equipment installed outside the spray booth. A carbon adsorption system or an incineration system, for example, are acceptable methods for collecting VOCs.

Traditional code inspections deal with the design of the spray booth. Inspectors evaluate hardware and installation methods for compliance with the Occupational Safety and Health Administration (OSHA) standards, National Fire Protection Association (NFPA) Bulletins 33 (Spray Applications) and 70 (National Electrical Code or NEC), and any local ordinances. A separate environmental quality review is conducted to determine the amount of pollutants the installation will emit.

A new spray booth installation is approved or denied by the authority having jurisdiction. For example, in areas dealing with public and employee safe-



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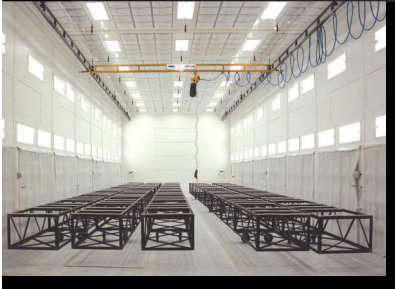
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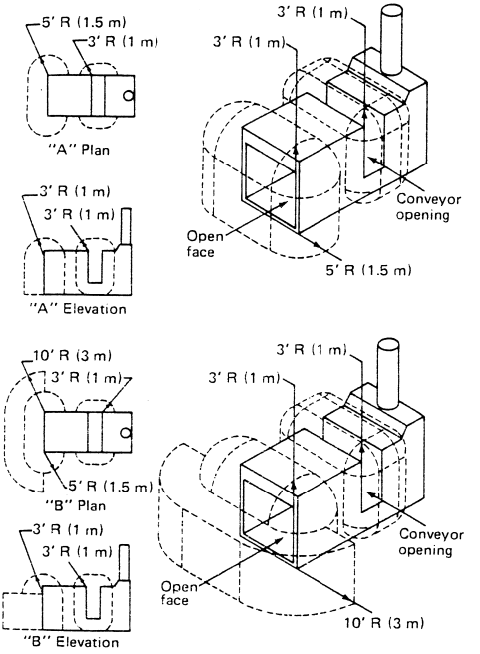


Fig. 1. Clearances required for spraying with (a) and without (b) exhaust fan interlock.

ty, the authority may be an official of a federal, state, or local agency. Or the authority having jurisdiction may be a regional official, such as a fire chief or marshall, building or electrical inspector, fire prevention bureau inspector, or labor or health department inspector. For insurance purposes, the authority may be an insurance inspector or representative of a rating bureau. Greater environmental concern has also led to increasing involvement by new agencies having jurisdiction. There are many agencies that dictate compliance. Depending on state and region, one or more of the following federal state and local agencies may play a part in approving a new booth installation.

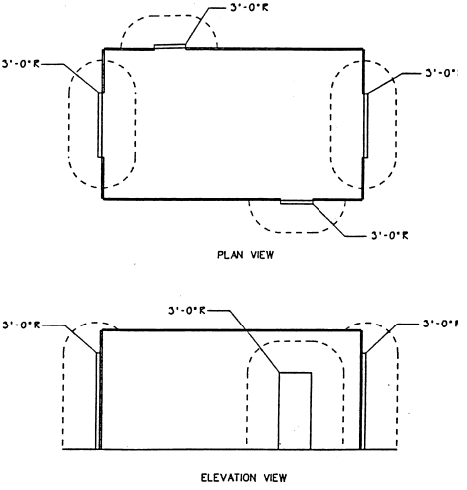


Fig. 2. Clearances required for Class I or II, Division 2 locations adjacent to openings in an enclosed spray booth or room.

Federal Agencies

OSHA is concerned with employee health and safety. Familiarization with the following OSHA codes and the booth design and safety requirements that each governs is important. The relevant OSHA codes are OSHA 1910.107 Spray Finishing, OSHA 1910.94 Ventilation and OSHA 1910.95 Noise Exposure. OSHA relies on the current National Fire Prevention Association (NFPA) Bulletin 33 to formulate guidelines on fire prevention.

In addition to NFPA-33, OSHA also bases compliance decisions on the electrical guidelines outlined in the current NFPA-70 (National Electrical Code). For guidelines on the acceptability of certain spray booth components, OSHA refers to Underwriters Laboratory (UL), ETL Testing Laboratories (ETL), Factory Mutual (FM), and Industrial Risk Insurers (IRI). These organizations evaluate equipment according to fire and safety standards.

The Environmental Protection Agency regulates the allowable amount of toxic material in exhaust stack emissions, liquid, and solid waste streams. The EPA has no jurisdiction over booth design, which is designated by NFPA-33.

State Agencies

Federal agencies, such as OSHA, often maintain state offices to enforce their own federal regulations and to administer any state mandated variations in those regulations. Also, each state has an environmental agency (such as Georgia Environmental Department) that conducts a review of all installations. The purpose of the review is to obtain a disclosure or prediction regarding the level of pollutants the booth will emit.

If the level is acceptable, the state agency issues a permit to operate an air contaminant source. If the pollutant level is unacceptable, the agency may deny the permit, require the use of exhaust air treatment equipment, or require the use of a different coating material.

Filing an application for a permit to operate an air contaminant source can cause delays in installing and operating the equipment. The permit to operate is needed before the equipment can be used, and often before installation and assembly can begin. The application forms are usually complicated, and when completed the application is subject to administrative review before approval.

Local Agencies

City and county authorities conduct code inspections to evaluate hardware and installation methods for compliance with OSHA, NFPA-33 (Spray Applications), NFPA-70 (National Electrical Code), and any local ordinances. Some municipalities are now writing EPA compliance into their local ordinances as well.

The burden of compliance falls on the end user. Ignorance of the regulations and procedures is not a defense against prosecution, and penalties for noncompliance are becoming more severe. Become familiar with all the agencies having jurisdiction, including the environmental agency review and application requirements.

Spray Booth Classifications

Spray booth classifications are outlined in NFPA-33. NFPA classifies booth areas according to the types of electrical equipment and other possible ignition sources that can safely be used within those areas.

Class I covers flammable gases and vapors and Class II covers combustible dusts.

$$\text{Grains/ft}^3 = \frac{\text{solids by weight in lb} \times \text{transfer ineff} \times \text{collection ineff} \times 7{,}000}{60 \text{ minutes} \times \text{cfm}}$$

Grain count is normally expressed in grains/1,000 ft^3; therefore

$$\text{Grain count} = \text{grains/ft}^3 \times 1{,}000$$

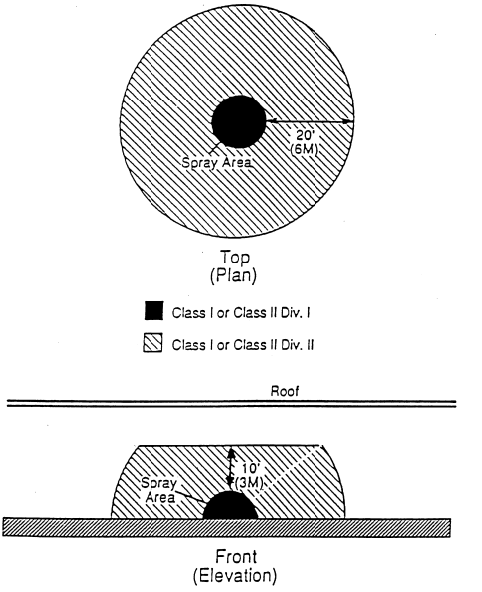
Divisions 1 and 2 cover locations in the classified area in which these flammable gases, vapors, and dusts are handled. Most industrial booths are Class I. Class I, Division 1 areas are the inside of the spray booth and the inside of the ductwork. Class I, Division 2 is any area within a 10-ft radius of the open face of a spray booth when the spray gun is not interlocked with the exhaust fan to prevent spraying unless the fan is operating. When the spray gun and fan are interlocked, the Class I, Division 2 area extends five feet back from the open face. This area also extends three feet from a conveyor opening and includes the area above the ceiling of the booth (see Figs.1 to 3).

Equipment located in the Class I, Division 1 atmosphere must be classified as explosion proof. In practice there should be no electrical items inside a spray booth. Electrical equipment in the Class I, Division 2 atmosphere must be third-party listed (such as UL, ETL, ER) and must not produce sparks under normal operating conditions.

MEASURING BOOTH EFFICIENCY

By design, a spray booth collects solids known as particulate emissions. Efficiency factors, specifically grain count, measure how effectively a spray booth and filter system will be in trapping these particulate emissions.

The following formula is used to determine the relative efficiency of a specific system.



The grain count, or relative efficiency, can be altered by making changes in equipment (transfer efficiency), coating material (percent of solids in paint), and the air flow (cfm), rather than changes only in booth design. For example, if a painter switched from conventional air spray equipment to HVLP equipment, the higher transfer efficiency possible with HVLP would lower the grain count. Because of its ability to trap particulate matter, a spray booth can help the end user meet EPA requirements. Unfortunately efficiency factors

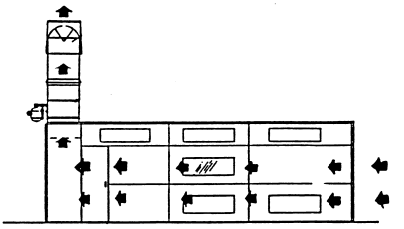


Fig. 4. Cross-draft air flow.

have at times been misrepresented as providing an assurance that a spray booth will meet EPA requirements. Although some spray booth designs are more efficient than others at preventing material from entering the environment, high-efficiency factor ratings do not automatically ensure EPA compliance.

TYPES OF SPRAY BOOTHS

A spray booth consists of a work compartment where spraying takes place, an exhaust chamber for collecting particulate, an exhaust fan and motor, and an exhaust duct to the exterior of the building. Paint booths are categorized by the method of collecting the overspray and the direction of air flow in the booth. There are subcategories in each case.

Dry-Filter Booths

There are several types of dry filters available for use in spray booths. The rectangular pad type is available in many grades and types. The roll media type is also available in many sizes, grades, and types. This designation is a slight misnomer as the media is rolled for ease of shipment but is unrolled and applied as a large rectangular block of filter media. Roll media filters should not be confused with continuous roll. Continuous roll media come on spools in large, long rolled coils. As the filter becomes contaminated, the clean section is advanced. This can be hand or motor operated.

Cardboard baffle and light density Styrofoam filters are also available; however, dry baffle exhaust systems have almost entirely disappeared, except when used with paint filters as prebaffles. A single or double row of baffles is placed vertically in front of a normal paint arrestor bank. This provides the primary collection surface for overspray and effectively protects the filters from rapid loading; however, they now become part of the collection system and must be cleaned and maintained. This application originated with the collection of high solids paints that caused heavy loading and forced rapid change of filter media. The physical characteristics of the high solids materials allow collection through a trough at the base of the baffles. In some cases, this reclaimed material is reusable or it can be returned to the manufacturer.

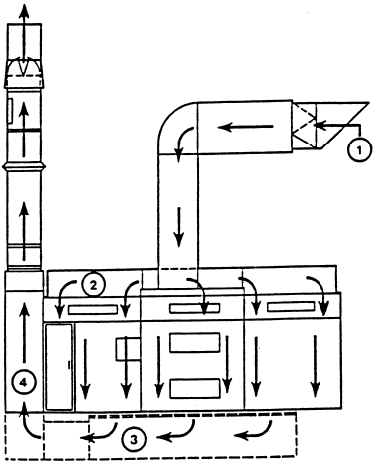


Fig. 5. Downdraft air flow.

Water-Wash Booths

These booths may use pumps or be pumpless. Low static pressure-pump-type

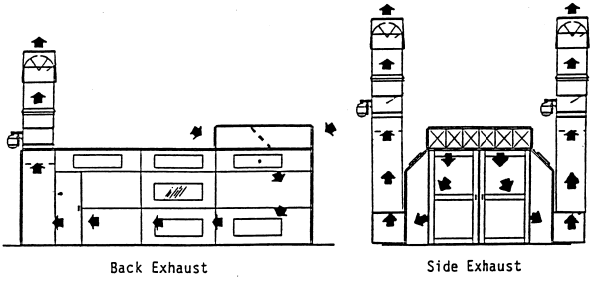


Fig. 6. Semidowndraft air flow.

booths with recirculating headers and piping are the most common types of water-wash booths. In contrast, high static pressure-pump-type booths are usually found in automotive plants and are described as *grain-count booths*, meaning that they are considered to have a higher collection efficiency than standard water-wash booths because of higher internal static pressure and scrubbing action. For a booth to be considered a grain-count booth, it should not release more than 3 grains (weight) to the atmosphere per 1,000 cfm of exhaust air. Test procedures are necessary to measure washer efficiency.

Pumpless booths also come in two forms, those requiring high pressure and those with low pressure. In pumpless types that require high internal static pressure as a means to circulate and scrub water, high velocity air moves water up through the exhaust chamber. It is then released at a high point and returns to the water tank through an exposed water curtain. Pumpless types with low static pressure usually are fitted with a water holding pan and little or no water movement through the exhaust plenum. Collection depends on an abrupt change of air direction to impinge overspray onto the water surface.

Draft Classifications

Booths are also classified by the method of draft. *Cross-draft booths* are characterized as having air flow designed in a horizontal movement (Fig. 4). Air travels parallel to the floor, from the face of the booth to the rear of the exhaust chamber. The majority of booths are designed as cross-draft. The booth can have the face open to the atmosphere, closed with input plenum, or closed with filter doors.

In the *downdraft* booth, the air flow is from overhead and moves down toward the building floor (Fig. 5).The building floor normally has a sunken pit to accept either dry-filter or water-wash exhaust. A bar-type grating is laid over the pit opening. The booth can also be placed on an elevated platform to avoid pit construction. The top of the booth may be open or enclosed with a filter input plenum. Most downdraft booths have overhead, filtered input plenums. A booth with a filter plenum is normally used in conjunction with a heated air make-up unit. This is considered a must for a clean paint job.

A *semidowndraft booth* combines features of the cross-draft and downdraft booths. The method of inputting the air to the booth makes it a semidowndraft. Air is introduced to the booth through the ceiling in the first 25% to 30% of booth length (Fig. 6). This input air may be introduced by relying on the suction of the exhaust fan or it can be pressurized. For the best results, air make-up should be used and the booth should be positively pressurized. The exhaust is placed at the booth rear as would be the case in a normal cross-draft booth.

A second style of semidowndraft places a floor level filtered exhaust plenum down each side of the booth. A full air input plenum is located in the booth

ceiling as would be the case of a normal downdraft booth. The air flow is from the ceiling of the booth down and out through each side plenum. No pit or elevated platform is required for this booth.

SPRAY BOOTH DESIGN AND SIZING

Selecting the booth and sizing it for an application requires review of several areas. Knowledge about the facility and production process are important in choosing the right equipment. Take the time to understand the application, and do not forget future plans that may influence the choice of spray booth design. The following are some general guidelines for selection and sizing.

1. *Maintenance:* All booths require regular maintenance for optimum performance. As a first step, determine the capability of the maintenance department or maintenance contractor. This will determine the sophistication level of the equipment required.
2. *Budget:* Always take the budget into consideration when choosing the spray booth. Balancing the application requirements and available funds will help identify the most effective exhaust chamber, air flow, and booth options for the job.
3. *Selecting the Booth Design:* The first step in selecting an appropriate booth design for an application begins with an investigation of the finish quality level and the production requirements. This step will help determine the direction of air flow through the booth, as well as the appropriate filtration method, either dry filter or water wash.

Production Requirements

Part Size and Configuration

The size and style of the part, the carrier that conveys it through the booth, and the relationship of the spray gun to the part, all play a role in determining the direction of air flow as well as the velocity or speed of air through the booth. Air flow and velocity are needed to transport paint overspray into the filters. There are three types of air flow through a booth as discussed above: cross-draft, semi-downdraft, and downdraft.

Production Rate and Transfer Efficiency

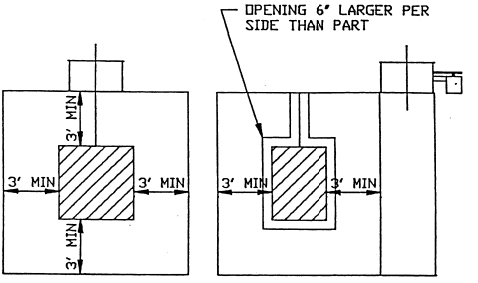


Fig. 7. Manual booth sizing.

Production rate is a measure of the number of parts that can be finished within a certain time frame, usually per hour or per shift. Transfer efficiency is the percentage of material being sprayed that adheres to the part; the remainder is overspray. The type of application equipment—conventional, electrostatic, or HVLP (high volume, low pressure)—deter-

mines how efficiently paint is transferred from the gun to the part. Together, production rate and transfer efficiency influence the choice of air flow.

Material Being Sprayed

The type of material being sprayed affects the choice of filtration or exhaust method, either dry filter or water wash, to remove overspray from the booth. A dry-filter or paint-arrestor booth traps airborne paint particles (overspray) in disposable filters. A dry-filter is used in the majority of applications. Depending on the material being sprayed, removal efficiency ranges from 95% to 99%. If more than one type of material is being sprayed, be sure that the materials are compatible. The combination of incompatible materials in the dry filter can be a cause of spontaneous combustion. In a water-wash booth, air washing action traps the paint solids from overspray. Water-wash systems should be used for very heavy spray rates (over 20 gal/8-hr shift/10 ft of exhaust chamber width). Removal efficiency for a water-wash booth can be as high as 98% to 99%, depending on the type of material being sprayed.

Finish Quality

The quality of the finish on the completed part has become more critical as customer's expectation levels have increased. The total process must now be considered in order to achieve first-time-through quality levels.

The spray booth design is one key aspect. Air flow, direction, filtration, air velocity, and balance are critical to accomplishing the various desired quality levels. Unpressurized cross flow designs would be at the low end and pressurized downdrafts at the high end of quality potential.

One key thing to consider is that a spray booth is only one part of the process. Many other phases of the process must be designed and controlled to achieve the desired quality level. That would include the preparation and cleanliness of the object going into the booth, the maintenance of the booth and surrounding processes, the quality of compressed air to the tools (including spray gun), the quality of clothing and equipment the painter uses, and the quality of the paint preparation activities. The finish quality can only be as good as the design and control of the process.

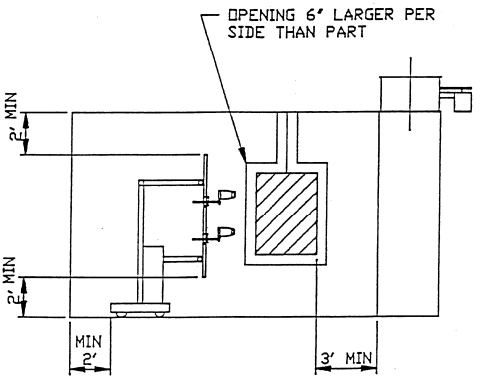


Fig. 8. Booth sizing for automated lines.

Determining the Booth Size

Determining booth size is the second step in selecting the application. It is dependent on booth location and the type of operation (manual or automatic). Review of the facility layout and proposed booth location is recommended to determine whether the allotted space is adequate for the size and style booth. The type of finishing operation, either manual or automatic, also determines the size

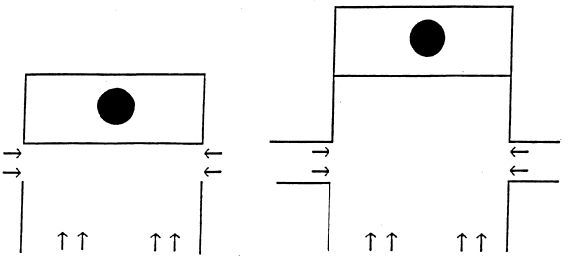


Fig. 9. Open-front booth design. On the left is a poor booth design; the conveyor openings are too large and too close to the exhaust chamber resulting in less air flow past the painter. A better design, on the right, makes use of entrance and exit vestibules.

of the booth (see Figs. 7 and 8). A properly sized booth for manual spray operations will give the operator and the finishing equipment adequate room in which to work. Adequate means enough space for the operator to move around, stoop down, bend over, and allow an even, fluid arm motion. For an automated application, the correct booth size will provide enough space for automatic equipment to operate effectively. This includes allowing for the operation of side-to-side and overhead reciprocators, and providing the necessary clearances for electrostatic equipment. During finishing, there should be sufficient velocity through the booth and past the equipment to keep it in clean operating condition. When conveyors are transporting parts through the booth, the booth size is directly related to conveyor speed.

Minimum and maximum part dimensions determine the booth width, height, and depth. Acceptable booth width will allow at least 3 ft on either side of the part, at least 6 ft of work space for each operator in multiple-operator applications, and a minimum of 2 ft from all conveyor openings. To determine the width, measure the diagonal dimension of the largest part, including the fixture or pallet it is on, and add a 2- to 4-ft clearance on each end. This space permits the part to be turned if necessary and enables the operator to work comfortably.

Adequate booth height will allow at least 2 ft above the largest part and allow for conveyor height or include a housing for the conveyor rail. Booth height is determined by the overall height of the largest part, plus 2 to 3 ft clearance. Add the height of the holding fixture if the part is moved by a conveyor. This measurement gives the operator suf-

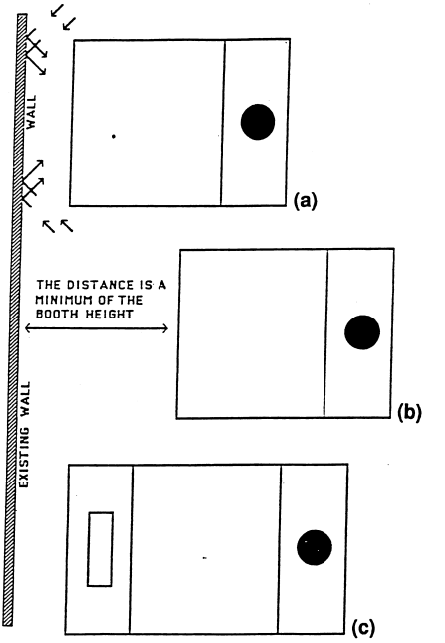


Fig. 10. Booth placement. Booths should not be placed too close to building walls (a); place the booth front at a distance front he wall that is equal to the height of the booth (b); or place the booth next to the wall with a direct connected air-input plenum.

Table I. Recommended Velocities for Floor-Type Booths

Velocity (fpm)	*Equipment and Application*
50–100	Automotive refinish
100–125	Hand electrostatic, batch operation
100–125	Hand spray, batch operation
80–100	Automatic electrostatic, conveyor system
125–150	Hand-spray conveyor system up to 10 fpm, small parts
125–150	Hand-spray conveyor system up to 20 fpm, small parts
150	Hand spray, large parts
150–175	Automatic, air atomized/airless

ficient room to coat the top of the part without coating the booth ceiling. The part should also be high enough above the floor to allow the operator room to spray the lower edges and the underside easily.

Sufficient working depth will allow at least 3 ft between the rear of the part and the water-wash tank or filter pads, at least 3 ft between the front of the part and the booth face or intake filters, and allow for automatic machines, such as reciprocators, in conveyorized applications. Working depth should be sufficient for the part, including the fixture or pallet, to be entirely within the booth enclosure during finishing, plus allow for clearance at the rear. There should be a minimum of 3 ft between the part and the tank in a water-wash booth or the filters in a dry-filter booth.

Conveyor openings are required when a conveyor moves parts through the spray booth. Conveyor openings should allow 6-in. minimum clearance around the part. A vestibule is a protected entry into the booth (see Fig. 9). It provides better air flow control through the booth by effectively blocking the tunnel leading into and out of the booth with the product. The vestibule length should be a minimum of the gap between parts so the vestibule always contains a part.

Booth Air Requirements

The final step in selecting the booth is establishing the minimum air velocity and volume requirements. The spray booth should be located to allow for proper air entry and flow through the booth. An open-faced booth should be located with the face at least booth height dimension from any wall (see Fig. 10). When this placement is not possible, air input plenums will provide adequate air flow.

A spray booth requires a minimum air draft or velocity, measured in lineal feet per minute (fpm), to carry overspray through the booth, past the operator or the automatic equipment, and deposit it into either the water curtain or filter pads. As a rule, OSHA inspectors rely on the guidelines specified in NFPA-33 requirements in the booth during spraying operations. Although the NFPA-33 guideline covers most spray operations, greater air flow may be required when specific types of finishing equipment are used. The high-pressure atomization equipment used to break up higher solids materials, for example, produces high atomization pres-

Table II. Recommended Velocities for Downdraft Booths

Velocity (fpm)	*Equipment and Application*
35–60	Automotive refinish
50–100	Pressurized, large objects only
75–100	Pressurized, large and small objects
75–125	Unpressurized

sures and consequently high fluid stream velocity at the tip of the spray gun. This can cause overspray tore bound and may expose the operator to toxic materials present in the paint. Velocity should always be sufficient to carry the overspray away from the operator and into the exhaust chamber.

The velocity possible in a booth depends on the fan size. Most standard booths offered in the market come equipped with fan and motor packages sized to deliver the necessary draft. Draft requirements take into account real-world static pressures including resistance to air flow from entry losses, stack filters, and duct work.

Static pressure is the amount of resistance air must overcome while moving from point A to point B. Static pressure in a spray booth is encountered in two areas: intake and exhaust filters and intake and exhaust duct work. The static pressure of any filter is determined by how much air will pass through that filter. Air-intake filters for downdraft spray booths are denser and pass less air than air-intake filters for either cross-draft or semi downdraft booths. Consequently, air-intake filters for downdraft spray booths have a higher static pressure rating than the air-intake filters for other booths.

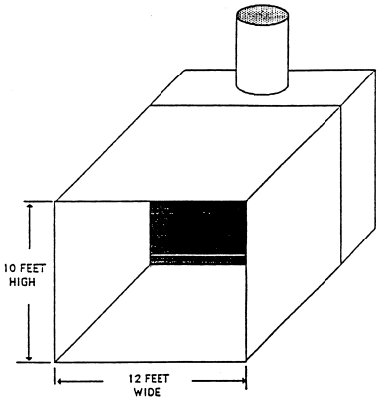


Fig. 11. To determine the size of the booth in cubic feet per minute, multiply the cross-sectional area of the booth in square feet by the velocity of the air through the booth in feet per minute (i.e., 10 ft x 12 ft = 120 ft^2; 120 ft^2; 120 ft^2 x 100 fpm = 12,000 cfm).

When intake or exhaust filters become clogged with dirt or material overspray, the amount of air that can pass through the filter decreases. When air flow is restricted, the filter's static pressure or resistance to air flow increases. Air intake and exhaust ducts also influence static pressure.

Air volume and velocity are decreased when elbows, reducers, transitions, and long runs are added to ducts. Elbows introduce angles and increase resistance to air flow. Reducers and transitions also increase the static pressure in duct work. The ideal situation is to keep duct work to a minimum.

Static pressure is also a factor when choosing an air replacement unit. Because of the similarities to an exhaust booth, pressure drops in and out of the unit must be considered.

Tables I and II give recommended spray booth velocities covering average conditions. The figures are all based on empty booths and include the face opening plus any conveyor openings. These are recommendations only, and are not meant to replace local or state regulations on minimum air velocity.

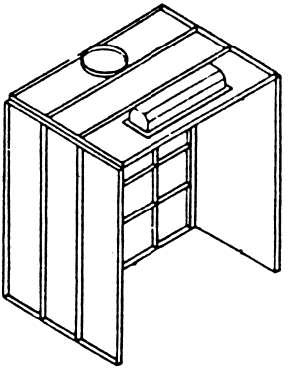


Fig. 12. Paint-arrestor spray booth.

In NFPA-33 (section 5–2) air velocity requirements are defined. According to the guidelines, a booth needs to "provide adequate ventilation to maintain the concen-

tration of flammable vapors or combustible vapors or mists in the exhaust stream below 25% of the lower flammable limit (lfl) of the paint." Lower flammable limit is defined as the concentration level at which a particular atomized solvent will ignite.

The volume of air needed to move through the booth and into the exhaust chamber is measured in cubic feet per minute (cfm). Use the following formula to determine the volume of exhaust air:

Area x Velocity = cfm of air

where area is the cross-sectional area in square feet of all openings in the spray booth. When air input plenums are used the conveyor openings may be ignored. When connecting vestibules are used, the opening between adjacent booths may be ignored. *Velocity* is the speed or velocity of air required by code. Speed of air movement is measured in feet per minute (fpm). Cubic feet per minute (cfm) is the volume of air moving through the booth. This relationship between booth size, the velocity of the air movement, and the volume of air being moved is shown in Fig.11.

INDUSTRIAL-TYPE SPRAY BOOTHS

Dry-Filter Booths

As with any type of paint-arrestor spray booth (see Fig. 12), the booth's main function is to remove the airborne particles from the spray booth exhaust air by means of disposable filters. The standard booth is typically designed to operate at 125 fpm air velocity. The booth normally provides an enclosure to accommodate a spraying operation. It limits the escape of spray and residue and safely directs them to a filter and exhaust system.

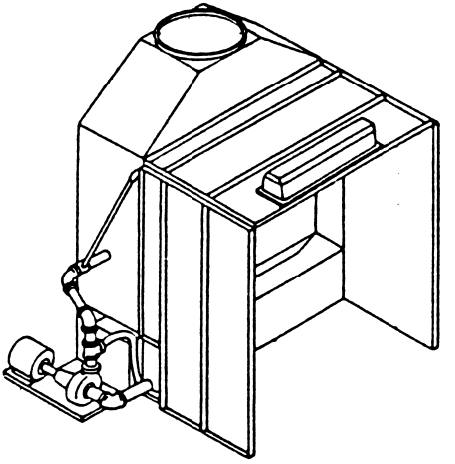


Fig. 13. Water-wash spray booth.

Dry-filter spray booths are ideally suited for low- to high-production operations; lighter spray rates; materials that stay wet, such as enamels, high solids, and water-base coatings; materials that do not react chemically with each other; and limited budgets.

Some of the styles of dry-filter booths include the floor-type, bench-top, and bench models. While the *floor-type booth* is available in a wide variety of sizes, this booth is designed for the work place where space is limited. The *bench-top booth* is perfectly suited to sit on top of an existing work bench. Depending on available space, this booth may fit the requirements perfectly. Some booths come with a leg kit for free-standing applications. The *bench booth* provides greater paint arrestor frontal area for in-

creased capacity in comparison to the bench-top booth. It is designed with a table height shelf. Both the bench-top and bench booths are perfect for spraying small objects and decorating and stenciling.

Use of the dry-filter spray booths requires a regular schedule of filter replacement. Codes require that filters be inspected after each period of use and that clogged filters be discarded and replaced immediately. Used filters must be removed to a safe, well-detached location or placed in a water-filled metal drum and disposed of at the close of the day's operation.

A draft gauge is typical standard equipment with dry-filter spray booths. The gauge is designed to indicate when paint filters have become sufficiently loaded and replacement is required.

Keep in mind that high-transfer-efficiency spray systems, when used in combination with high-holding-capacity dry filters, result in lower operating costs and higher production rates. There are two filtration principles that apply to dry filters, baffle and strainer, each having advantages and disadvantages.

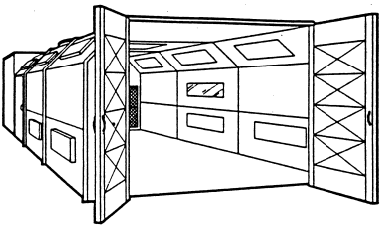


Fig. 14. Vehicular cross-draft spray booth.

Baffle Filters

The baffle principle creates a high turbulence in the air flow as the air moves through the filter. The heavier overspray particulates are forcefully deposited at various depths in the filter. This process, called depth loading, is optimized with the slit and expanded kraft filter. Baffle filters are available in metal panels, corrugated filters, pleated and expanded kraft, and Styrofoam pads. Metal panels have excellent holding capacity, but their ability to trap a high percentage of solids from the spray booth is limited and the exhaust air is poor. Also their efficiency is low. The metal panels are most efficient when intermittent production exists, or when used as a precollector to reduce the replacement frequency of more efficient filters. Corrugated filters also have excellent holding capacity and poor efficiency/performance. Pleated kraft filters have excellent holding capacity with fair efficiency. Generally, pleated kraft is used in light production situations and with slow-drying coatings. Expanded kraft filters exhibit good efficiency but only fair holding capacity. And lastly, Styrofoam pads have excellent holding capacity with fair efficiency.

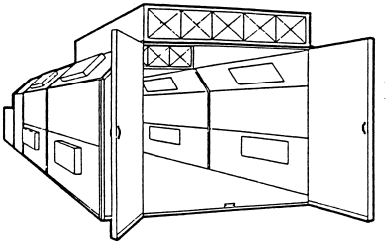


Fig. 15. Vehicular semidowndraft spray booth.

Strainer Filters

The second primary filtration principle is the strainer filter. This filter simply screens overspray from the air stream. Particles finer than the screen work through the screen, where as larger particles become trapped. Strainer filters come in two types.

Nonwoven cloth filters have excellent efficiency but poor holding capacity. Another disadvantage is that they are face loaded. Fiberglass filters are a little less efficient, showing good efficiency and a somewhat better,but still only fair, holding capacity. The front surface loads quickly, which is also disadvantageous.

Combination Baffle/Strainers

Any time you combine the best technologies from two different sources, the end product is one that's better than each component. So it only makes sense that the combination of the superior properties of baffle filters and strainer filters produces a filter with the highest effectiveness possible. These high-capacity filters can range as high as 99.5% efficiency, depending on paint formulation.

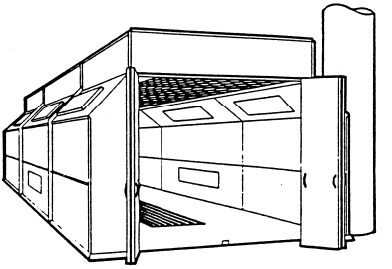


Fig. 16. Vehicular downdraft spray booth.

Water-Wash Booths

Water-wash spray booths (see Fig. 13) use a type of air washing action to trap paint particles. They are designed to continually break up paint accumulating on the surface of the tanks into minute, easier to handle solid particles of paint or a skimming system.

Overspray laden air is first drawn into the exhaust chamber. The heavier paint particles are separated from the air and forced into a water curtain at the chamber front. The air then enters a washer where it passes in front of a manifold containing numerous water-spray nozzles where it is washed a second time. In addition to passing these water nozzles, the air is forced to make numerous turns throughout its journey. Centrifugal force discards water and solid particles at each turn. The deposited water and solid particles to this point fall back into the water tank.

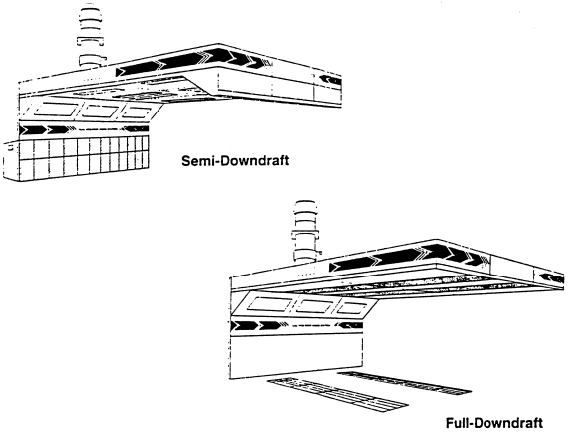


Fig. 17. Prep work stations.

Water-wash booths are ideally suited for heavier spray rates (over 20 gal/8-hr shift/10 ft of chamber width); all types of paints including primers, topcoats, enamels, epoxies, urethanes, and water reducibles; finishing operations that

are conveyorized and where automatic coating equipment is used or large amounts of coating material are sprayed; and high-production applications.

Features of water-wash booths include up to 99.6% collection efficiency, depending on paint formulation; continuous ventilation rate (constant static pressure); and agitation systems for more effective paint-killing action.

The water-wash action removes the liquid from most paints and reduces it to extremely small particles. It is a nonflammable, nonsticky waste, which may be nonhazardous. The sludge formed is skimmed from the tank top, or scooped from the tank bottom, and placed in drums.

There are several potential challenges associated with water-wash systems such as maintenance downtime, operating costs, and sludge disposal costs. The addition of a sludge removal system can greatly minimize these problems. The benefits of a proper sludge removal system are numerous and include reduction in the overall volume of disposed material because the end product is a drier sludge; the final water content, with some systems, may be low enough to permit the dried sludge to be classified as nonhazardous; the result of cleaner booth water can eliminate nozzle clogging in the air-wash section of the booth; and higher production due to increased up time.

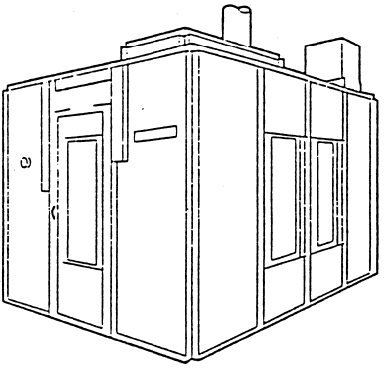


Fig. 18. Paint mixing room.

AUTOMOTIVE, TRUCK, AND TRAILER BOOTHS, PREP STATIONS, AND PAINT MIX ROOMS

There are a variety of vehicular spray booths available, including cross-draft, downdraft, and semidowndraft, which were discussed above. Figures 14, 15, and 16 show models of these three types of vehicular spray booths.

The prep work station (see Fig. 17) is a filter exhaust system that traps sanding dust at the source, returning a clean, even flow of air to the work areas around the part. They are also used to exhaust paint overspray on some light painting applications. They come in semidowndraft and downdraft designs.

During sanding or prep work, the overhead plenum recirculates clean, filtered air to the work station. During priming, the inside/outside damper vents solvent vapors to the outside. The advantages of utilizing a prep work station include a quick return on investment; a cleaner work area because a prep work station can be equipped to control both dust and vapors; increased productivity due to lower maintenance and easy cleanup; and lower energy costs (shop air is recirculated after filtering, so heating and air conditioning bills are lower).

A paint mix room (see Fig. 18) is designed to provide a bright, clean, well-ventilated area for mixing paints and related materials. These "clean-air" rooms help provide a contaminant-free mixing operation and a safe work environment.

The paint mix room downdraft ventilation system pulls in air from around

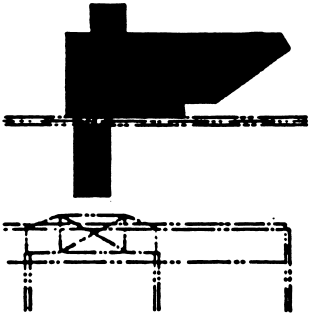


Fig. 19. Roof-mounted horizontal intake blast.

the mixing room and through a first-stage filter to collect large dirt and dust particles. The prefiltered air then moves through the ceiling fan for continuous air exchanges. Air then moves through the ceiling plenum filter to further purify room air of contaminants for a clean air mixing environment.

AIR MAKE-UP

An air make-up unit can lower heating and cooling costs. When air make-up is added, the building exhaust system works more efficiently. The information in this section will help to determine when an air make-up system is needed.

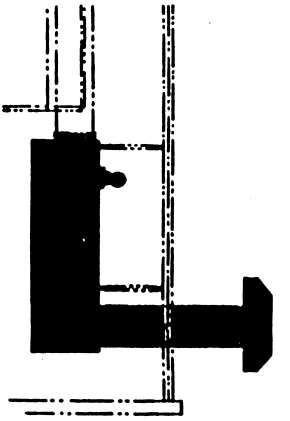


Fig. 20. Inside ceiling mount vertical intake.

Air make-up is the air required to maintain safe and effective building operation by replacing exhausted air. When an exhaust fan is installed in a building, exhausted air must be replaced from outside. This is done either through the cracks and openings in a building or with an air make-up, or air replacement, unit, which introduces outside air into the building. This air is usually filtered, cooled, or heated.

Installing an exhaust system without an air make-up unit is a good example of heating ventilation air by accident rather than by design. Air always flows from a higher pressure area to a lower pressure area. Installing an exhaust fan in a building creates negative pressure within the interior space. Air will flow from the higher pressure outside the building to the lower pressure inside. Because most buildings are closed in, the flow is restricted, but not completely. Cracks around doors and windows and in the

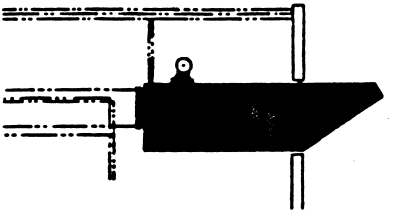


Fig. 21. Inside ceiling mount horizontal intake.

$$\text{Annual fuel cost} = \frac{\text{cfm} \times (T - T_o) \times 1.08 \times H \times C}{F \times E}$$

masonry and vent stacks allow air to flow into the building. This air creates drafts and cold spots until it can mix sufficiently with space air to reach room temperature. The normal heating system must work longer and at higher temperature to heat the air seeping from the outside. In addition to the increased heating cost, the negative pressure keeps the exhaust fan from doing its job—ex-

$$\frac{7 \text{ months of operation} \times 52 \text{ weeks} \times 60 \text{ hr/week}}{12 \text{ months/year}} = 1{,}820 \text{ hr}$$

Translate the heating value into BTU/100 ft^3

$$1{,}021 \text{ BTU/ft}^3 \times 100 = 102{,}100 \text{ BTU/100 ft}^3$$

Figure the annual costs

$$\frac{10{,}000 \times (65 - 43.1) \times 1.08 \times 1{,}820 \times 0.40}{102{,}100 \times 0.92} = \$1{,}833.10$$

hausting contaminants from the space.

Exhaust fans are rated for a certain air delivery measured in cubic feet per minute (cfm). This rating is based on a specific static pressure. Static pressure is the friction the fan must overcome to exhaust air. The more cracks and openings in the building (and the larger they are), the easier it is for air to move into the building. As the static pressure rises, the exhaust air decreases.

When to Install an Air Make-Up Unit

Use the following checklist to determine if a building needs an air make-up unit.

1. Gravity systems, such as vent stacks from a gas-fired furnace or water heater that normally draw air out of the building, are pulling outside air in.
2. Exhaust systems are not operating efficiently, resulting in a build-up of contaminated air within the facility.
3. The inside perimeter of the building is cold because the outside air is being pulled into the building.
4. Exterior doors are hard to open or close because of the pressure exerted by outside air entering the building through them.
5. It is difficult to maintain an even temperature throughout the interior space.

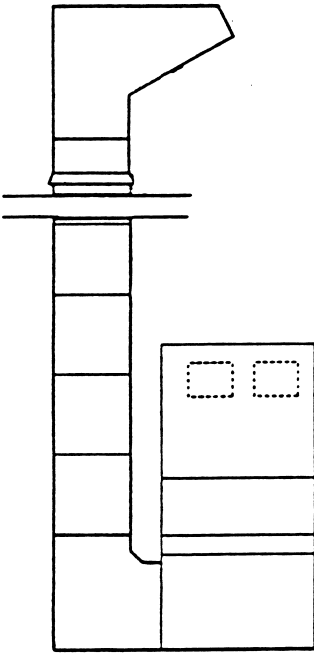


Fig. 22. Vertical air replacement.

OSHA requires the work compartment of a spray booth to be maintained at a minimum temperature of 65°F. To meet this regulation, it is mandatory that heated air make-up be used during the winter months.

Installing an air make-up unit sized to the building will improve exhaust system efficiency and provide greater control over the interior temperature. With the correct balance of air, it is easier to control air pressures to alleviate problems in opening or closing doors. Balance also prevents contaminants or odors from

travelling to different areas of the building. The air make-up unit reduces fuel bills by eliminating drafts.

Sizing

The air make-up system should be sized according to the spray booth exhaust volume plus 10%. If the air make-up duct will be physically connected to the spray booth, then the 10% extra capacity can be disregarded; however, some means of volume adjustment must be allowed so that a proper input/exhaust volume balance can be obtained. This can be in the form of an adjustable drive on the air make-up and/or exhaust fan or volume dampers in the system. If the installation is new, then the manufacturer will know the needs of both the exhaust fan and the air make-up system. If the booth is older, the exhaust volume can be determined from the manufacturer's literature, computing from known booth velocity or from fan curves.

Air make-up is most easily sized during initial booth purchase and installation. To determine if you require an air replacement unit, multiply your spray booth's exhaust fan rated capacity (cfm) by 20 (based on three changes per hour: 60 minutes/3 = 20). Using a 10 ft wide x 8 ft high spray booth rated at 125 fpm (with a total of 10,000 cfm exhausted) would be 20 times 10,000, or 200,000 ft^3 of air.

If your shop's cubic foot area is less than 200,000 ft^3 of air, you should install an air replacement system.

Types of Heaters

An air make-up unit contains a heater to heat the air. The heater may be gas-fired (direct or indirect), steam or hot water, or electric units. Direct gas-fired heaters are the most economical choice. Indirect gas-fired heaters are only used when there are restrictions against the use of direct units. Steam or hot water heaters are the least efficient. They should only be used when there is an existing boiler that has additional capacity to handle the air make-up system. Electric units should only be used when alternative fuels are not available. The cost of this fuel is quite expensive. The formula for calculating costs is as follows:

where cfm is the actual cubic feet of air delivered by the air make-up per minute, *T* is the temperature of the air leaving the unit (same as the space temperature), T_o is the average outside air temperature during heating season, 1.08 is the constant arrived by multiplying 0.075 (air density) by 0.24 (specific heat) by 60 min/hr, *H* is the total hours of operation from October through April inclusive, *F* is the BTU value of one unit of fuel (generally1,021 for natural gas per cubic foot), *E* is the efficiency of the unit (0.92 for a direct fired air make-up unit), and *c* is the cost of one unit of fuel (expressed in the same units as those used for *F*). The following example illustrates how the fuel cost formula works.

A 10,000 cfm air make-up unit in a building in St. Louis operates 60 hr per week at 65°F space temperature. It is fueled by natural gas at \$0.40/ft^3. We find the annual operating hours by

Remember, this represents the greatest cost to operate the air make-up unit. Actual cost could be less.

Types of Air Make-Up Units

There are four basic air make-up styles available. They are defined by their intake and discharge mechanisms and include horizontal intake/downdraft dis-

charge, horizontal intake/horizontal discharge, vertical intake/horizontal discharge, and the floor-mounted vertical unit.

The horizontal intake/downblast discharge unit is an air replacement unit for inside or outside installation (see Fig. 19). The unit, when weather proofed may go on the building roof, has a horizontal intake with a down blast discharge, and is curb mounted. The horizontal intake/horizontal discharge unit is an air replacement unit generally used indoors (see Fig. 20). The horizontal intake allows the unit to be mounted through the side wall of a building. The unit has a horizontal discharge. The vertical intake/horizontal discharge unit is used indoors (see Fig. 21). The vertical intake allows for mounting through the roof of the building. It has a horizontal discharge. The floor-mounted vertical unit is an upblast furnace (see Fig. 22). All horizontal intake and floor-mounted vertical units are available in either inside or outside models.

SUMMARY

This has been a basic overview of spray booths. Hopefully, an appreciation for their complexity of application into a total finishing process has been conveyed. Too often, the finishing process is not designed; it evolves, and the purchase of any spray booth is considered as "all that is required." Finishing and refinishing expertise should always be sought early in the process when initiating a new system or upgrade to an existing system.

DESIGN AND OPERATION OF CONVECTION DRYING AND CURING OVENS

BY DAVID CARL
GEORGE KOCH SONS INC., EVANSVILLE, IND.

he three major processes at work in a finishing operation are the surface pretreatment, the coating application, and the drying and curing of the coating. There are several proven methods from which to choose. The processes are dependent upon each other and are subject to design considerations, such as coating specifications, substrates, factory space availability, capital budget, environmental concerns, and many others. Several options for the process are available. There are air-dry applications, low-temperature cures for woods, plastics, and even electrocoated parts, and the more traditional higher temperatures for solids and powders.

The equipment required to properly dry and/or cure the coating is just as varied. Infrared (gas and electric), radiant wall, conventional convection, and high-velocity convection are but a few of the available options. Applications that combine methods are becoming increasingly popular. From the point of view of an equipment supplier, by far the most often applied process is the direct gas-fired conventional convection oven. Infrared or radiant wall designs are often incorporated for preheating; however, the completion of the cure still is accomplished by traditional means.

The purpose of a drying and/or curing oven is to elevate the product and coating to a particular temperature and hold this temperature for a set period of time. The combination of time and temperature serves to drive off solvents and set the coating. The desired outcome is for the combination of pretreatment, application, and cure to produce a coating with specific physical and chemical properties.

Understanding the operation of a convection oven requires the examination of the systems at work within the unit. There are five major components in an oven: the shell, the heater, the supply system, the recirculation system and the exhaust system. Each of these has an essential function, is comprised of several interlocking parts, and is subject to problems from misadjustment and misapplication. When they work together properly, they produce the process necessary for the successful cure of a coating.

OVEN SHELL

The purpose of an oven shell is to contain the environment necessary for the curing process. The shell consists of the supporting structure, insulating and sealing materials, and openings. It must be of proper dimensions to house the product and process equipment while exposing the product to the required times and temperatures.

A steel structure supports the enclosure and the product-conveying equipment. Most often the structure is built using wide flange or tubular steel on 10 foot centers. For ease of construction, the steel is located within the enclosure, exposing it to the elevated temperatures and cycling of the oven environment. Expansion becomes a problem. The beams in an oven that is 40 feet wide, operating at 450°F, will grow about 1 in. as the oven temperature is elevated. Special slotted-hole connections must be used to allow the structure to compensate for the expansion.

To contain the heat, the process must be enclosed with proper insulating materials. Panels that are 30 in. wide are used with the necessary fiber insulation (1 in. of 4-lb density insulation for every 100°F) sandwiched between aluminized metal skins. The

assembled panels are tongue-and-groove design for ease of installation. The outer skins are connected with formed metal channels. These channels form a through-metal condition, allowing a significant loss of heat at the joint. This panel joint can become too hot. To solve this problem, the channel is slotted, greatly reducing the area available for the migration of heat. This technique can reduce the joint temperature to less than 100°F in a 450°F oven, without losing the structural integrity of the channel.

Personnel access must be provided into the enclosure. The door and hardware must seal the opening without the use of a positive latching device for safety reasons. (Any panic hardware with positive latching features must allow the door to be opened from the inside.) A good rule of thumb is to locate access doors so that when someone is working in an oven, once he reaches a wall, an exit is never more than 25 feet away. Windows in oven doors are a good way to make them easy to locate.

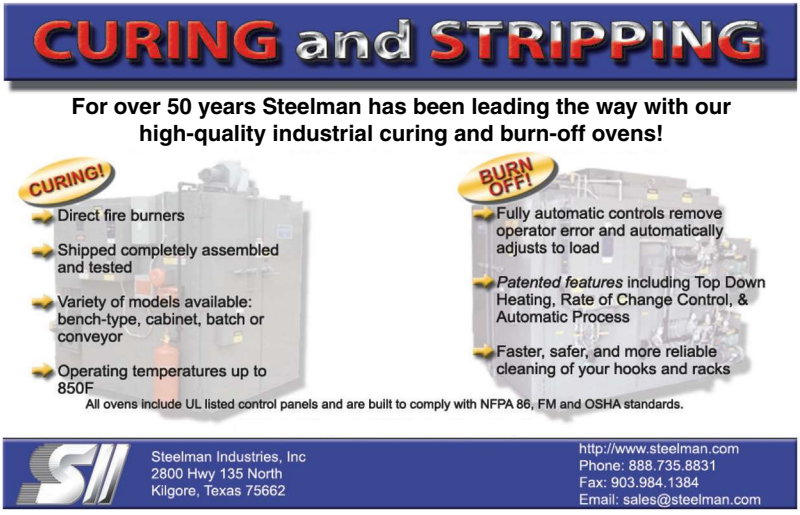
A great source of oven problems are the enclosure openings. These are required for the product to enter and exit the enclosure. These holes are designed using a minimal clearance for the ware. Bottom entry/exit designs make use of the natural sealing features of hot air and present no real problems. Openings in the sides of ovens require mechanical air seals to contain the environment.

To seal an opening, it is best to draw hot air from the oven and force it back into the opening. For this to work, a significant velocity must be developed at the center of the opening. Additionally, the oven must be run on negative relative to the production environment. These two requirements draw factory air into the oven. This pressurization must be relieved by exhausting the enclosure, a considerable source of heat loss. An alternative to traditional construction methods is the oven module, but it is rarely practical due to its configuration.

HEATER SYSTEM

The second system at work in an oven is the heater unit, which generates the energy necessary for curing the coating and begins the distribution of the energy. The most significant components of the heater are the burner, the supply fan, and the filters.

To properly size heater equipment, a detailed heat load must be carefully calculat-



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ed. Energy losses for the ware load, conveyor load, enclosure, and exhaust must be considered. These losses, expressed in BTUs per hour, are used for selection of the burner and corresponding electrical devices necessary for burner control. The burner, most often a direct-flame device, provides the energy for the cure.

The heat-load calculation also provides information for the selection of the oven supply fan. The heat required to maintain a good oven temperature is delivered by heating the supply air to no more than 100°F above the oven operating temperature and distributing this air to the oven proper. The fan volume must be expanded for the elevated temperatures. The supply fan should turn over the oven volume approximately two times every minute. Because the fan is a constant-volume device, the fan motor is sized for cold starts to avoid overloading. These rules will provide an oven temperature profile ±10°F throughout the enclosure.

Another feature of many heater units is filtration to continuously clean the oven environment. The efficiency of the filters varies with the application, but the most effective are the types used to final filter make-up air, modified for the elevated temperatures. Filters require velocities, which are much lower than in normal heater units. Including these means increasing the size of the heater unit to accommodate this requirement. Oven filters continuously clean the air and, as a result, load very slowly. It is not necessary to prefilter high-efficiency filters.

Sometimes, the products of combustion are not compatible with the coating. In these cases, indirectly fired heater units are an option. These use air-to-air heat exchangers and are applied at the cost of the loss of efficiency. In practical applications, indirect heating equipment can require a third more energy.

As the heater unit discharges the supply air, it is directed into the oven supply system. The purpose of the supply system is to deliver and distribute the energy developed in the heater unit. The supply duct is constructed of aluminized metal and is rectangular in shape. For proper operation, velocities in the duct should not exceed 2, 500 fpm. This assures good laminar flow in the duct and good temperature control.

AIR SUPPLY SYSTEM

The actual delivery of the supply air into the oven is achieved through some type of discharge device. The simplest of these is a hole in the side or top of the duct; however, this provides no control over the air. A better design is to provide a control device or slide damper over the opening. The slide allows the size of the opening to be adjusted to change the amount of air leaving the supply duct at a particular opening. The total area of these openings should approximate the cross-sectional area of the ductwork. Because of the poor control available with these devices, more discharge area is not better as the air will leave the duct at the point of the highest pressure differential. Too many openings will allow a large volume of air to escape the duct near the heater, leaving very little air to do the work in remote locations.

Simple openings in the duct have a second problem. Simply allowing it to escape the duct does not assure that it will change directions, mix with the oven environment, and find its way back to the recirculation system. One effective tool to correct or change the direction of discharged air is a discharge nozzle. These devices are inserted over the discharge openings and give the air a new direction, away from problem areas.

RECIRCULATION SYSTEM

The purpose of the recirculating system is to return the oven air to the heater unit so the process of adding energy to the oven can continue. This is accomplished by using the duct with the supply fan to create a negative pressure condition within the enclosure. The oven air will naturally migrate to the areas of low pressure, be captured

by the duct system, and be returned to the heater. Recirculation duct is fabricated in much the same way as the supply. It is of aluminized metal construction and rectangular in shape. The duct is designed for slightly lower velocities. The velocity in the duct is held at 2,000 fpm and openings are 20 to 25% greater than the supply.

It is poor design to count on the recirculation duct for providing any control over the oven environment. The influence of suction pressure is negligible at even short distances from the source. While air naturally moves to the areas of lower pressure, this movement cannot be easily controlled. It is better to place a small amount of recirculation in the hottest part of the oven and let the supply air do the work.

EXHAUST SYSTEM

Every oven must be exhausted in order to create a negative environment so that air seals can properly operate and to remove the VOCs and other products of the cure from the oven, plus eliminate the build-up of smoke. These requirements exist in all types of curing ovens, whether powder, electrocoat, high solids, or waterborne. Additionally, the exhaust serves the purpose of purging the oven prior to startup. The requirement for purge is to change to enclosure atmosphere four times in a reasonable period of time (20 minutes) prior to ignition. The location of the exhaust is rarely critical because the supply and recirculation systems mix the oven atmosphere so effectively. As long as the exhaust intake does not improperly influence another part of the oven, such as an opening, one location is as good as the next.

It is the flexibility of convection curing that keeps it popular with today's finishers. A convection oven properly designed, installed, and put into operation requires little attention relative to pretreatment and application processes. It can run effectively with simple controls, can be combined with other curing methods, and can be operated efficiently. To conserve on factory space, ovens can be elevated, located outside, or on the building roof. This flexibility, not readily available with other applications, will continue to keep direct-fired convection curing the number one choice of general industry.

IMPORTANCE OF RACK DENSITY

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In any coating process there are four main requirements: careful surface preparation, the proper coating, a good application system, and a well-designed racking system. One may ask, "Why would a well-designed racking system be a requirement for any coating process?" It is one thing to coat a sample part for a customer to prove what your capabilities are; however, it is something else altogether to coat the same part on a full production line and make a profit doing it. Making a profit requires coating as many pieces as possible quickly and efficiently while maintaining the highest level of quality.

There are two keys to a profitable production finishing line: the line speed, which determines the number of cycles per hour per day, and the number of parts racked on the line for finishing. The reason that these two keys are so important to a profitable finishing line is that when you consider washing, rinsing, drying, cooling, coating, baking, and handling, along with building space, utilities, waste disposal, and rejects, each of these overhead factors is related to how many part scan be processed per hanger, or per cycle. In other words, part density directly affects profit. If there is anything that should stimulate your thinking about racking, it should be the impact that high-density racks can have on your production finishing line.

THE WELL-DESIGNED RACKING SYSTEM

A well-designed rack will address four areas: part density, proper grounding, rack maintenance, and flexibility.

Part Density

Most racks are welded structures designed to handle as many different parts as possible (see Fig. 1). Because they are welded, the vertical space between parts is set for the longest part to be hung. When shorter parts are hung, there is wasted vertical space between pieces. The same principle is true when applied to the horizontal spacing between pieces. Part hooks are welded at distances set for holding the widest part and thus, when smaller width parts are hung, the horizontal space between parts is wasted.

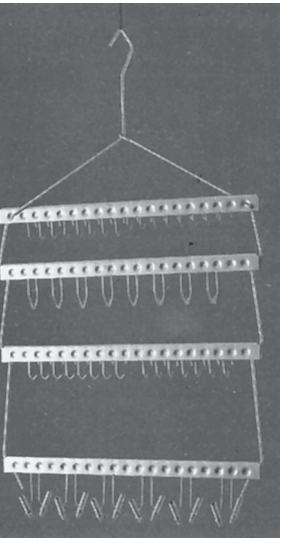


Fig. 1. Side bars adjust vertical spacing, and removable hooks adjust horizontal spacing.

With regard to part density, the best type of rack will be adjustable to allow for variables in both the vertical and horizontal spacing and maximize part density in both directions. The side bars of the rack should allow for up-and-down movement of the horizontal cross members to eliminate wasted vertical space. Part hooks should be adjustable at any time (even between cleanings), to

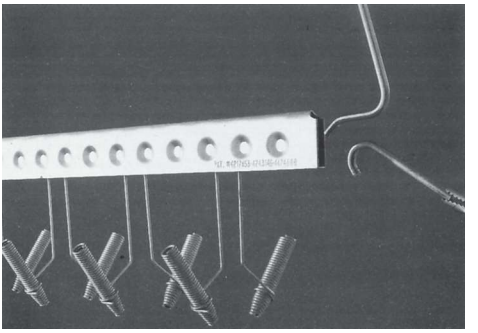


Fig. 2. Removable side bars protected inside the crossbar.

be repositioned as close as possible to eliminate wasted horizontal space between parts (see Fig. 2).

The overall width of a rack should be determined by maximizing the number of pieces on the rack in relation to the distance between conveyor pendants and the degree of incline related to any hills in the system. Most racks are designed to be 20 in. wide and to be center hung on 24-in. centers, assuming a 30° maximum incline/decline.

Proper Grounding for Electrostatic Applications

Nearly all part hooks eventually lose their ground between the part and the hook as they are used through the finishing system. The ground may be lost within as little as 2–3 cycles or as many as10–12 cycles, depending on the amount of paint being applied and whether the same kind of part is hung. A loss of ground causes loss of paint wrap, uneven paint distribution, blemishes, rejects, scrap, and wasted paint, particularly if there is no recovery system.

When loss of ground occurs, it is necessary to either clean the hook or, if possible, remove it and replace it with a clean one. In most cases cleaning requires either burning or chemically stripping the entire rack or burning or grinding just the hook end. The other option,replacing the hook, may be faster depending on the design of the rack and hook connection. There is a rack available that uses spring steel hooks that can be quickly and easily removed even after many cycles (see Fig. 3). The contact to the rack is shielded from paint and always remains clean for grounding.

Rack Maintenance

Optimizing rack density automatically reduces rack maintenance. Fewer cycles automatically means less cleaning. A common problem with welded racks is the hook breakage that occurs due to the annealing at the weld point of the hook to the rack. This problem causes less product to be painted and gives an inaccurate count of finished parts. Hooks that can be removed and easily replaced are desirable.

Part hooks made of stainless steel will retain strength for a longer period of time, particularly if cleaned in a burn-off oven. Stainless steel is also a requirement if spring steel is used to avoid annealing. Most burn-off ovens operate at approximately 800°F, whereas the annealing temperature of stainless steel is approximately 1,900°F.

Flexibility

Flexibility in racking is very important in any finishing job, large or small. The flexibility achieved with modular racking gives one the ability to concentrate on density and obtain it quickly. Moving part hooks around is not the important part of flexibility. It is having the ability to put a rack together quickly, without

welding,and to clean and reuse rack materials for multiple jobs. Modular racking systems offer the ability to stock rack materials for new designs or quick changeover when needed. Some rack companies offer design and engineering for custom rack needs. They can also supply custom hooks that will work with your existing racks.

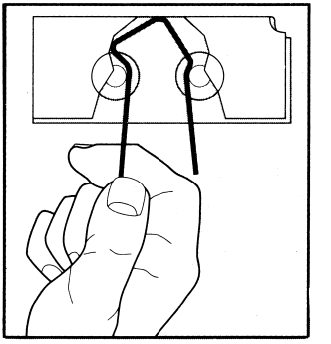


Fig. 2. Crossbar covers removable hook.

SUMMARY

Racking parts for density will significantly increase profits. If the parts being finished lend themselves to modular racking, it is well worth the time to address the issues of density, ground, maintenance,and flexibility. Most finishing systems have been designed to run faster than they actually do.

appendix a

DEFENSE & CIVILIAN SPECIFICATIONS*

The following listing has been compiled from the latest available edition of the Department of Defense Index of Specifications and Standards (DODISS), which includes unclassified Federal and Military specifications, standards, and related documents as well as non-government standards adopted for DOD use. Note: Only "active" files are included here.

ALUMINUM & ALUMINUM ALLOYS

AMS2477—Conversion Coating for Aluminum Alloys, Low Electrical Resistance
ASTM-B136-84(2003)—Standard Method for Measurement of Stain Resistance of Anodic Coatings on Aluminum
ASTM-B253-87(2005)e1—Standard Guide for Preparation of Aluminum Alloys for Electroplating
ASTM-B449-93(2004)—Standard Specification for Chromates on Aluminum
ASTM-B921-02—Standard Specification for Non-hexavalent Chromium Conversion Coatings on Aluminum and Aluminum Alloys
ASTM-D1730-09—Standard Practices for Preparation of Aluminum and Aluminum-Alloy Surfaces for Painting
ASTM-D1731-09—Standard Practices for Preparation of Hot-Dip Aluminum Surfaces for Painting
MIL-A-8625F(1)—Anodic Coatings for Aluminum & Aluminum Alloys
MIL-DTL-512C NOT 1—Aluminum Powder, Flaked, Atomized
MIL-DTL-5541F—Chemical Conversion Coatings on Aluminum/Alloys
MIL-DTL-83488D—Aluminum Coating (High Purity)
MIL-HDBK-341—Process for Coating Aluminum & Silicon Diffusion
MIL-M-17999C NOT 1—Metal, Expanded, Aluminum

BLACK OXIDE

AMS2485J—Coating, Black Oxide
MIL-DTL-13924D NOT-1 Black Oxide Coating for Ferrous Metals

CARC COATINGS

MIL-DTL-53039B—Aliphatic Polyurethane, Single Component, Chemical Agent Resistant Coating
MIL-DTL-53072C—Application of CARC Coating; Quality Controls
MIL-DTL-53084A—Primer, Cathodic Electrodeposition (CARC)
MIL-DTL-64159— Water Dispersable Aliphatic Polyurethane, Chemical Agent Resistant Coating

CHROMIUM AND CHROMIUM ALLOY PLATING

AMS2438B—Chromium Plating: Thin, Hard, Dense Deposit
ASTM B177-01(2006)e1—Standard Guide for Engineering Chromium Electroplating
ASTM-B630-88(2006)—Standard Practice for Preparation of Chromium for Electroplating with Chromium
ASTM-B650-95(2002)—Standard Specification for Electrodeposited Engi-

neering Chromium Coatings on Ferrous Substrates
ASTM-B921-02—Standard Specification for Non-hexavalent Chromium Conversion Coatings on Aluminum and Aluminum Alloys

MIL-C-20218F NOT 1—This specification covers porous, electrodeposited chromium plating applied to surfaces where a lubricating film must be sustained, such as cylinder bores.

MIL-DTL-14538D NOT 1—Chromium Plating, Black (Electrodeposited). Generally applied to steels but may be used as a plating for other metals such as brass, copper, iron, and chromium.
MIL-DTL-23422F—Chromium Plating (Electrodesposited)

CLEANING & SURFACE PREPARATION

AMS1377—Remover for Paint Epoxy and Polyurethane Paint System Non-Chlorinated Solvent
AMS1375B—Remover for Paint, Epoxy and Polyurethane Paint Systems
AMS1374A—Remover for Polyurethane/Epoxy Paint Alkaline, Hot-Tank Type
AMS1385A—Compound, Hot Carbon and Paint Remover for Aircraft Turbine Engine Components
AMS2480—Phosphate Treatment Paint Base
AMSC27725—Coating, Corrosion Preventative for Aircraft Integral Fuel Tanks
AMSC83231A—Coatings, Polyurethane, Rain Erosion Resistant for Exterior Aircraft and Missile Plastic Parts
AMSC83445A—Coating System: Polyurethane, Nonyellowing, White, Rain Erosion Resistant, Thermally Reflective
AMSR81903— Acid Activated Remover for Amine-Cured Epoxy Coating Sys tems
AMS1388A—Remover for Temporary Coating Alkaline Type, Water Base
AMS1376B—Remover for Epoxy Paint Acid-Type, Thickened
AMS3167—Solvents, Wipe for Cleaning Prior to Primer & Topcoat
AS7109/4—NADCAP Requirements for Stripping of Coated Material
AMSP38336—Primer Coating, Inorganic, Zinc Dust Pigmented, Self-Curing, for Steel Surfaces
ASTM-A967-05el—Standard Specification for Chemical Passivation Treatments for Stainless Steel Parts
ASTM-B322-99(2004)—Standard Guide for Cleaning Metals Prior to Plating
ASTM-B851-04—Standard Specification for Automated Controlled Shot Peening of Metallic Articles Prior to Nickel, Autocatalytic Nickel, or Chromium Plating, or as Final Finish
ASTM-D7055-04—Standard Practice for Preparation (by Abrasive Blast Cleaning) of Hot-Rolled Carbon Steel Panels to Test Coatings
DOD-P-15328D(1) NOT 1—Primer, Pretreatment for Metal Surfaces
MIL-B-23958A(1)—Metal Brightening for Aircraft (Brush, Cleaning)
MIL-C-8514C(1)—Coating Compound Metal Pretreatment Resin Acid
MIL-C-43616C(2)—Cleaning Compounds Aircraft Surface
MIL-C-46487 NOT2—Cleaning & Preparation, Organic Coatings
MIL-DTL-053022C—Primer, Epoxy Coating (Lead, Chromate Free)
MIL-P-53022B—Primer: Epoxy Coating (Chromate free)

MIL-P-81985(1)—Peening of Metals
MIL-P-85499—Primer Material
MIL-P-85891A(2)—Plastic Media (For Removal of Organic Coatings)
MIL-PRF-6864E—Cleaning Compound, Solvent, Oil Cooler
MIL-PRF-9954B—Glass Beads for Cleaning & Peening
MIL-PRF-11090H(1)—Degreasing & Depreserving Solvent
MIL-PRF-26915D—Primer (Coating Steel)
MIL-PRF-83756D—Blast Cleaning Machines
MIL-PRF-83936C—Paint Remover (Aircraft Wheels & Landing Gear Components)
MIL-PRF-85582D(1)—Primer Coatings: Epoxy, Waterborne
MIL-PRF-87937D—Cleaning Compound (Aerospace Equipment)
MIL-PRF-87978A—Paint Remover (Aircraft Wheels & Landing Gear Components)
TT-P-1757B—Primer Coating: One-Component Alkyd Base
TT-P-2760A—Primer Coating: Polyurethane, High Solids
TT-R-2918A-NOT 1—Paint Removal (No Hazardous Air Pollutants)

COATING MATERIALS, METHODS

A-A-59166—Coatings for Non-Slip Walkways on Aircraft Surfaces
AMS2447C—Thermal Spray Coating, High Velocity Oxygen/Fuel Process
AMS2526B—Molybdenum Disulfide Coating, Thin Lubricating Film, Impingement Applied
AMS2506—Coating of Fasteners, Aluminum Filled, Ceramic Bonded Coating
AMS2516D—Polytetrafluoroethylene (ptfe) Resin Coating, High Build, 370-400Mdc (698-752Mdf) Fusion
AMS2515E—Polytetrafluoroethylene (ptfe) Resin Coating, Low Build, 370-400Mdc (698-752Mdf) Fusion
AMS3678B—Polytetrafluoroethylene (PTFE) Moldings and Extrusions, Unfilled, Pigmented, and Filled Components
AMS3095A—Paint: High Gloss for Airline Exterior System
AMS3120F—Glyceryl Phthalate, Black Baking Enamel
AMS3125F—Glyceryl Phthalate, Engine Gray Baking Enamel Impingement Applied
AMS3143—Powder Coating Materials, Epoxy
AMS3145C—Paint, Marking Epoxy
AMS2525C—Graphite Coating: Thin Lubricating Film Impingement Applied
AMS2437C—Coating: Plasma Spray Deposition
AMS3143A—Powder Coating Materials, Epoxy
AMSP21600—Paint System, Fluorescent, Removable, for Aircraft Application
AMS3108E—Primer, Ocher, Phenolic
AMS3116—Primer Coating Epoxy, Chemical & Solvent Resistant, Non-Chromate
AMS3138D—Fluorocarbon Elastomeric Coatings (various)
AMS3136E—Coating Material: Phenolic Resin, ptfe Filled Pigmented, 150Mdc (302Mdf) Cure
AMS3130F—Vehicle Paint, Glyceryl Phthalate
AMS3140—Coating: Urethane, Aliphatic Isocyanate, Polytetrafluoroethylene Filled
AMSC83231—Coatings, Polyurethane, Rain Erosion Resistant, Aircraft & Missiles
AS4984—Coating Requirements for Aerospace Hand Tools

AS133341—Process for Barrier Coating of Anti-Friction Bearings
ASTM-D16-07—Standard Terminology for Paint, Related Coatings, Materials, and Applications
MIL-C-17504B(2)—Coating Compound (Acrylic Clear)
MIL-C-83466 NOT-1—Polyurethane Coatings for Aircraft Applications
MIL-C-85322B(2)—Elastomeric Polyurethane Coating for Rain-Erosion
MIL-DTL-24631—(1C, 2B, 3B) Epoxy Paint for Navy Coating Formulas
MIL-HDBK-808—Finishing for Protective Ground Support Equipment
MIL-HDBK-1110/1—Handbook for Protective Coatings for Facilities
MIL-HDBK-1884—Plasma Spray Coating Deposition
MIL-P-14105D—Heat-Resistant Paint for Steel Surfaces
MIL-P-85089A—Painting Aircrew Escape Propulsion Systems
MIL-PRF-6799K—Sprayable, Strippable Coatings
MIL-PRF-19565C(1)—Coating Compounds (Thermal Insulation)
MIL-PRF-22750F—Coating Epoxy, High Solids
MIL-PRF-24712A(1)—Powder Coatings
MIL-PRF-32239—Coating Systems, Advanced Aerospace Applications
MIL-PRF-81352C—Aircraft Touch-up
MIL-PRF-85285D(1)—Polyurethane Coating for Aircraft & Support Equipment
MIL-STD-7179—Finishes, Coatings to Protect Aerospace Weapons Systems
TT-C-490E—Chemical Conversion Coatings & Pretreatments for Ferrous Surfaces, Base for Organic Coatings
TT-P-2756A—Polyurethane Coating, Self Priming Top Coat (Low VOC)

COBALT ALLOYS

MIL-C-24248B(1) NOT 1—Cobalt Alloy Castings, Wear- and Corrosion-Resistant
MIL-C-24252D—Cobalt Chromium Alloy Bars & Forgings
MIL-C-24689B—Cobalt Alloy Castings (Wear, Corrosion-Resistant)

COPPER

ASTM-B281-88(2001)—Standard Practice for Preparation of Copper and Copper-Base Alloys for Electroplating and Conversion Coatings
ASTM- B368-97(2003)e1—Standard Method for Copper-Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS Test)
ASTM-B734-97(2003)e1—Standard Specification for Electrodeposited Copper for Engineering Uses
MIL-C-16555D—Coating Compounds (Strippable, Sprayable)
MIL-C-24679—Copper Nickel Alloy Forgings
MIL-F-495E(1) NOT 2—Chemical Finish for Black, Copper Alloys
MIL-HDBK-698A NOT 1—Copper & Copper Alloy

CORROSION PREVENTION, COMPOUNDS

AMS3116A—Primer Coating: Epoxy, Chemical and Solvent Resistant Non-Chromated, Corrosion Preventive
AMSC27725A—Coating: Corrosion Preventive, Polyurethane for Aircraft Integral Fuel Tanks for Use to 250 Mdf (121 Mdc)
MIL-C-11796C—Corrosion Preventive Compound (Hot Application)
MIL-HDBK-729 NOT 1—Corrosion & Corrosion Prevention Metals

MIL-HDBK-1568—Materials & Processes for Corrosion Prevention in Aerospace Weapons Systems
MIL-HDBK-46164 NOT 1—Sealing & Coating Compounds (Corrosion Inhibitive)
MIL-PRF-81733D—Sealing & Coating Compound (Corrosion Inhibitive)

GOLD

ASTM-B488-01(2006)—Standard Specification for Electrodeposited Coatings of Gold for Engineering Uses
MIL-DTL-45204D—Gold Plating (Electrodeposited)

IRON OXIDE

MIL-I-85370—Iron Oxide, Yellow (Monohydrate)

MAGNESIUM ALLOYS

AMS2466A—Hard Anodic Coating of Magnesium Alloys Alkaline Type, High Voltage
ASTM-B480-88(2006)—Standard Guide for Preparation of Magnesium and Magnesium Alloys for Electroplating
ASTM-B879-97(2003)e1—Standard Practice for Applying Non-Electrolytic Conversion Coatings on Magnesium and Magnesium Alloys
ASTM-B893-98(2003)—Specification for Hard-Coat Anodizing of Magnesium for Engineering Applications
ASTM-D1732-03—Standard Practices for Preparation of Magnesium Alloy Surface for Painting
MIL-HDBK-305 NOT 1—Alloy for Temper Designation System
MIL-HDBK-693A NOT 1—Magnesium & Magnesium Alloy
MIL-M-46130(1) NOT 1—Magnesium-Lithium Alloy Plate, Sheet, & Forgings

MOLYBDENUM & MOLYBDENUM ALLOYS

ASTM-B629-77(2003)—Standard Practice for Preparation of Molybdenum and Molybdenum Alloys for Electroplating

NICKEL & NICKEL ALLOYS

ASTM-B343-92a(2004)e1—Standard Practice for Preparation of Nickel for Electroplating with Nickel
ASTM-B558-79(2003)—Standard Practice for Preparation of Nickel Alloys for Electroplating
ASTM-B733-04—Standard Specification for Autocatalytic (Electroless) Nickel-Phosphorus Coatings on Metal
MIL-C-24615A—Nickel Chromium-Columbium Alloy
MIL-C-24723—Nickel Copper Alloy Castings
MIL-DTL-23229E—Nickel Chromium Iron Alloy Bars & Forgings
MIL-DTL-32119—Electroless Nickel Coatings
MIL-HDBK-506—Process for Coating Chrome Aluminide
MIL-N-24106C & MIL-N-24549B(1)—Nickel-Copper Alloy Bars, Rods, & Forgings
MIL-N-24271A NOT 1—Nickel-Chromium-Iron Alloy Castings
MIL-N-24390B(1) NOT 1—Nickel Molybdenum Chromium Iron Sheet & Low-Carbon, Low-Silicon Nickel-Molybdenum-Chromium-Iron Plate

MIL-P-27418 NOT 3—Plating of Soft Nickel (Electrodeposited, Sulfamate Bath)
MIL-P-18317—Plating of Black Nickel on Brass, Bronze, or Steel (Plated)

PALLADIUM

ASTM-B679—Plating w/Palladium (Electrodeposited)
ASTM-B679-98(2004)e1—Standard Specification for Electrodeposited Coatings of Palladium for Engineering Use
ASTM-B867-95(2003)—Standard Specification for Electrodeposited Coatings of Palladium-Nickel for Engineering Use

PHOSPHATE COATINGS

MIL-DTL-16232G—Phosphate Coating: Heavy, Manganese or Zinc Base
MIL-HDBK-205A—Phosphatizing and Black Oxide Coating of Ferrous Metals

PLATING ON PLASTICS

ASTM-B532-85(2002)—Standard Specification for Appearance of Electroplated Plastic Surfaces
ASTM-B533-85(2004)—Standard Test Method for Peel Strength of Metal Electroplated Plastics
ASTM-B604-91(2003)e1—Standard Specification for Decorative Electroplated Coatings of Copper, Plus Nickel & Chromium on Plastics
ASTM-B727-04—Standard Practice for Preparation of Plastics Materials for Electroplating

RHODIUM

ASTM-B634-88(2004)e1—Standard Specification for Electrodeposited Coatings of Rhodium for Engineering Use

SILVER

ASTM-B700-97(2002)—Standard Specification for Electrodeposited Coatings of Silver for Engineering Use

STEEL

ASTM-B183-79(2004)e1—Standard Practice for Preparation of Low-Carbon Steel for Electroplating
ASTM-B242-99(2004)e1—Standard Guide for Preparation of High-Carbon Steel for Electroplating
ASTM-B254-92(2004)e1—Standard Practice for Preparation of and Electroplating on Stainless Steel
ASTM-B850-98(2004)—Standard Guide for Post-Coating Treatments of Steel for Reducing the Risk of Hydrogen Embrittlement
ASTM-B912-02—Standard Specification for Passivation of Stainless Steels Using Electropolishing
MIL-C-24637—Corrosion-Resistant Steel Castings (Martensitic)

TESTING

ASTM-B117-07a—Standard Practice for Operating Salt Spray Apparatus (Accelerated Corrosion Test)
ASTM-B201-80(2004)—Standard Practice for Testing Chromate Coatings on Zinc and Cadmium

ASTM-B244-97(2002)—Standard Test Method for Measurement of Thickness of Anodic Coatings on Aluminum and of Other Nonconductive Coatings on Nonmagnetic Basis Metals with Eddy-Current Instruments

ASTM-B457-67(2003)—Standard Test Method for Measurement of Impedance of Anodic Coatings on Aluminum

ASTM-B487-85(2007)—Standard Test Method for Measurement of Metal and Oxide Coating Thickness by Microscopical Examination of a Cross Section

ASTM-B489-85(2003)—Standard Practice for Bend Test for Ductility of Electrodeposited and Autocatalytically Deposited Metal Coatings on Metals

ASTM-B499-96(2002)—Standard Test Method for Measurement of Coating Thicknesses by the Magnetic Method: Nonmagnetic Coatings on Magnetic Basis Metals

ASTM-B504-90(2007)—Standard Test Method for Measurement of Thickness of Metallic Coatings by the Coulometric Method

ASTM-B537-70(2002)e1—Standard Practice for Rating of Electroplated Panels Subjected to Atmospheric Exposure

ASTM-B555-86(2007)—Standard Guide for Measurement of Electrodeposited Metallic Coating Thicknesses by Dropping Test

ASTM-B567-98(2003)—Standard Test Method for Measurement of Coating Thickness by the Beta Backscatter Method

ASTM-B568-98(2004)—Standard Test Method for Measurement of Coating Thickness by X-Ray Spectrometry

ASTM-B571-97(2003)—Standard Practice for Qualitative Adhesion Testing of Metallic Coatings

ASTM-B578-87(2004)—Standard Test Method for Microhardness of Electroplated Coatings

ASTM-B588-88(2006)—Standard Test Method for Measurement of Thickness of Transparent or Opaque Coatings by Double-Beam Interference Microscope Technique

ASTM-B602-88(2005)—Standard Test Method for Attribute Sampling of Metallic and Inorganic Coatings

ASTM-B636-84(2006)e1—Standard Test Method for Measurement of Internal Stress of Plated Metallic Coatings with the Spiral Contractometer

ASTM-B680-80(2004)—Standard Test Method for Seal Quality of Anodic Coatings on Aluminum by Acid Dissolution

ASTM-B764-04—Standard Test Method for Simultaneous Thickness and Electrode Potential Determination of Individual Layers in Multilayer Nickel Deposit (STEP Test)

ASTM-B767-88(2006)—Standard Guide for Determining Mass Per Unit Area of Electrodeposited and Related Coatings by Gravimetric and Other Chemical Analysis Procedures

ASTM-B809-95(2003)—Standard Test Method for Porosity in Metallic Coatings by Humid Sulfur Vapor ("Flowers-of-Sulfur")

ASTM-B839-04—Standard Test Method for Residual Embrittlement in Metallic Coated, Externally Threaded Articles, Fasteners, and Rod—Inclined Wedge Method

ASTM-B877-96(2003)—Standard Test Method for Gross Defects and Mechanical Damage in Metallic Coatings by the Phos-

phomolybdic Acid (PMA) Method
ASTM-B905-00(2005)—Standard Test Methods for Assessing the Adhesion of Metallic and Inorganic Coatings by the Mechanized Tape Test
ASTM-C756-87(2006)—Standard Test Method for Cleanability of Surface Finishes
ASTM-D268-01(2007)—Standard Guide for Sampling and Testing Volatile Solvents and Chemical Intermediates for Use in Paint and Related Coatings and Materials
ASTM-D609-00(2006)—Standard Practice for Preparation of Cold-Rolled Steel Panels for Testing Paint, Varnish, Conversion Coatings, and Related Coating Products
ASTM-D662-93(2005)—Standard Test Method for Evaluating Degree of Erosion of Exterior Paints
ASTM-D2201-99 —Standard Practice for Preparationof Zinc Coated & Zinc Alloy Coated Steel Panels for Testing Paint
ASTM-D2369-07 —Standard Test Method for Volatile Content of Coatings
ASTM-D3322-82(2005)—Standard Practice for Testing Primers and Primer Surfacers Over Preformed Metal
ASTM-D4146-96(2003)—Standard Test Method for Formability of Zinc-Rich Primer/Chromate Complex Coatings on Steel
ASTM-D4548-91 (2009)—Standard Test Method for Anion-Cation Balance of Mixed-Bed Ion Exchange Resins
ASTM-D5065-07 —Standard Guide for Assessing the Condition of Aged Coatings on Steel Surfaces
MIL-HDBK-728/1 NOT 1—Non-Destructive Testing

THINNERS

MIL-T-81772B(1)—Requirements for Three Types of Thinner to be Used in Reducing Aircraft Coatings

TIN & TIN ALLOYS

ASTM-B545-97(2004)e1—Standard Specification for Tin Coatings (Plated)
ASTM-B579-73(2004)—Standard Specification for Electrodeposited Coatings of Tin-Lead Alloy (Solder Plate)
ASTM-B605-95a(2004)—Standard Specification for Electrodeposited Coatings of Tin-Nickel Alloy

TITANIUM & TITANIUM ALLOYS

MIL-HDBK-697A NOT 1—Finishing Titanium & Titanium Alloys

TUNGSTEN & TUNGSTEN ALLOYS

ASTM-B481-68(2003)e1—Standard Practice for Preparation of Titanium and Titanium Alloys for Plating
ASTM-B482-85(2003)—Standard Practice for Preparation of Tungsten and Tungsten Alloys for Electroplating

ZINC & ZINC ALLOY

AMSC81562—Zinc Coatings (Mechanically Deposited)

ASTM-B252-92(2004)—Standard Guide for Preparation of Zinc Alloy Die Castings for Electroplating and Conversion Coatings
ASTM-B633-07—Standard Specification for Electrodeposited Coatings of Zinc on Iron and Steel
ASTM-B840-99(2004)—Standard Specification for Electrodeposited Coatings for Zinc Cobalt Alloy Deposits
ASTM-B841-99(2004)—Standard Specification for Electrodeposited Coatings for Zinc Nickel Alloy Deposits
ASTM-B842-99(2005)—Standard Specification for Electrodeposited Coatings for Zinc Iron Alloy Deposits
MIL-C-17711B—Chromate Coatings for Zinc Alloy Castings & Hot-Dip Galvanized Surfaces

** Active documents as of 11/1/12. Inactive specifications are omitted; superseding files for cancelled documents are noted where applicable. To download full PDFs, or to view a complete listing of specifications, visit the Department of Defense Index of Specifications at https://assist.daps.dla.mil/online/start//; www.sae.org for AMS Standardss; or www.astm.org for ASTM documents.*

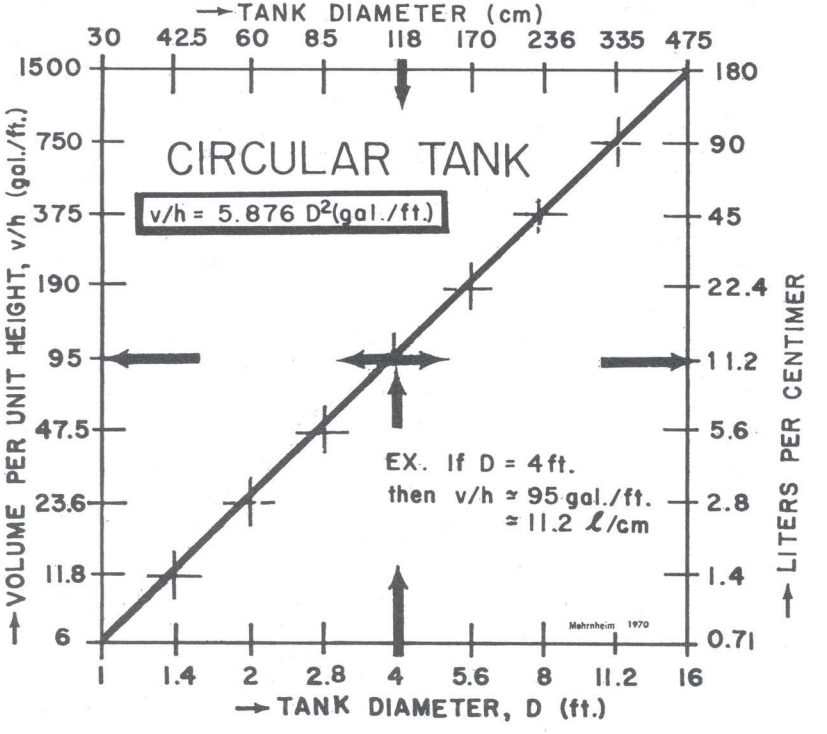
DETERMINING TANK CAPACITY

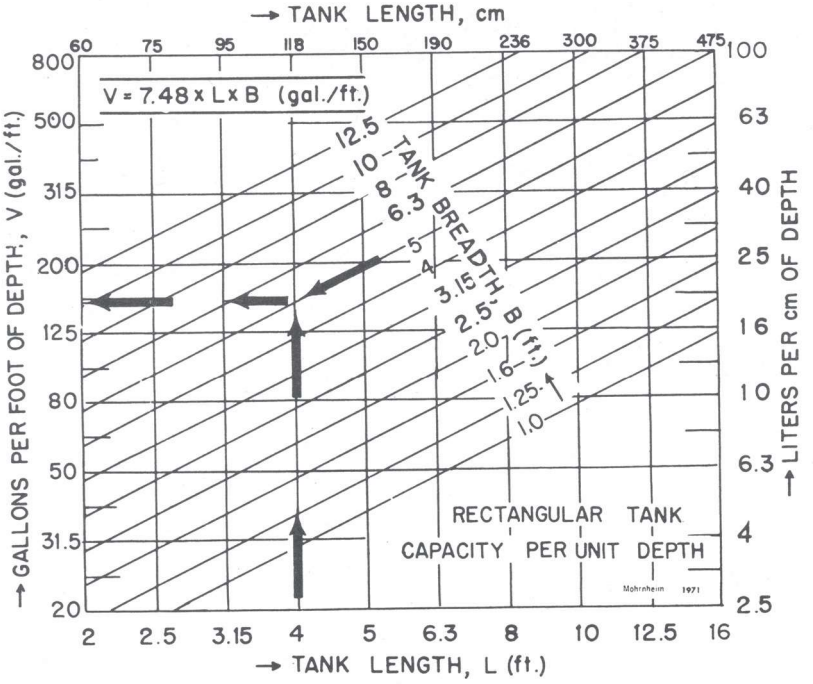
The two graphs shown offer visual guidelines for orientation and quick approximation of the quantity of solution in circular and rectangular containers. The graph "Circular Tank" shows, for round containers, the given diameter in feet at the lower scale. For convenience, the corresponding approximate metric diameter (cm) is shown opposite at the upper scale. Following the direction of the heavy arrows, shown for the Example, D = 4 ft (118 cm), one reads, at the height of the intersection of the corresponding vertical and the diagonal line, the solution volume per unit height (v/h) at the left ordinate, for example 95 gal/ft, corresponding to about 11.2 liters per centimeter shown at the right ordinate.

The graph "Rectangular Tank" shows the given breadth and length of the tank at the lower scale and at the diagonals, for example, B = 5 ft and L = 4 ft. At the intersection of the corresponding vertical and diagonal line, one reads 150 gal/ft at the left ordinate, or about 19 liters per centimeter at the right ordinate.

The solution level (height) is measured either by reading fixed height markings at the inside tank wall or from a ruler dipped to the bottom of the tank. The total solution volume, V (gal), is then equal to the solution height, h (ft), multiplied by V/h (gal/ft).

Note: The *preferred number sequences*, shown on the graphs, represent simplified evenly-divided log scales involving inaccuracies up to about 3 per cent. In most practices this





may be considered as inconsequential. For numerical exact results, the use of the equation at the upper left of the corresponding graph is recommended.

ESTIMATING PLATING TIME

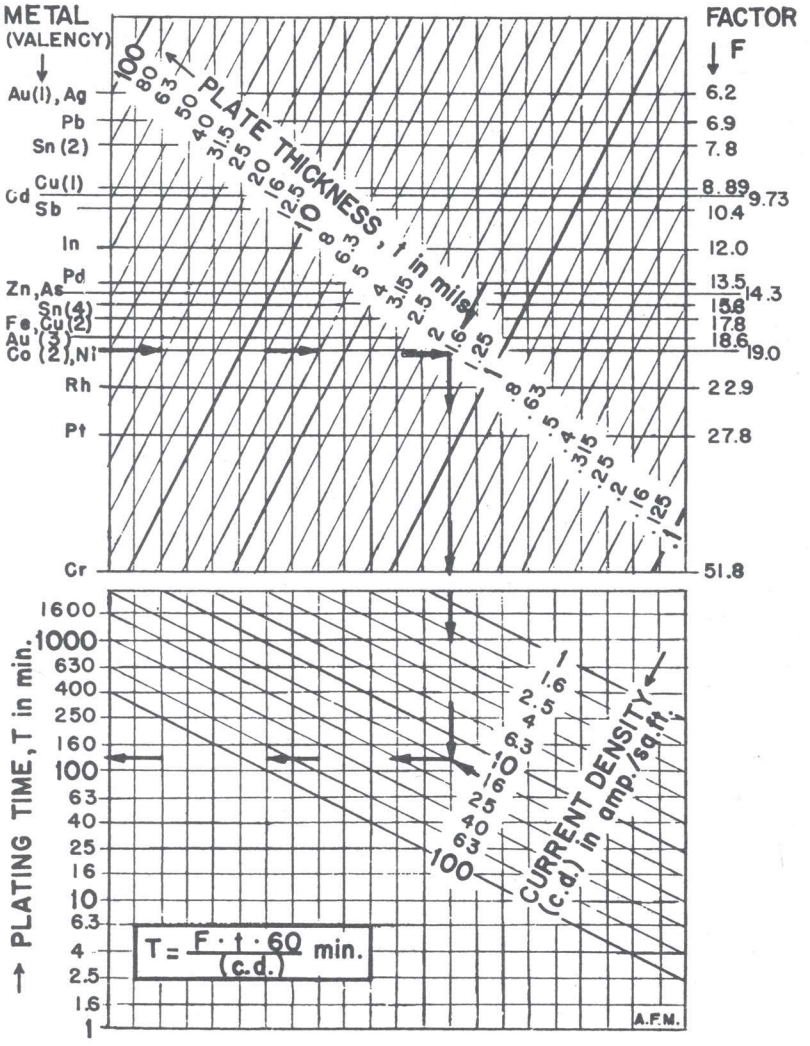
This nomograph is for the practical plater for convenient orientation and approximation of the plating time required to produce a specified plate thickness. The main factors involved are: the kind of metal, its valency in the bath (electrochemical equivalent), density of electroplate, and current density employed.

For using the diagram, one starts from the given plating bath at the upper left ordinate, as illustrated for nickel by the heavy arrows as an example, and goes horizontally to the right to the diagonal indicating the desired plate thickness, for example 1.6 mils. From the point of interception one goes vertically down to the diagonal indicating the applied current density, for example 16 amp./sq. ft. Following the arrow direction to the left, the approximate plating time can then be read from the ordinate, and is for the example somewhat larger than 100 minutes.

In order to obtain numerically exact values, the formula shown in the lower left corner of the diagram should be used. The factor F at the upper right ordinate is equal to the amp.

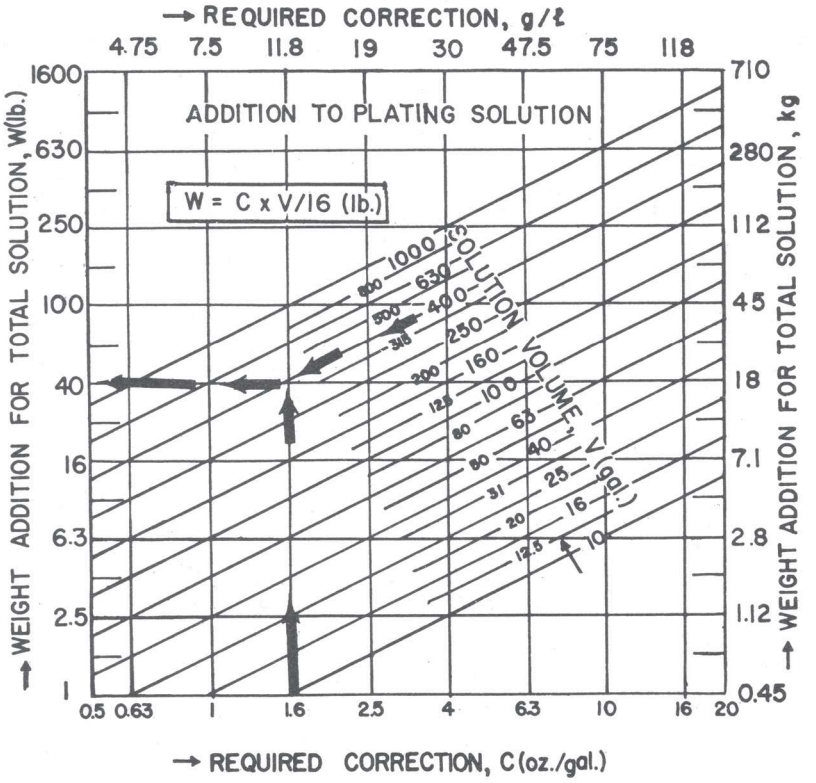
hr./sq. ft. to deposit 0.001 inch of electroplate thickness. The computation using F(Ni) = 19, t = 1.6 mils, c.d. = 16 amp./sq. ft. results in 114 minutes required plating time.

The diagram and the formula are based on 100% cathode efficiency. If the efficiency is less, for example 95% = 0.95, the theoretical plating time must be divided by this value, that is, 114/0.95 = 120 minutes = 2 hours.

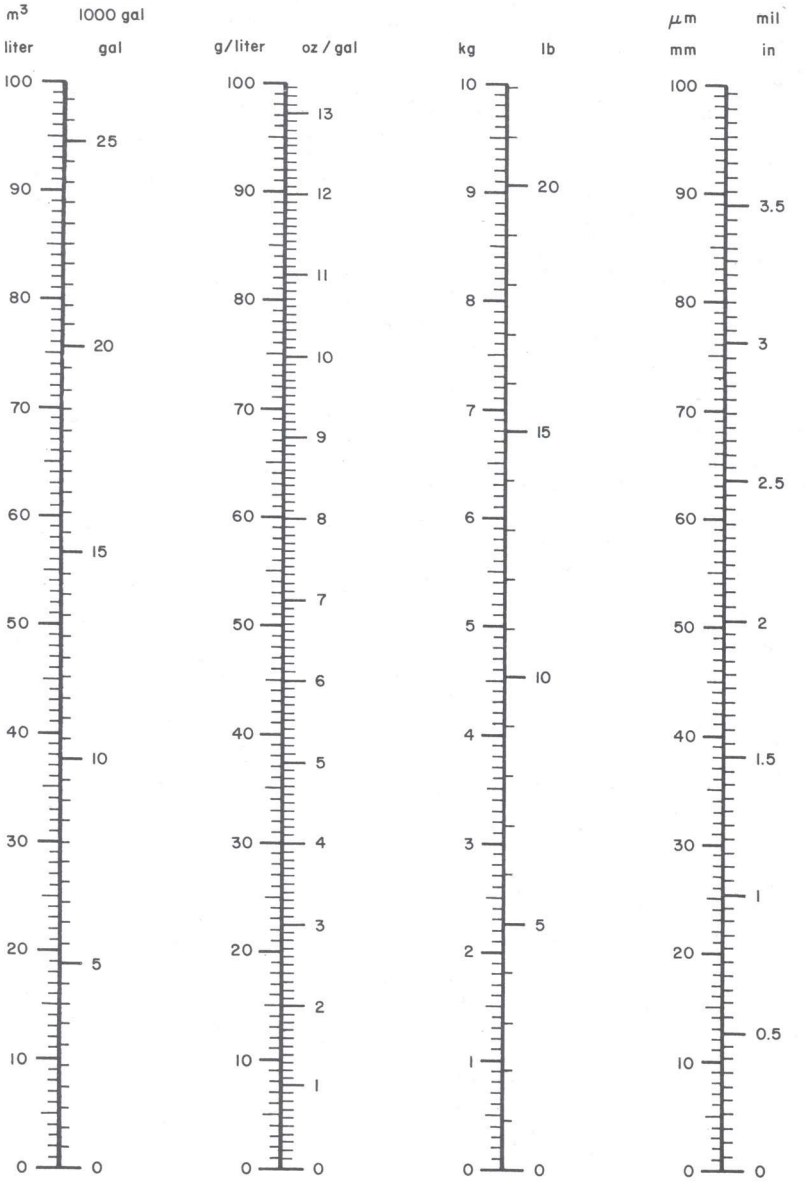


MAKING ADDITIONS TO PLATING SOLUTIONS

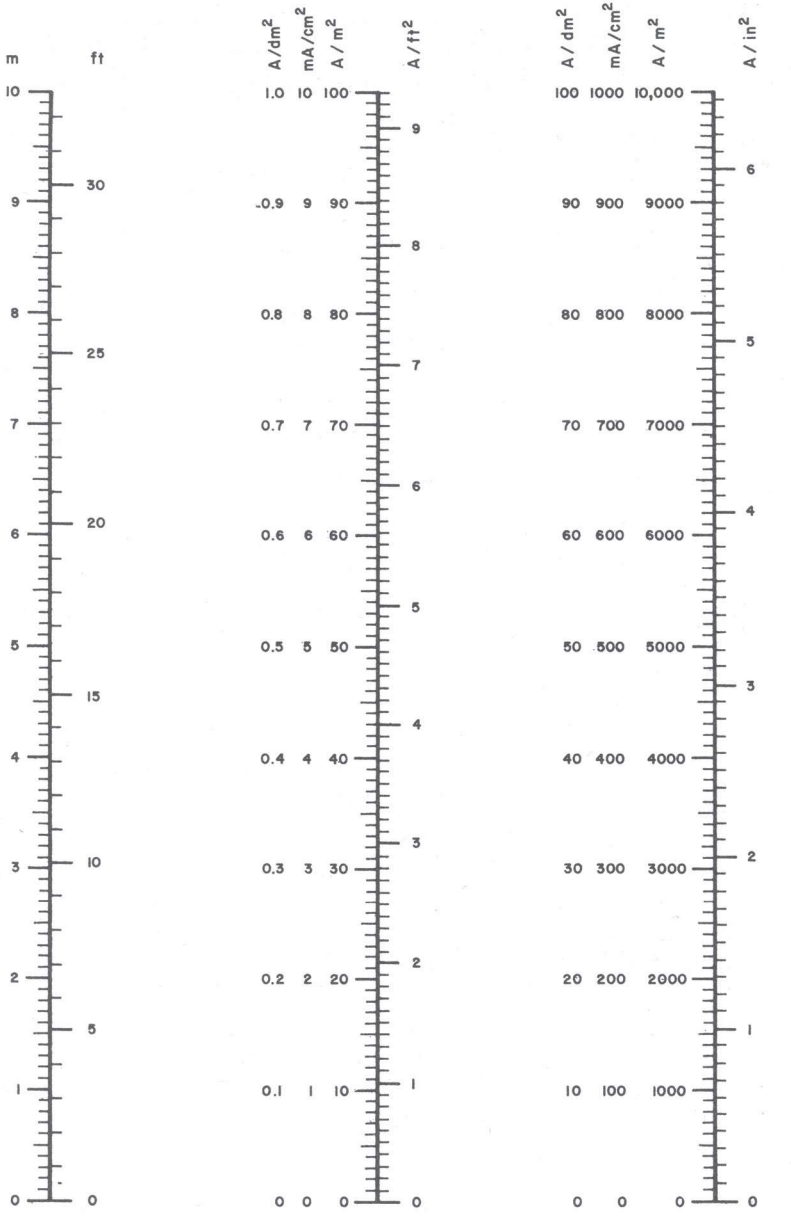
The directions of the heavy arrows show the problem solution for the example: if the required addition is 1.6 oz/gal (lower abscissa) for a 400 gal bath (diagonal) then 40 lbs of chemicals must be added (left ordinate). Numerically accurate solutions are obtained by using the inserted equation. For convenience, approximately corresponding metric values are shown at the upper abscissa and right ordinate.



English to Metric Conversion of Units
(Courtesy Fielding Ogburn, Consultant)



English to Metric Conversion of Units
(Courtesy Fielding Ogburn, Consultant)



METAL CONTENTS OF COMMON PLATING SALTS

(Note: Technical products usually vary slightly from stated percentages. Actual metal contents of precious metal salts are usually marked on package.)

Technical Name of Salt	Chemical Formula	Percent Metal
Aluminum chloride	$AlCl_3 \cdot 6H_2O$	11.1
Aluminum chloride (anhydrous)	$AlCl_3$	20.3
Aluminum sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$	8.1
Antimony trichloride	$SbCl_3$	53.4
Arsenic trioxide	As_2O_3	75.9
Cadmium chloride	$CdCl_2 2\frac{1}{2}H_2O$	49.3
Cadmium cyanide	$Cd(CN)_2$	68.3
Cadmium oxide	CdO	87.5
Cadmium sulfate	$3CdSO_4 \cdot 8H_2O$	43.3
Chloroplatinic acid	$H_2PtCl_6 \cdot 6H_2O$	37.7
Chromic acid	CrO_3	52.0
Cobalt chloride	$CoCl_2 \cdot 6H_2O$	24.8
Cobalt sulfate	$CoSO_4 \cdot 7H_2O$	21.0
Copper acetate	$Cu(C_2H_3O_2)_2 \cdot H_1O$	31.8
Copper carbonate (basic)	$CuCO_3 \cdot Cu(OH)_2$	57.5
Copper chloride (ic)	$CuCl_2 \cdot 2H_2O$	37.3
Copper cyanide (ous)	$CuCN$	71.0
Copper fluoborate	$Cu(BF_4)_2$	26.8
Copper potassium cyanide	$K_2Cu(CN)_3$	28.9
Copper pyrophosphate	$Cu_2P_2O_7$	42.3
Copper sodium cyanide	$Na_2Cu(CN)_3$	33.9
Copper sulfate	$CuSO_4 \cdot 5H_2O$	25.5
Ferric chloride (anhydrous)	$FeCl_3$	34.5
Ferric chloride	$FeCl_3 \cdot 6H_2O$	20.6
Ferric sulfate (anhydrous)	$Fe_2(SO_4)_3$	27.9
Ferrous ammonium sulfate	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	14.2
Ferrous chloride	$FeCl_2 \cdot 4H_2O$	28.1
Ferrous sulfate	$FeSO_4 \cdot 7H_2O$	20.1
Gold chloride (ic)	$AuCl_3 \cdot 2H_2O$	58.0
Gold cyanide (ous)	$AuCN$	88.3
Gold potassium cyanide	$KAu(CN)_2$	68.3
Gold sodium cyanide	$NaAu(CN)_2$	72.5
Indium chloride	$InCl_3$	51.8
Indium cyanide	$In(CN)_3$	59.4
Indium fluoborate	$In(BF_4)_3$	30.6
Indium sulfate	$IN_2(SO_4)_3$	44.3
Lead carbonate (basic)	$Pb(OH)_2 \cdot 2PbCO_3$	80.1
Lead fluoborate	$Pb(BF_4)_2$	54.4
Nickel acetate	$Ni(C_2H_3O_2)_2 \cdot 4H_2O$	23.6
Nickel ammonium sulfate	$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	14.9
Nickel carbonate (basic)	$2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$	50.0
Nickel chloride	$NiCl_2 \cdot 6H_2O$	24.7
Nickel cyanide	$Ni(CN)_2 \cdot 4H_2O$	32.1
Nickel fluoborate	$Ni(BF_4)_2$	25.3

(Continued on next page)

Technical Name of Salt	Chemical Formula	Per Cent Metal
Nickel sulfamate	$Ni(NH_2SO_3)_2$	23.4
Nickel sulfate	$NiSO_4 \cdot 6H_2O$	22.3
Palladium chloride	$PdCl_2$	60.0
Palladium diaminodinitrite (P Salt)	$Pd(NH_3)_2(NO_2)_2$	45.8
Platinum chloride (Commercial salt is often chloroplatinic acid)	$PtCl_4 \cdot 5H_2O$	45.7
Platinum diaminodinitrite (P Salt)	$Pt(NH_3)_2(NO_2)_2$	60.8
Potassium stannate	$K_2SnO_3 \cdot 3H_2O$	39.6
Rhodium chloride	$RhCl_3 \cdot 3H_2O$	39.1
Rhodium sulfate	$Rh_2(SO_4)_3$	20.8
Silver chloride	$AgCl$	75.2
Silver cyanide	$AgCN$	80.5
Silver nitrate	$AgNO_3$	63.5
Silver oxide	Ag_2O	93.3
Silver potassium cyanide	$KAg(CN)_2$	54.2
Silver sodium cyanide	$NaAg(CN)_2$	59.0
Silver sulfate	Ag_2SO_4	34.6
Sodium stannate	$Na_2SnO_3 \cdot 3H_2O$	44.5
Sodium tungstate	$Na_2WO_4 \cdot 2H_2O$	55.8
Tin chloride (ous)	$SnCl_2 \cdot 2H_2O$	52.6
Tin fluoborate (ous)	$Sn(BF_4)_2$	40.6
Tin sulfate (ous)	$SnSO_4$	55.3
Tungstic acid	H_2WO_4	73.6
Tungstic oxide	WO_3	79.3
Zinc carbonate	$ZnCO_3$	52.2
Zinc chloride	$ZnCl_2$	48.0
Zinc cyanide	$Zn(CN)_2$	55.7
Zinc fluoborate	$Zn(BF_4)_2$	27.3
Zinc oxide	ZnO	80.3
Zinc pyrophosphate	$Zn_2P_2O_7$	42.9
Zinc sulfate	$ZnSO_4 \cdot 7H_2O$	22.7
Zinc sulfate (anhydrous)	$ZnSO_4$	40.4
Zinc sulfate (exsiccated)	$ZnSO_4 \cdot H_2O$	36.5

CONVERSION FACTORS FOR PLATING CALCULATIONS

Grams per liter (g./L.) multiplied by 0.134 = avoirdupois ounces per gallon (oz./gal.).
Avoirdupois ounces per gallon (oz./gal.) multiplied by 7.5 = grams per liter (g./L.).
Grams per liter (g./L.) multiplied by 0.122 = troy ounces per gallon (tr. oz./gal.).
Troy ounces per gallon (tr. oz./gal.) multiplied by 8.2 = grams per liter (g./L.).
Grams per liter (g./L.) multiplied by 2.44 = pennyweights per gallon (dwt./gal.).
Pennyweights per gallon (dwt./gal.) multiplied by 0.41 = grams per liter (g./L.).
Amperes per square decimeter (amp./$dm.^2$) multiplied by 9.29 = amperes per sq. ft. (amp./$ft.^2$).
Amperes per square foot (amp./$ft.^2$) multiplied by 0.108 = amperes per square decimeter (amp./$dm.^2$).
Fluid ounces per gallon (fl. oz./gal.) multiplied by 7.81 = cubic centimeters per liter (cc./L.).

CENTIGRADE—FAHRENHEIT TEMPERATURE CONVERSION

Look up known temperature in center (bold face type) column. Its equivalent in either F or C can then be found in the appropriate column at left or right.

°F.		°C.	°F.		°C.	°F.		°C.
+ 32.0	± 0	−17.78	230.0	**110**	43.33	428.0	**220**	104.44
+ 35.6	+ 2	−16.67	233.6	**112**	44.44	431.6	**222**	105.56
+ 39.2	+ 4	−15.56	237.2	**114**	45.56	435.2	**224**	106.67
+ 42.8	+ 6	−14.44	240.8	**116**	46.67	438.8	**226**	107.78
+ 46.4	+ 8	−13.33	244.4	**118**	47.78	442.4	**228**	108.89
+ 50.0	+10	−12.22	248.0	**120**	48.89	446.0	**230**	110.00
+ 53.6	+12	−11.11	251.6	**122**	50.00	449.6	**232**	111.11
+ 57.2	+14	−10.00	255.2	**124**	51.11	453.2	**234**	112.22
+ 60.8	+16	− 8.89	258.8	**126**	52.22	456.8	**236**	113.33
+ 64.4	+18	− 7.78	262.4	**128**	53.33	460.4	**238**	114.44
+ 68.0	+20	− 6.67	266.0	**130**	54.44	464.0	**240**	115.56
+ 71.6	+22	− 5.56	269.6	**132**	55.56	467.6	**242**	116.67
+ 75.2	+24	− 4.44	273.2	**134**	56.67	471.2	**244**	117.78
+ 78.8	+26	− 3.33	276.8	**136**	57.78	474.8	**246**	118.89
+ 82.4	+28	− 2.22	280.4	**138**	58.89	478.4	**248**	120.00
+ 86.0	+30	− 1.11	284.0	**140**	60.00	482.0	**250**	121.11
+ 89.6	+32	± 0.00	287.6	**142**	61.11	485.6	**252**	122.22
+ 93.2	+34	+ 1.11	291.2	**144**	62.22	489.2	**254**	123.33
+ 96.8	+36	+ 2.22	294.8	**146**	63.33	492.8	**256**	124.44
+100.4	+38	+ 3.33	298.4	**148**	64.44	496.4	**258**	125.56
+104.0	+40	+ 4.44	302.0	**150**	65.56	500.0	**260**	126.67
107.6	**42**	5.56	305.6	**152**	66.67	503.6	**262**	127.78
111.2	**44**	6.67	309.2	**154**	67.78	507.2	**264**	128.89
114.8	**46**	7.78	312.8	**156**	68.89	510.8	**266**	130.00
118.4	**48**	8.89	316.4	**158**	70.00	514.4	**268**	131.11
122.0	**50**	10.00	320.0	**160**	71.11	518.0	**270**	132.22
125.6	**52**	11.11	323.6	**162**	72.22	521.6	**272**	133.33
129.2	**54**	12.22	327.2	**164**	73.33	525.2	**274**	134.44
132.8	**56**	13.33	330.8	**166**	74.44	528.8	**276**	135.56
136.4	**58**	14.44	334.4	**168**	75.56	532.4	**278**	136.67
140.0	**60**	15.56	338.0	**170**	76.67	536.0	**280**	137.78
143.6	**62**	16.67	341.6	**172**	77.78	539.6	**282**	138.89
147.2	**64**	17.78	345.2	**174**	78.89	543.2	**284**	140.00
150.8	**66**	18.89	348.8	**176**	80.00	546.8	**286**	141.11
154.4	**68**	20.00	352.4	**178**	81.11	550.4	**288**	142.22
158.0	**70**	21.11	356.0	**180**	82.22	554.0	**290**	143.33
161.6	**72**	22.22	359.6	**182**	83.33	557.6	**292**	144.44
165.2	**74**	23.33	363.2	**184**	84.44	561.2	**294**	145.56
168.8	**76**	24.44	366.8	**186**	85.56	564.8	**296**	146.67
172.4	**78**	25.56	370.4	**188**	86.67	568.4	**298**	147.78
176.0	**80**	26.67	374.0	**190**	87.78	572.0	**300**	148.89
179.6	**82**	27.78	377.6	**192**	88.89	590.0	**310**	154.44
183.2	**84**	28.89	381.2	**194**	90.00	608.0	**320**	160.00
186.8	**86**	30.00	384.8	**196**	91.11	626.0	**330**	165.56
190.4	**88**	31.11	388.4	**198**	92.22	644.0	**340**	171.11
194.0	**90**	32.22	392.0	**200**	93.33	662.0	**350**	176.67
197.6	**92**	33.33	395.6	**202**	94.44	680.0	**360**	182.22
201.2	**94**	34.44	399.2	**204**	95.56	698.0	**370**	187.78
204.8	**96**	35.56	402.8	**206**	96.67	716.0	**380**	193.33
208.4	**98**	36.67	406.4	**208**	97.78	734.0	**390**	198.89
212.0	**100**	37.78	410.0	**210**	98.89	752.0	**400**	204.44
215.6	**102**	38.89	413.6	**212**	100.00	770.0	**410**	210.00
219.2	**104**	40.00	417.2	**214**	101.11	788.0	**420**	215.56
222.8	**106**	41.11	420.8	**216**	102.22	806.0	**430**	221.11
226.4	**108**	42.22	424.4	**218**	103.33	824.0	**440**	226.67

ATOMIC WEIGHTS OF THE ELEMENTS

	Symbol	Atomic number	Atomic weight
Aluminum	Al	13	26.97
Antimony	Sb	51	121.76
Argon	A	18	39.944
Arsenic	As	33	74.91
Barium	Ba	56	137.36
Beryllium	Be	4	9.02
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Carbon	C	6	12.010
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Columbium	Cb	41	92.91
Copper	Cu	29	63.57
Dysprosium	Dy	66	162.46
Erbium	Er	68	167.2
Europium	Eu	63	152.0
Fluorine	F	9	19.00
Gadolinium	Gd	64	156.9
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	197.2
Hafnium	Hf	72	178.6
Helium	He	2	4.003
Holmium	Ho	67	164.94
Hydrogen	H	1	1.0080
Indium	In	49	114.76
Iodine	I	53	126.92
Iridium	Ir	77	193.1
Iron	Fe	26	55.85
Krypton	Kr	36	83.7
Lanthanum	La	57	138.92
Lead	Pb	82	207.21
Lithium	Li	3	6.940
Lutecium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.93
Mercury	Hg	80	200.61
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Nickel	Ni	28	58.69
Nitrogen	N	7	14.008
Osmium	Os	76	190.2
Oxygen	O	8	16.0000
Palladium	Pd	46	106.7
Phosphorus	P	15	30.98
Platinum	Pt	78	195.23
Potassium	K	19	39.096
Praseodymium	Pr	59	140.92
Protactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.31
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.43
Scandium	Sc	21	45.10
Selenium	Se	34	78.96
Silicon	Si	14	28.06
Silver	Ag	47	107.880
Sodium	Na	11	22.997
Strontium	Sr	38	87.63
Sulfur	S	16	32.066
Tantalum	Ta	73	180.88
Tellurium	Te	52	127.61
Terbium	Tb	65	159.2
Thallium	Tl	81	204.39
Thorium	Th	90	232.12
Thulium	Tm	69	169.4
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	183.92
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

For most calculations in electroplating the nearest whole numbers may be employed.

ELECTROCHEMICAL EQUIVALENTS

Calculated on Basis of 100% Cathode Efficiency

Metal	*Symbol*	*Valence*	*Atomic Weight (1971)*	*Specific Gravity*	*Weight oz./sq. ft. for 0.001"*	*Thickness in inches of 1 oz./ sq. ft.*	*Grams Deposited Per Amp. Hr.*	*Ounces Per Amp. Hr.*	*Amp. Hr. Per. Sq. Ft. to Deposit 0.001"*
Antimony	Sb	3	121.75	6.62	.56	.00180	1.514	.053	10.4
Arsenic	As	3	74.92	5.72	.47	.00213	0.932	.033	14.4
Cadmium	Cd	2	112.40	8.65	.71	.00139	2.097	.074	9.73
Chromium	Cr	6	52.00	7.2	.59	.00169	0.323	.011	51.8
Cobalt (ous)	Co	2	58.93	8.9	.74	.00135	1.099	.039	19.0
Copper (ous)	Cu	1	63.54	8.96	.74	.00134	2.370	.084	8.89
Copper (ic)	Cu	2	63.54	8.96	.74	.00134	1.186	.042	17.8
Gold (ous)	Au	1	197.0	19.3	1.47*	.00068*	7.348	.236*	6.2
Gold (ic)	Au	3	197.0	19.3	1.47*	.00068*	2.449	.079*	18.6
Indium	In	3	114.82	7.31	.56*	.00182*	1.428	.045*	12.0
Iron (ous)	Fe	2	55.85	7.86	.65	.00153	1.042	.037	17.9
Lead	Pb	2	207.19	11.34	.94	.00106	3.865	.136	6.9
Nickel	Ni	2	58.71	8.90	.74	.00135	1.095	.039	19.0
Palladium	Pd	2	106.4	12.0	.86*	.00116*	1.985	.064*	13.5
Platinum	Pt	4	195.09	21.41	1.60*	.00062*	1.819	.058*	27.8
Rhodium	Rh	3	102.91	12.4	.95*	.00106*	1.280	.041*	22.9
Silver	Ag	1	107.87	10.5	.79*	.00126*	4.024	.129*	6.2
Tin (ous)	Sn	2	118.69	7.30	.61	.00164	2.214	.078	7.8
Tin (ic)	Sn	4	118.69	7.30	.61	.00164	1.106	.039	15.6
Zinc	Zn	2	65.38	7.14	.59	.00168	1.219	.043	14.3

*These figures are for 1 troy ounce per square foot.

appendix b
CALCULATION OF VOC IN COATINGS

This appendix provides an overview of the most important calculations, which environmental engineers and paint facility staff need to perform on a regular basis.

The calculations are actually quite easy to perform, and for each new concept one example is provided.

CALCULATING THE VOC OF A SIMPLE COATING MIXTURE

You wish to calculate the VOC content for a mixture comprising 1 gal of red alkyd enamel and 1/4 gal (0.25 gal) thinners. The respective VOC levels are 2.5 lb/gal for the enamel and 6.8 lb/gal for the thinners.

To perform the calculation, set up a table where the first column lists the names of the components that you will be mixing together and the second contains the number of gallons to be added. In the third, you enter the VOC content as given to you by the paint manufacturer on the Material Safety Data Sheet (MSDS) and the last column is the total amount of solvent (or VOC) for each of the components. In this case, the table would appear as shown in Table I.

Because the EPA assumes that all of the VOC (mostly the solvents) evaporates to cause emissions, the last column is headed "Emissions," instead of "VOC."

Step 1: Multiply the number of gallons by the VOC content to arrive at the total amount of VOC (or Emissions) for each component.

Step 2: After completing the last column, total the number of gallons in Column 2 as well as the lb of VOC (Emissions) in the mixture, Column 4. In this case the total number of gallons is 1.25 and the total Emissions 4.2 lb. Note that you do not need to total Column 3 as the result is meaningless.

Step 3: The final step requires you to divide the number of gallons in the mixture into the total Emissions.

Therefore, the VOC of one gallon of the mixed coating is:

VOC = 4.2 lb/1.25 gal = 3.36 lb/gal

In other words, if someone were to sample the coating you have just mixed, the VOC content would be 3.36 lb for one gallon of the mixture.

If your state coating rule specifies a maximum VOC content of 3.5 lb/gal, your mixture is in compliance.

CALCULATING THE VOC OF A TWO-COMPONENT COATING MIXTURE

You wish to mix a two-component coating in the ratio four parts Component A

Table I. Calculating VOC for a Simple Coating

Component	*Volume (gal)*	*VOC Content (lb/gal)*	*Emissions (lb)*
Red Alkyd Enamel	1.0	2.5	2.5
Thinner	0.25	6.8	1.7
Total	1.25		4.2

Table II. Calculating VOC for a Two-Component Coating Without Thinners

Component	*Volume (gal)*	*VOC Content (lb/gal)*	*Emissions (lb)*
Component A	4	3.6	14.4
Component B	1	1.5	1.5
Total	5		15.9

and one part Component B. For the time being, you will not add any thinners.

From the MSDS you get the following information:

Component A = 3.6 lb/gal

Component B = 2.2 lb/gal

Set up the same table as before and insert the given information into columns 1, 2 and 3 as shown in Table II. Following the same steps given in the previous example, you simply divide the total number of gallons of the mixture into the total Emissions.

Therefore, the VOC of one gallon of the mixture is:

VOC = 15.9/5 = 3.18 lb/gal

Once again, if someone were to sample the coating, the VOC content would be 3.18 lb for 1 gal of the mixture. Because the VOC content of the mixture is *below* 3.5 lb/gal, you are allowed to add thinners, if necessary, but under no circumstances are you allowed to exceed the 3.5 lb/gal limit.

CALCULATING THE VOC OF A TWO-COMPONENT COATING MIXTURE PLUS THINNERS

Suppose you do want to add thinners having a VOC of 6.4 lb/gal to the coating mixture in Table II. How much can you add before exceeding the regulatory limit?

There are two methods for making this determination. The first is quite simple and does not require any knowledge of algebra. The second is slightly more difficult, but a whiz for those who still remember their high school math.

Here is the simpler of the two methods. Suppose you were to add only one quart (0.25 gal) of thinner, would you exceed the VOC limit?

Solution Using Trial and Error

The results of the first trial are shown in Table III.

Following the same steps as given in the previous examples,

VOC = 17.5/5.25 = 3.33 lb/gal

Because the VOC content of the mixture is still *below* 3.5 lb/gal, you can afford to add slightly more, if necessary, but remember that under no circumstances may you exceed the 3.5 lb/gal limit.

Repeat the calculations by adding another quart (0.25 gal) of thinners. In re-

Table III. Calculating VOC for a Two-Component Coating With Thinners (First Trial)

Component	*Volume (gal)*	*VOC Content (lb/gal)*	*Emissions (lb)*
Component A	4.0	3.6	14.4
Component B	1.0	1.5	1.5
Thinners	0.25	6.4	1.6
Total	5.25		17.5

Table IV. Calculating VOC for a Two-Component Coating With Thinners (Second Trial)

Component	*Volume (gal)*	*VOC Content (lb/gal)*	*Emissions (lb)*
Component A	4.0	3.6	14.4
Component B	1.0	1.5	1.5
Thinners	0.5	6.4	3.2
Total	5.5		19.1

calculating the problem, a total of 1/2 gal of thinners has been added. (See Table IV).

$$VOC = 19.1/5.5 = 3.47\backslash \text{ lb/gal}$$

This is as far as you should go. By adding any more thinner to the coating, you will overshoot the 3.5 lb/gal limit.

It is important to understand that you should only add thinners if you cannot properly atomize the coating. By adding thinners you might be able to overcome a problem such as orange peel, or excessive film build (dry film thickness), but the trade off is that you are adding to air pollution.

Note

These regulations have been written for the sole purpose of reducing air pollution; therefore, *you should avoid adding thinners unless it is really required.*

There is one other critical point that must be borne in mind. When an EPA or state inspector takes a sample, it is sent to an analytical laboratory where the VOC content is determined. In the analytical test, a few drops (approximately 0.3–0.5 g) of the mixed coating are weighed into a small aluminum dish and heated to 230°F for 1 hr, after which the sample is weighed again. The loss of weight between the first and second weighing is due to the loss of VOC from the mixture. At this relatively high temperature, it is possible for some of the coating resin and other ingredients to evaporate.

According to the EPA definition of VOC, *everything* that evaporates, with the exception of water, inorganic compounds, and a few select number of exempt organic compounds, is considered to be VOC. Therefore, even though you calculated the VOC content of the mixture to be 3.47 lb/gal, it is possible that if you subjected a sample of the mixture to the laboratory procedure, the VOC content could be higher than 3.47 lb/gal. In fact, it could exceed the regulatory 3.5 lb/gal limit, which would cause you to be in violation of the regulation. For this reason you should always be cautious when adding thinners to ensure that you stay well below the regulatory limit. In the case of this problem, add less than 1/2 gal of thinners, thereby playing it safe.

Solution Using Algebra

This method assumes that the amount of thinners added is the unknown "y." Set up the table as before. The result is shown in Table V.

$$VOC = (15.9 + 6.4y)/(5.0+y)$$

Because you are constrained by the regulatory limit of 3.5 lb/gal, you can solve for y.

$$3.5 = (15.9 + 6.4y)/(5.0+y)$$
$$y = 0.55 \text{ gal}$$

Table V. Calculating VOC for a Two-Component Coating With Thinners (Algebraic Solution)

Component	*Volume (gal)*	*VOC Content (lb/gal)*	*Emissions (lb)*
Component A	4.0	3.6	14.4
Component B	1.0	1.5	1.5
Thinners	y	6.4	6.4y
Total	5.0 + y		15.9 + 6.4y

If you wanted to add thinners right up to the limit, you could add 0.55 gal, which is slightly higher than the 0.5 gal that was calculated by trial and error, but it is strongly advised not to go so close to the limit as you can easily overshoot the mark and find yourself with a costly violation. More importantly, since pollution prevention is now the name of the game, it is good practice to keep your addition of thinners to a minimum.

PROBLEMS THAT INCLUDE WATER

The following calculations will demonstrate how the EPA and states differentiate between solvent-borne and waterborne coatings.

If the coating is solely based on organic solvents, there is only one VOC content to report, such as 3.5 lb/gal. If you are dealing with a waterborne coating, such as a latex or water reducible, most EPA or state regulations require that the coating contain less than, e.g., 3.5 lb/gal, *less water*. What this means is that if you were able to remove the water from the coating, then the new "hypothetical" coating would need to have a VOC content less than 3.5 lb/gal.

To clarify this, imagine that you have a 1-gal can of waterborne coating, which contains a small amount of VOC, and a large amount of water. The coating is represented by Figure 1a, for which the volume solids is, say 25%. Assume that the ratio of VOC to solids is 1:10 by volume.

Now suppose you had another 1-gal can with identically the same solid ingredients (resins, pigments, extenders, and additives), and maintained the VOC to solid ratio at 1:10, such as in Figure 1b. Imagine now that you wanted to paint two *identical* large walls so that you would deposit exactly 1 mil (0.001 in.) of *solid* coating onto each.

The first wall will be painted using the waterborne coating, and the second with the solvent-borne. In each case, you would stop painting as soon as the entire surface had a coating film of exactly 1-mil dry film thickness. Which of the two coatings will emit more VOC into the air?

They will both emit exactly the same amount of VOC, because in each case the *amount of solid coating deposited* is identical, and in each case the ratio of VOC to solid is the same. For instance, if you were to apply 1 gal of solid of the waterborne coating you would emit 0.1 gal of VOC (ratio of VOC to solid is 1:10). In the case of the solvent-borne coating, you would also need to apply 1 gal of solid coating to achieve the 1 mil thickness, and for the same reason you would emit 0.1 gal of VOC.

In other words, *regardless of how much water is in the coating*, the amount of VOC emitted will solely depend on the ratio of VOC to solid, in this case 1:10. For this reason, the regulations are written such that the coating may not contain more

Table VI. Calculating VOC for a Two-Component Solvent-Borne Coating Plus Water (Example 2)

Component	*Volume (gal)*	*VOC Content (lb/gal)*	*Emissions (lb)*
Component A	3	3.1	9.3
Component B	1	1.8	1.8
Water	7	0.0	0.0
Total	4		11.1

VOC than "x" lb/gal, *less water*. In the case of a 3.5 lb/gal limit, the regulation would specifically state that the coating may not contain more than 3.5 *lb/gal, less water*.

The following calculations will demonstrate this concept.

Example 1: Single-Component Solvent-Borne Coating Plus Water

A state regulation limits you to a coating for which the VOC is less than 3.5 lb/gal, less water. You purchase 1 gal of solvent-borne coating, which contains no water, but has a VOC content of 5.0 lb/gal. To bring down the VOC content you decide to add 1 gal of water. What is the VOC content, less water, of the mixed coating? Would it now meet the regulatory requirement?

Regardless of how much water is added, the VOC content remains 5.0lb/gal, less water, and continues to be in violation of the regulation.

Example 2: Two-Component Solvent-Borne Coating Plus Water

What is the VOC content of the following two-component epoxy? Is it in compliance with a regulatory limit of 2.8 lb/gal, less water? The coating consists of three parts of Component A at 3.1 lb/gal, one part of Component B at 1.8 lb/gal, and 7 parts of water. (See Table VI.)

Neither Component A nor B contains water.

Notice that when you calculate the VOC of the coating mixture for *compliance* purposes, you must ignore the water altogether. Hence, in Column 2 the total is 4 and not 7.

$$VOC = 11.1/4 = 2.75 \text{ lb/gal, less water}$$

The mixture is in compliance with the regulation.

Example 3: Two-Component Solvent-Borne Coating Plus Water

You are provided with the following information concerning a waterborne coating. What is the VOC content, less water? The volume of water is 52%, the volume solids is 42%, and the density of the VOC only is approximately 7.36 lb/gal.

The % volume of VOC in the coating = 100 - 42 - 52 = 6%. For 1 gal of coat-

Table VI. Calculating VOC for a Two-Component Solvent-Borne Coating Plus Water (Example 2)

Component	*Volume (gal)*	*VOC Content (lb/gal)*	*Emissions (lb)*
Component A	3	3.1	9.3
Component B	1	1.8	1.8
Water	7	0.0	0.0
Total	4		11.1

APPENDIX C
CONVERSION CHARTS

Linear Measure Factors

	Meters (m)	*Deci-meters (dm)*	*Centi-meters (cm)*	*Milli-meters (mm)*	*Microns (μm)*	*Feet (ft)*	*Inches (in.)*	*Mils*
Meters	1	10	100	1,000	1,000,000	3.281	39.37	39,370
Decimeters	0.1	1	10	100	100,000	0.3281	3.937	3,937
Centimeters	0.01	0.1	1	10	10,000	0.03281	0.3937	393.7
Millimeters	0.001	0.01	0.1	1	1,000	0.003281	0.03937	39.37
Microns	1.0×10^{-6}	1.0×10^{-5}	1.0×10^{-4}	0.001	1	3.281×10^{-6}	3.937×10^{-5}	0.03937
Feet	0.3048	3.048	30.48	304.8	304,800	1	12	12,000
Inches	0.02540	0.2540	2.540	25.40	25,400	0.08334	1	1,000
Mils	2.54×10^{-5}	2.54×10^{-4}	0.002540	0.02540	25.4	8.334×10^{-5}	0.001	1

Notes: A micrometer is equivalent to one micron.
One kilometer equals 1,000 meters equals 0.6214 miles.
One mile equals 5,280 feet.

Surface Area Factors

	Square Meters (m^2)	*Square Deci-meters (dm^2)*	*Square Centi-meters (cm^2)*	*Square Milli-meters (mm^2)*	*Square Feet (ft^2)*	*Square Inches (in^2)*
Square Meters	1	100	10,000	1,000,000	10.76	1,550
Square Decimeters	0.01	1	100	10,000	0.1076	15.50
Square Centimeters	0.0001	0.01	1	100	0.001076	0.1550
Square Millimeters	1.0×10^{-6}	0.0001	0.01	1	1.076×10^{-5}	0.001550
Square Feet	0.09289	9.289	928.9	92,890	1	144
Square Inches	6.452×10^{-4}	0.06452	6.452	645.2	0.006944	1

Notes: One acre equals 43,560 ft^2.
One hectare equals 2.471 acres equals 1,000 m^2.
One square mile equals 2.590 km^2.

Volumetric Factors

	U.S. Gallons (gal)	*Liters (L)*	*Fluid Ounces (fl. oz.)*	*Pints*	*Quarts*	*Cups*	*Cubic Feet (ft^3)*
U.S. gallon	1	3.785	128	8	4	16	0.1337
Liters	0.2642	1	33.8	2.11	1.057	4.22	0.03531
Fluid ounces	7.813×10^{-3}	0.02957	1	0.0625	0.03125	0.125	0.001044
Pints	0.125	0.4732	16	1	0.5	2	0.01671
Quarts	0.25	0.9463	32	2	1	4	0.03342
Cups	0.0625	0.237	8	0.5	0.25	1	0.008354
Cubic feet	7.481	28.32	957.6	59.85	29.92	119.7	1

Notes: One cubic foot equals 1,728 cubic inches.
One liter equals 1,000 cubic centimeters or 61.025 cubic inches.
One gallon equals 231 cubic inches.
One Imperial gallon equals 1.2 U.S. gallons.

Weight Factors

	Pounds (lb)	*Ounces (oz)*	*Troy Ounces (tr. oz)*	*Kilograms (kg)*	*Grams (g)*	*Milligrams (mg)*	*Micrograms (μg)*
Pounds	1	16	14.58	0.4536	453.6	453,600	4.536×10^8
Ounces	0.06250	1	0.9115	0.02835	28.35	28,350	2.835×10^7
Troy ounces	0.06857	1.097	1	0.03110	31.10	31,100	3.110×10^7
Kilograms	2.205	35.28	32.15	1	1,000	1,000,000	1.0×10^9
Grams	0.002205	0.03527	0.03215	0.001	1	1,000	1,000,000
Milligrams	2.205×10^{-6}	3.527×10^{-5}	3.215×10^{-5}	1.0×10^{-6}	0.001	1	1,000
Micrograms	2.205×10^{-9}	3.527×10^{-8}	3.215×10^{-8}	1.0×10^{-9}	1.0×10^{-6}	0.001	1

Notes: One tonne is one metric ton and equals 1,000 kilograms.
One ton is 2,000 pounds.
One troy ounce equals 20 pennyweights.
One pound equals 7,000 grains.
One troy pound equals 12 troy ounces.
One gallon of water weighs 8.34 pounds at 60°F.
One g/m^2 equals 92.89 mg/ft^2

appendix d
FINISHING CALCULATOR

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"Reduce costs while maintaining or improving quality" is a common cry heard in the finishing industry. Finishers are required to provide a high-quality product at an ever-reduced cost. Reducing costs can be tricky or impossible if the right information is not known. A hidden cost might be missed or an area with a higher return could be overlooked. This section will discuss how to calculate and determine some of the major costs that are associated with a finishing system. Calculations discussed range from energy consumption to paint usage. The formulas and methods used in this section are for estimation purposes — actual cost could vary.

The formulas and calculations are presented in an easy-to-follow, step-by-step format, with explanations and examples. Worksheets that simplify the use of the formulas and calculations are included at the end of the paper.

ELECTRIC

Motors consume the majority of electrical energy in a finishing system. Calculations for energy consumption of a motor are straightforward. A formula for calculating energy consumption is listed below. Motors are used on pumps, blowers, conveyors, and cooling equipment. Motors consume a lot of electricity and it is beneficial to review the cost of operating them along with possible changes.

Energy consumption for an electric motor can be calculated using the following formula:

$$\frac{0.746 \times \text{horsepower of motor}}{\text{efficiency of motor}} \times \frac{\text{hours}}{\text{day}} \times \frac{\text{days}}{\text{year}} \times \frac{\text{cost}}{\text{Kilowatt hour}} = \frac{\$ \text{ to operate motor}}{\text{year}}$$

The 0.746 is used to convert horsepower to kilowatts. This formula can be used to determine the cost savings for a motor if it was turned off when not needed. The savings for switching to a higher efficiency motor can also be calculated. Examples on how to apply the formula are listed below. These are only two examples; many other applications of this formula exist.

Turning a Motor Off

Finishing systems contain pumps that operate 24 hours a day. Motors that consume electricity run these pumps. Do all of the pumps have to operate 24 hours a day? If a pump were only needed during production, what cost savings would be incurred if it were shut off during nonproduction hours? Hours of nonproduction equal

$$\frac{0.746 \text{ kW/hp} \times 20 \text{ hp}}{0.90 \text{ eff}} \times \frac{88 \text{ hr.}}{\text{week}} \times \frac{52 \text{ wk.}}{\text{year}} \times \frac{\$0.05}{\text{Kilowatt hour}} = \frac{\$3{,}793.00}{\text{year}}$$

88 hours a week — 8 hours a day during the week and 48 hours on the weekend.

Savings of $3,793 a year would be incurred if this pump were shut off during nonproduction hours.

High-Efficiency Motors

When replacing a motor is it worth upgrading to a high efficiency motor?

$$\frac{0.746\ \text{kW/hp} \times 20\ \text{hp}}{0.90} \times \frac{24\ \text{hours}}{\text{day}} \times \frac{365\ \text{days}}{\text{year}} \times \frac{\$0.05\ \text{cost}}{\text{Kilowatt hour}} = \frac{\$7{,}261}{\text{year}}$$

Assume motor efficiencies of 90% and 92%, a cost difference of $300, between the

$$\frac{0.746\ \text{kW/hp} \times 20\ \text{hp}}{0.92} \times \frac{24\ \text{hours}}{\text{day}} \times \frac{365\ \text{days}}{\text{year}} \times \frac{\$0.05\ \text{cost}}{\text{Kilowatt hour}} = \frac{\$7{,}103}{\text{year}}$$

two motors.

The cost of operating the 90% efficient motor:

The cost of operating a 92% efficient motor:

Annual savings for using a higher efficiency motor:

$7,261 - $7,103 = $157/year

Pay back for the higher efficiency motor:

$300/$157 = 1.91 years

After 1.91 years the high-efficiency motor has paid for its self. Savings incurred after 1.91 years and until the motor is replaced could be consider profit.

GAS

Heaters and ovens consume gas in a finishing system. Determining total gas consumption for an oven or heater is complicated and beyond the scope of this paper. The cost associated with the temperature adjustments of an oven, up or down, can be easily calculated. The temperature at which an oven operates de-

$$\frac{\text{SCFM of exhaust} \times \text{Temp change} \times 1.1 \times \text{hours/day} \times \text{days/year} \times \text{cost/million BTUs}}{1{,}000{,}000}$$

termines the amount of gas consumed by the oven. Many factors effect the temperature settings, type of parts being cured, bake time, air flow, product, etc.

Calculating the cost change when the temperature of the oven is changed can be accomplished using the following formula:

SCFM is standard cubic feet per minute and can be attained from drawings for the oven or the blower supplier. The factor 1.1 is used to convert SCFM and °F of air to BTU/hour. Example of how to use this formula is illustrated below.

$$\frac{30{,}000\ \text{SCFM} \times 10°\text{F} \times 1.1\ (\text{BTU/hour/SCFM °F}) \times 20\ \text{hours/day} \times 245\ \text{days/year} \times \$4.00\ \text{cost/million BTUs}}{1{,}000{,}000} = \$6{,}468/\text{year}$$

Oven Temperature Reduction

The temperature of an oven was lowered 10°F due to an air duct modification. What are the cost savings? The SCFM is 30,000, the cost/MBTU is $4.00, the oven operates 20 hours a day, and the plant operates 245 days a year.

Reducing the air temperature of the oven saved $6,468 dollars a year for this example. Gas savings are not the only savings that occur when the oven temperatures are reduced.

PAINT USAGE PER SQUARE FOOT

Paint usage per square foot can be calculated by totaling the amount of paint used then dividing it by the square footage of parts produced. Calculating paint per square foot using this method is accurate if the filmbuild is the same throughout the part and from part to part. If the filmbuild varies, the above method calculates the average paint used per square foot for all the pieces produced.

To accurately calculate the paint per square foot, for the different pieces produced, the filmbuild needs to be considered. Calculating the paint per square foot using the filmbuild is more complicated then the above method, but the results are more useful. The method using filmbuild is listed below.

$$\frac{144\ \text{in}^2/\text{ft}^2 \times \text{coating thickness in mils}}{\%\ \text{of volume solids of paint} \times 231\ \text{in}^3/\text{gal}} = \frac{\text{Gallons of paint}}{\text{ft}^2}$$

Calculating Paint Usage per Square Foot

Gallons of paint per square foot/Transfer efficiency
= Actual paint usage per square foot

The following formula uses the filmbuild to calculate paint usage per square foot:

One square foot is equal to 144 square inches. The factor 231 is used to convert cubic inches to gallons. Percent volume solids are available from the paint supplier.

The above formula provides the theoretical usage for a perfect paint system; the amount of paint used is equal to the amount applied. Real-world system losses are not considered. When calculating the actual usage, which takes into account the system losses, use the following formula:

Transfer efficiency is the percentage of paint that actually makes it to the part. How to determine transfer efficiency will depend on the type of paint and equipment used to apply the paint. Contact the equipment supplier and paint supplier for assistance on determining transfer efficiency. Knowing paint usage per square foot can be very beneficial. Usage for a new part can be calculated. The cost impact of a process modification could be calculated. The actual cost of coating a part could be determined. An example of how this formula follows.

Example

A plant produces 1,000,000 ft^2 of painted parts a month. It coats two parts, a large one and a small one. The large part accounts for 750,000 ft^2 a month, the small part 250,000ft^2. The large part has a paint thickness of 1.0 mil. The small part specification is a thickness of 1.0 mil, but because of the way the parts are mixed the small part has a paint thickness of 1.2 mils. If the parts where processed differently and the paint thickness of the small part was reduced to 1.0 mil, what reduction in paint would occur? Assume the percent volume solids are 35, the transfer efficiency is 90%.

Large part usage per ft^2
= [(144in^2/ft^2 x 0.001 in)/(35/100 x 231 in^3/gal)]/90/100 x 1.0 mil
= 0.001979 gal/ft^2 @ 1.0 mils

Total usage per month for the large part
= 0.001979 gal/ ft^2 x 750,000 ft^2
= 1,484 gals of paint per month

Small part paint usage per ft^2 @ 1.2 mils
= [(144 in^2/ft^2 x 0.001 in)/(35/100 x 231 in^3/gal)]/90/100 x 1.2 mil
= 0.002375gal/ft^2 @ 1.2 mils

Small part electrocoat usage per ft^2 @ 1.0 mils
= [[(144 in^2/ft^2 x 0.001in)/(35/100 x 231 in^3/gal)]/90/100) x 1.0 mil
=0.001979 gal/ft^2 @ 1.0 mils

Total paint usage per month for the small part @ 1.mils
= 0.002375 gal/ft^2 x 250,000 ft^2
= 593.7 gals per month

Total paint usage per month for the small part @ 1.0mils
= 0.001979 gal/ft^2 x 250,000 ft^2
= 494.75 gals of coating per month

If the small parts where coated at 1.0 mil instead of 1.2 mil the paint usage would be reduced about 100 gallons per month. To determine the percentage of the reduction divide 100 by the total usage.

Usage per square foot is a valuable tool when determining costs and changes in costs. The calculations should be used to determine how much paint is used and how changes might effect costs.

Work Sheet Electric Motor

Horsepower	_____A	Motor Efficiency	_____B
Hours/Day	_____C	Days/Year	_____D
Cost/kW	_____E	0.746 / B	_____F

Annual cost of operating a Motor

_____F * _____A * _____C * _____D * _____E = _____

Horsepower	_____A	Motor Efficiency	_____B
Hours/Day	_____C	Days/Year	_____D
Cost/KW	_____E	0.746 / B	_____F

Annual cost of operating a Motor

_____F * _____A * _____C * _____D * _____E = _____

Work Sheet Reducing Temperature of Oven

SCFM of Exhaust	_____A	Temperature Change	_____B
Hours/day	_____C	Days/Year	_____D
Cost/million BTUs	_____E		

Annual Savings for Temperature Reduction

0.000001 * _____A * _____B * _____C * _____D * _____E = _____

SCFM of Exhaust	_____A	Temperature Change	_____B
Hours/day	_____C	Days/Year	_____D
Cost/million BTUs	_____E		

Annual Savings for Temperature Reduction

0.000001 * _____A * _____B * _____C * _____D * _____E = _____

Work Sheet Paint Usage per Square Foot

% volume solids of paint _____A Coating thickness in mils _____B

% transfer efficiency _____C Square foot per part _____D

Total number of parts _____E

Paint usage per part:

144 * _____B /1000 = _____F _____A/100 * 231 = _____G

_____F / _____G = _____H _____H / _____C / 100 = _____I

_____I * _____D = _____J (Paint usage per part)

Total paint usage for a part:

Paint usage per part:

_____E * _____J = _____Total paint usage for a part

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Zinc Plating	black	Zylite® HT, Tridur® Zn H2, Sealer 3500 WL
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ZnNi Plating	black	Zinni AL 450, Unifix Ni 3-30 L, Sealer 3500 WL

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