THE SURFACE TREATMENT AND FINISHING OF ALUMINUM AND ITS ALLOYS

by P. G. SHEASBY
and R. PINNER

SIXTH EDITION

VOLUME 1

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by

P. G. SHEASBY, B.Sc., F.I.M.F.
R. PINNER, B.Sc., F.I.M.F., F.I.Corr.T.

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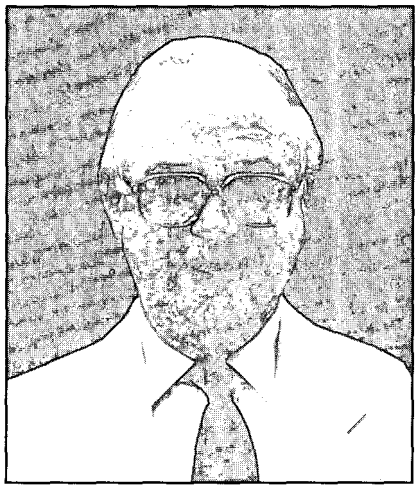
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Mr. Peter G Sheasby

Peter Sheasby, the principal Editor of this edition, has been involved in the finishing of aluminium since he joined the research staff of Alcan in 1960. He was educated at the University College School, Hampstead and University College, London, where he graduated with an Honours Degree in Chemistry in 1960. He then joined Aluminium Laboratories Ltd in Banbury to work in the metal finishing group on anodizing problems. Aluminium Laboratories, now Alcan International Ltd., is the European research centre for Alcan Aluminium Ltd. and Peter held several positions including Principal Scientist in the field of surfaces and interfaces and was Programme Manager in the automotive development area. In his last ten years at Alcan he was deeply involved in the development of weld-bonded aluminium automotive vehicle structures, for which he was recognised, with Jerry Powell of Ciba-Geigy Ltd., by the award of the Welding Institute Lillicrap Medal in 1994. He retired from full-time work at Alcan in 1997, but continues to work as a consultant.

Internationally known in the field of anodizing, Peter has published more than 60 papers in journals and at national and international conferences. With A.W. Brace he was the author of "The Technology of Anodizing Aluminium" and he was the main contributor to the 5th Edition of the present work. He is the author of some 12 patents on aluminium finishing and joining. In his work with Alcan he has travelled widely to provide technical support to Alcan's anodizing plants and to give advice on licensees and customers. He was also closely involved in Alcan's electrolytic colouring and adhesive bonding developments. He has been a Fellow of the Institute of Metal Finishing for many years and has been awarded their Westinghouse Prize and the Canning Bicentennial Medal. He was the first recipient of the Aluminium Federation Quality and Excellence Award for lifetime achievement in the aluminium field.

Peter has long been active in the production of standards for anodizing and has been Chairman of the British Standards committee on anodizing for over 20 years. He led the British delegation for the production of the ISO standards and is Chairman of the CEN committee (CEN TC132 WG 15) which has produced the equivalent European Standards.

He has also represented the Aluminium Federation at the Qualanod meetings in Zurich for many years. In his spare time, he is an enthusiastic botanist.

Preface to the Sixth Edition

It is now almost 50 years since this work was first published. Simon Wernick had a major involvement in its production and in the revision of subsequent editions. His wide-ranging knowledge, his many contacts with other experts around the world and his own fund of experience were invaluable. Latterly, however, his failing health followed by his death in 1998,precluded any involvement in this, the 6th Edition. The 17 years since the writing of the 5th edition have seen major advances, both in our understanding of the science underlying the subject, and the technologies as used in the finishing industry.

Work started on the 6'" edition almost 6 years ago and early on, it became apparent that no one person could be expected to undertake the revision single-handed. I therefore involved several specialist colleagues at Alcan International Ltd in the fields where they had more detailed knowledge than myself. Their input, backed by the general support and moral encouragement from Alcan, has been invaluable. Thus in the field of pretreatment, Dr. John Treverton has completely revised Chapter 5 to include details of extensive developments of chromium-free conversion coating systems. In Chapter 6, Dr. Robin Furneaux has succinctly summarised the substantial volume of literature which now gives a far better understanding of the mechanism of anodic film formation. Much of this is based on the extensive work carried out at the University of Manchester Institute of Science and Technology (UMIST) under Professor George Thompson, where Robin studied for his Ph.D. degree. Chapter 16 discusses effluent treatment, a topic which threatens to become more important than the surface treatment processes which precede it. Ted Short's first-hand knowledge of this would have been hard to find elsewhere. Ted has also been involved in the revision of Chapter 4 which covers cleaning and etching. Finally David Arrowsmith has again been a significant contributor, revising Chapters 2, 3 and 13. In his revision, David decided to combine the four relevant chapters in the 5th edition into the more concise single Chapter 13 which covers all aspects of plating onto aluminium and associated processes.

In all these areas the input of these authors has greatly enhanced the authority of the book, and their contributions are gratefully acknowledged. The many detailed changes which have been made are summarised below:–

Chapter 1 now includes a section on the mechanism of filiform corrosion.

Chapters 2 and 3 have minor revisions to bring them into line with current practices.

Chapter 4 has revised sections on cleaning, long-life etching and etch recovery, and includes new information on electrolytic cleaning and electrograining for lithographic purposes.

Chapter 5 has been modified, omitting much of the detail on the chemical oxidation processes which is now of only historic interest. Our increased knowledge of chromate-based conversion coatings and more recent developments of chromate- (and chromium)-free processes for pretreatment purposes is covered in depth.

In Chapter 6, accounts of many of the early theories of anodizing mechanism now proved to be incorrect have been condensed or omitted. The emphasis is on our current knowledge and theories of anodic film formation mechanisms, to which staff at UMIST have so greatly contributed.

Many additions have been made to Chapter 7, most notably those covering the increased use of phosphoric acid anodizing as a pretreatment in the aerospace industry and wherever adhesive bonding is involved. **A** new section on functional anodizing, covering anodizing for applications such as memory discs and filter membranes, has also been added.

Revisions in Chapter 8 include changes in architectural specifications and standards, recent advances in electrolytic colouring processes, including continuing development of interference finishes.

Chapter 9 includes details of the new British and European hard anodizing standards, recent work on abrasion and hardness testing and the use of lubricants with hard anodized finishes.

Chapter 10 expands earlier treatments on defects in dyeing, while Chapter 11 updates our knowledge of the mechanism of conventional sealing, and reflects the increased understanding of cold impregnation processes.

Chapter 12 reports changes in standard test methods for anodic coatings, including sections on the new paper abrasion test and new image clarity measurement methods. The latest information on weathering performance of anodic coatings is included.

Chapter 13 now consolidates the four chapters on plating onto aluminium from the previous edition into one. There is emphasis on the zincate and stannate preparation processes used almost exclusively in plating onto aluminium.

Chapter 14 emphasises aspects of organic finishing specific to aluminium, and the extensive work on filiform corrosion is summarised. Important quality control developments such as the introduction of the Qualicoat specification in Europe are covered.

Chapter 15 (vitreous enamelling) , reflects the relative maturity of this area while Chapter 16, by contrast sets out the increasingly stringent demands on effluent treatment. It now includes practical aspects of most types of effluent treatment plant used in conjunction with aluminium finishing processes and the mass of recent environmental legislation relating to the subject.

Finally the Appendices on aluminium and finishing specifications have been updated and now cover all the appropriate International and European Standards.

Many new Figures have been included, and the extent of the overall revision can be judged from the fact that over 1000 new references have been added.

Banbury, Oxon, 2001 P.G.S

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CHAPTER 1

Introduction: Aluminium, Its Properties, Alloys and Finishes

1. HISTORY, PROPERTIES AND ALLOYS

The history of the light metal industry, as that of many other industries in this century, is one of notable and ever accelerating expansion and development. There are few people today who are not familiar with at least some modern application of aluminium and its alloys. The part it plays in our everyday life is such that it is difficult to realise that a century ago the metal was still a comparative rarity.

The excellent corrosion resistance of pure aluminium is largely due to its affinity for oxygen; this results in the production of a very thin but tenacious oxide film which covers the surface as soon as a freshly-cut piece of the metal is exposed to the atmosphere. This oxide coating is of great significance in the production of practically every type of surface finish for the metal. It is, of course, the basis of what is probably the most corrosion-resistant finish of all, namely, that group of finishes which involves the technique of anodic oxidation in its varied forms. Here, the natural film is, in effect, greatly thickened and strengthened by electrochemical means.

On the other hand, the tenacity of the natural oxide film is a serious adverse factor in the production of other finishes, such as those based on electrodeposition, and also, but to a lesser extent, the organic finishes, as it must be removed or transformed before the alternative coating can be successfully applied. Special techniques have had to be evolved to effect this.

History of aluminium

Aluminium is a strongly electro-negative metal and possesses a strong affinity for oxygen; this is apparent from the high heat of formation of its oxide. For this reason, although it is among the six most widely distributed metals on the surface of the earth, it was not isolated until well into the nineteenth century.

Alumina (Al_2O_3) was known, however, in the eighteenth century, and the first unsuccessful attempts to isolate the metal were made by Sir Humphry Davy in 1807, when the isolation of the alkali metals had made a powerful reducing agent available. It was not, however, until 1825 that the Danish Worker, H.C. Oersted, succeeded in preparing aluminium powder by the reduction of anhydrous aluminium chloride with sodium amalgam; two years later, F. Wohler replaced the amalgam by potassium, and between 1827 and 1847 discovered and listed many of the chemical and physical properties. However, many years passed before the metal could be produced commercially.

The father of the light metal industry was probably the French scientist, Henri Sainte-Claire Deville, who in 1850 improved Wohler's method of preparation by replacing potassium by sodium, and by using the double chloride of sodium and aluminium as his source of the metal, thus making the production of aluminium a commercial proposition; the price of the metal, however, was still comparable with that of gold.

The production of aluminium received a further impetus when Robert Bunsen and, following him, Deville, showed how the metal could be produced electrolytically from its ores.

In 1885, the brothers Cowle produced the first aluminium alloys containing iron and copper, soon after which the invention of the dynamo made a cheaper supply of electricity available and resulted, in 1886, in Héroult's and Hall's independent French and American patents for the electrolytic production of aluminium from alumina and molten cryolite (AlF_3NaF). Thenceforth, the production of aluminium in Europe centred round the first factory in Neuhausen, while Hall's process was applied in the U.S.A. in Pittsburgh. Modern production of aluminium begins from the mineral bauxite, which contains approximately 25% of aluminium. This is converted to alumina by digestion with a solution of sodium hydroxide under pressure (the Bayer process), and the purified alumina produced is added to a molten mixture of cryolite and fluorspar. This mixture is electrolysed in a cell with carbon anodes (Fig. 1-1) and the molten mixture is tapped from the bottom of the cell.

Properties of aluminium

The three main properties on which the application of aluminium is based are its low density of approximately 2.7, the high mechanical strength achieved

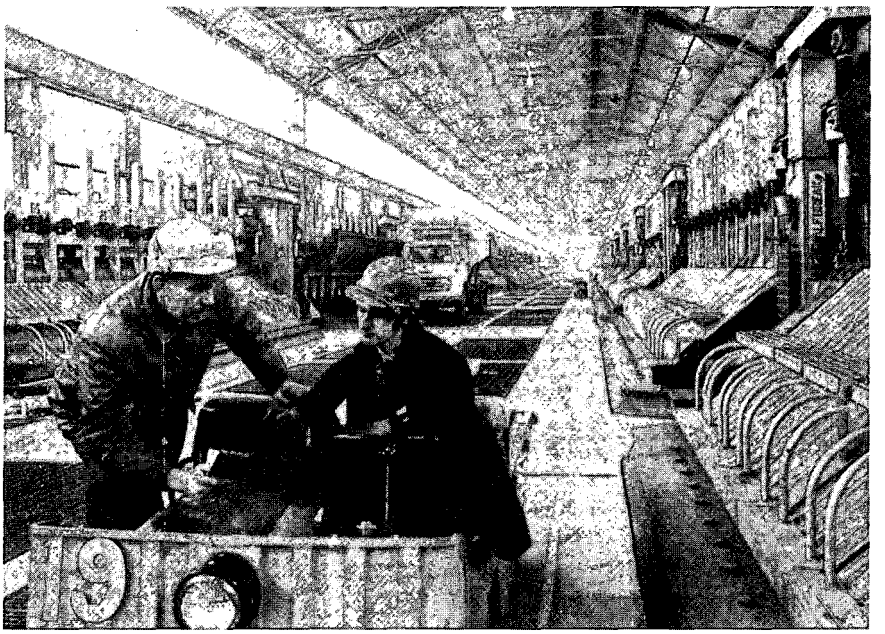


Fig. 1-1. Modern pot line at the British Alcan smelter at Lynemouth

by suitable alloying and heat treatments, and the relatively high corrosion resistance of the pure metal. Other valuable properties include its high thermal and electrical conductance, its reflectivity, its high ductility and resultant low working cost, its magnetic neutrality, high scrap-value, and the non-poisonous and colourless nature of its corrosion products which facilitates its use in the chemical and food-processing industries. Still further valuable features are obtained by various treatments of the metal; these will be considered when the applications of aluminium and its finishes are considered.

In its pure state, aluminium is, however, a relatively soft metal with a yield strength of only 34.5 N/mm^2 (5,000 lb/in^2) and a tensile strength of 90 N/mm^2 (13,000 lb/in^2). Through the development of a wide range of alloys, however, very varied strengths and ductility can be achieved, and this has led to the many applications of today. For example these range from the use of very thin foil material in the packaging industry, ductile materials for drink containers, and highly conductive alloys for electrical purposes, to relatively low-strength alloys for the building industry and high strength materials for aircraft and armoured vehicles.

The metal in its pure state has a relatively high corrosion resistance and needs less protection than most metals. On the other hand, the commercial metal and its alloys, though resistant, are distinctly more sensitive to corrosion, and the

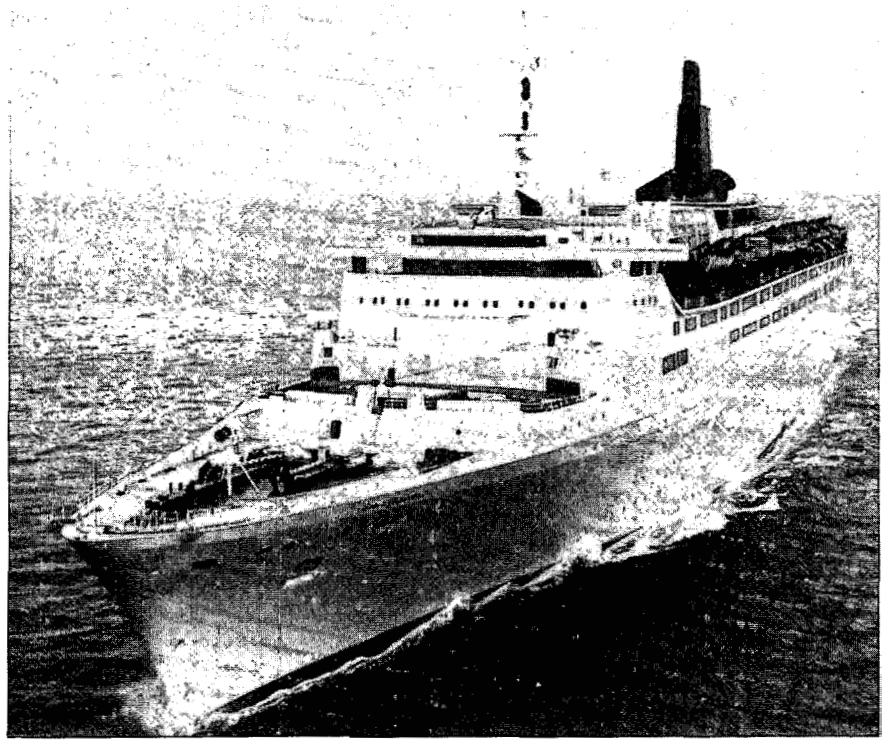


Fig. 1-2. The Queen Elizabeth 2, which incorporates 1000 tons of 5083 alloy plate and extrusions

[Courtesy Cunard Line]

development of high strength light alloys, containing quantities of heavy metals such as copper, zinc or nickel, has heightened the need for protective surface treatments. The nature of the heavy metal additions appreciably influences the alloy's susceptibility to corrosion, and high mechanical strength and corrosion resistance have so far proved largely incompatible. The development of satisfactory protective finishes for these metals has been, therefore, of very great importance.

Brief consideration is now given to the properties of the various aluminium alloys which are available in relation both to their corrosion resistance and applications.

Development of aluminium alloys

The chief alloying constituents added to aluminium are copper, magnesium, silicon, manganese, nickel and zinc. All of these are used to increase the strength of pure aluminium.

Two classes of alloys may be considered. The first are the 'cast alloys' which are cast directly into their desired forms by one of three methods (i.e., sand-casting, gravity die casting or pressure die casting), while the second class, the 'wrought alloys', are cast in ingots or billets and hot and cold worked mechanically into extrusions, forgings, sheet, foil, tube and wire. The main classes of alloys are the 2000 series (Al-Cu alloys), which are high-strength materials used mainly in the aircraft industry, the 3000 series (Al-Mn alloys) used mainly in the canning industry, the 5000 series (AI-Mg alloys) which are used unprotected for structural and architectural applications, the 6000 series (Al-Mg-Si alloys) which are the most common extrusion alloys and are used particularly in the building industry, and the 7000 series (Al-Zn-Mg alloys) which are again high strength alloys for aircraft and military vehicle applications.

The alloy used in any particular application will depend on factors such as the mechanical and physical properties required, the material cost and the service environment involved. If a finishing treatment is to be applied, then the suitability of the alloy for producing the particular finish desired will be an additional factor to be taken into account. The great benefit of aluminium is that such a wide variety of alloys with differing mechanical and protection properties is available, and these, together with the exceptional range of finishes which can be used, make aluminium a very versatile material.

2. THE OXIDE FILM

When a freshly formed aluminium metal surface is exposed to the atmosphere, it is immediately covered with a thin film of oxide, and this oxide film quickly re-forms when damaged. An important and beneficial feature of this oxide film is that its molecular volume is stoichiometrically 1.5 times that of the metal used up in oxidation. This then means that the oxide film is under compressive stress, and will not only cover the metal continuously, but can cope with a certain amount of substrate deformation without rupturing. It is to this protective surface layer that the aluminium industry owes its existence.

Reports of the structure of this low temperature, air-formed film have varied widely although, in general, it is assumed to be amorphous, with the outer surface being a hydrated aluminium oxide. At higher temperatures (above 450°C), crystalline γ-Al_2O_3 is formed, and then, in the molten state, α-Al_2O_3 can occur.

The kinetics of oxide growth on pure aluminium are complex. The currently accepted mechanism has been described recently by Wefers.[1] At ambient temperatures a limiting oxide film thickness of 2 to 3 nm will be produced within one day; thermal oxidation is controlled by diffusion of aluminium and oxygen ions at temperatures up to ~ 400°C and, in this temperature range, asymptotically decaying rate laws are observed. However, when the temperature

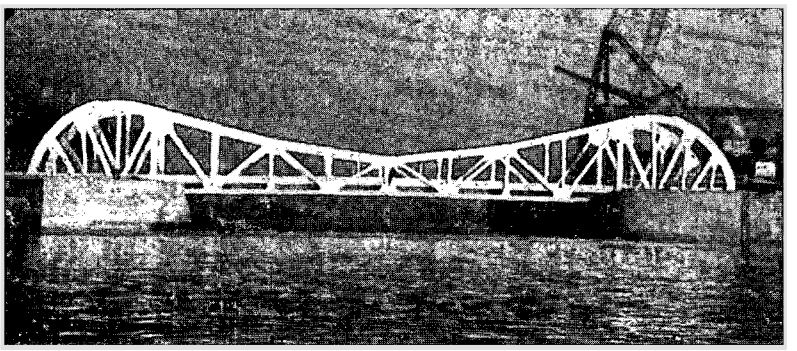


Fig. 1-3. The twin bascule bridge at Hendon Junction, Sunderland, Co Durham – the world's first all-aluminium structure of this type

is raised towards and above 450°C, the exponential oxidation rate changes to a linear relationship between weight gain and time. This change in mechanism represents crystallisation to γ-Al_2O_3, which will disrupt the continuity of the film. At temperatures above 500°C, it has been reported[2] that the preparation of the sheet, i.e. both metallurgical and surface roughness features, can alter the oxidation kinetics.

TABLE 1-1

Thickness of oxide coatings on aluminium

Natural oxide film on pure Al or Al-Mg alloy (formed at below 300°C)	1-3 nm
Natural oxide film on pure Al (formed at temperatures above 300°C)	up to 30 nm
Natural oxide film on **Al-Mg** alloy (formed at temperatures above 300°)	up to 3,000 nm (3 pm) (depending on temp. and bulk Mg content)
Normal chemical oxide coating (e.g. M.V.V., Alrok, etc.)	2.5-5 µm (2,500-5,000 nm)
Normal barrier layer anodizing	0.25-0.75 µm (250-750 nm)
Normal protective anodic coating (e.g. sulphuric acid anodizing)	5-30 µm (5,000-30,000 nm)
Hard anodic coatings (e.g. for engineering purposes)	25-150µm (25,000-150,000 nm)

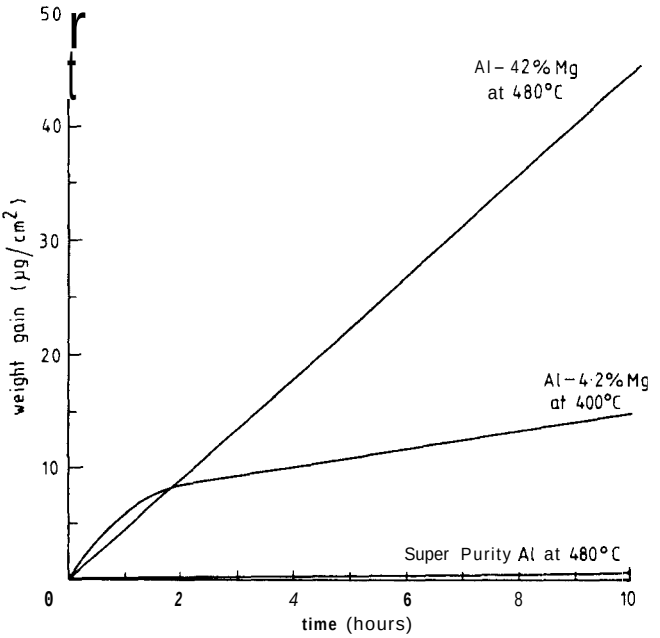


Fig. 1-4. **A** comparison of weight gain curves for oxidation under dry conditions[4]

The major alloying element incorporated within the oxide film is magnesium. At temperatures above 340°C,[3] magnesium diffuses from the bulk of the alloy and, even at levels less than 50 ppm magnesium, there is a competitive oxidation reaction between magnesium diffusion outwards and oxygen diffusion inwards. At higher levels of bulk magnesium (up to 4%), a duplex film of aluminium oxide close to the metal, and an outer layer of MgO, results. These oxide films will thicken until the bulk magnesium level is depleted. Typical weight gain curves for Al-4.2%Mg, as compared to super-purity aluminium, are shown in Fig. 1-4.[4] The current understanding of oxidation of aluminium-magnesium alloys is summarised by Wefers' and Field *et al.*[5]

Table 1-1 indicates the thickness of typical natural oxide coatings in comparison with chemical and anodic oxidation coatings.

Breakdown of the oxide film can result from mechanical rupture, or from chemical attack by anions such as chloride ions. In most cases repair is instantaneous and, depending on the moisture content of the environment, can either be accompanied by the oxygen reduction reaction or the hydrogen evolution reaction shown overleaf:

$$\left.\begin{array}{lll} 4Al - 12e^- \rightarrow & 4Al^{3+} & \\ 3O_2 + 12e^- \rightarrow & 6O^{2-} & \text{cathodic} \\ 2H_2O + 2e^- \rightarrow & 2OH^- + H_2 & \end{array}\right\} \quad \text{anodic}$$

In the first cathodic reaction aluminium oxide results, whereas in the second, hydroxide is formed.

There is growing evidence that flaws pre-exist in the oxide film, and can act as nucleation sites for film breakdown. Information has been gained both from electrochemical studies[6,7] **and** transmission electron microscopy.[8] It is proposed that, in solution, flaws are continually being developed and repassivated, and the presence of aggressive ions hinders the repassivation step, allowing pits to nucleate. Electrochemical noise generated prior to pit initiation provides strong evidence for this type of process. However, even with the existence of flaws, the aggressive ions would still have to penetrate the flaw bases. This could be by the formation of short-lived complex ions or by the development of islands of salts, e.g. $AlCl_3.6H_2O$, followed by currentless dissolution.[9] Alternatively, the local pH in the flaw may become sufficiently low to effectively defilm the base of the flaw and expose the aluminium. The latter mechanism is favoured at present. The result of film breakdown is corrosion and this is considered in the next section.

3. CORROSION OF ALUMINIUM

Whilst aluminium and its alloys generally have good corrosion resistance, localised forms of corrosion can occur, and it is important to understand the factors contributing to these forms of corrosion.

Corrosion may be defined as the reaction between a metal and its immediate environment, which can be natural or chemical in origin. The most recognisable form of corrosion is, perhaps, the rusting of iron. All metals react with natural environments but the extent to which this happens can vary; for noble metals like gold the amount is insignificant whereas for iron it is considerable. Aluminium is no exception but, fortunately, it has the propensity of self passivation and for many applications corrosion is not a problem.

Factors contributing to corrosion

There are two main factors which influence the general corrosion behaviour of aluminium; one is the type and aggressiveness of the environment and the

second is that of its chemical and metallurgical structure. Environments can vary from outdoor atmospheres to media such as soils, waters, building materials, food and chemicals etc. Outdoor atmospheres are usually classified as either rural, industrial or marine depending on their location. In rural atmospheres the degree of natural pollution is usually low, but industrial and marine environments are more aggressive, usually due to the presence of sulphates and chlorides respectively. Soils, waters and building materials vary in aggressiveness depending on such properties as composition, chemical activity, degree of aeration and electrical conductivity. Chemical environments usually have unique compositions and their corrosive effects can be fairly accurately determined.

Pure aluminium displays the highest corrosion resistance, but as purity decreases and alloying elements are added this resistance decreases.'" Copper lowers resistance more than other elements, whilst magnesium has the least effect. The influence of the main alloying elements and impurities on the corrosion resistance of aluminium is summarised in Table 1-2.

TABLE 1-2

General effect of major alloying elements on the corrosion resistance of aluminium

Element	*Effect*			
	Marked	Moderate	Slight	**V.** Slight
Copper	J			
Magnesium				✓
Zinc				✓
Silicon			✓	
Manganese				J
Chromium				✓
Zirconium				✓
Titanium				✓
Iron + Silicon		✓		

The metallurgical state of an aluminium alloy for a given composition is determined by its fabrication history. In the wrought form it will be made either by the procedure of work-hardening or by that of solution heat-treatment. Aluminium alloys are also available in the cast form. Briefly, work-hardening involves deformation at room or slightly elevated temperatures, and for semi-fabricated products the process used is that of rolling. The main features resulting from rolling are dislocations, in arrays varying from subgrains with ragged boundaries, to high density configurations of 'forests' and slip bands; Fig. 1-5

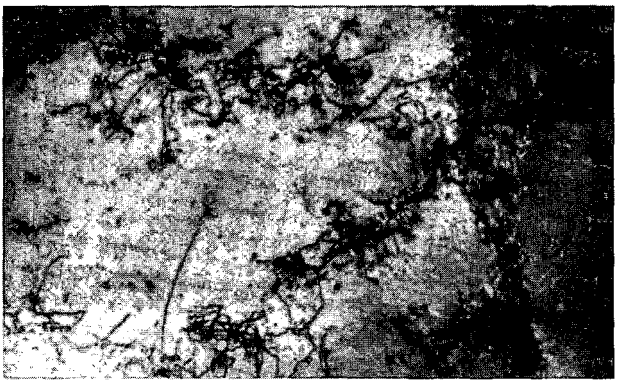


Fig. 1-5. 'Ragged' sub-grain boundaries resulting from small amounts of cold rolling (AI-Mg alloy) (210,000)

illustrates some of these. Cold worked structures also arise from processes such as shearing, stamping and forming. The two main work-hardening alloy groups are those based on Al-Mn (3000 series) and on Al-Mg (5000 series).

In general terms solution heat-treatment consists of two basic stages. The first involves soaking at temperatures between 450°C and 550°C for predetermined periods depending on the particular alloy composition, followed by quenching either into water or into air, again depending on the alloy. The second stage is that of ageing, which is carried out at temperatures between 20°C and about 175°C. During the first stage most of the alloying elements are taken into solid solution and then partly released from this state during ageing. Except at grain boundaries and other energetically favourable regions, material released from solid solution remains coherent with the matrix and by so doing increases strength. If the ageing period is prolonged or the temperature raised, coherency tends to break down and strength decreases. At the grain boundaries the ageing process is usually more advanced than that elsewhere and incoherent particles are precipitated. Grain boundary precipitates are illustrated in Fig. 1-6. The principal heat-treatable alloys are those based on Al-Cu (2000 series), Al-Mg-Si (6000 series), Al-Zn-Mg and Al-Zn-Mg-Cu (7000 series).

Although a fairly large number of casting alloys exist, most of them derive their properties from the addition of magnesium, silicon and copper either singly or in combination. The amount of magnesium can range from about 3 to 11%, that of silicon from 3 to 13% and that of copper from about 1 to 5%. They are produced in a range of tempers from 'as cast' to 'solution heat-treated' depending on alloy composition. Their basic structure is mainly that of dendritic cells in a matrix of aluminium. Some changes to the basic structure result from heat-treatment.

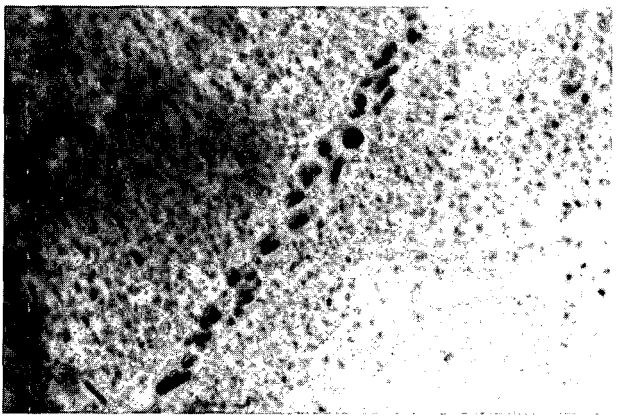


Fig. 1-6. Grain boundary precipitates in overaged Al-Zn-Mg-Cu material (x 50,000)

Types of corrosion

Pitting corrosion

Aluminium displays a number of different corrosion modes, sometimes within the same alloy, but the most common form, in natural environments, is that of pitting." This mode is a random process initiating from various sites on the metal surface where the air-formed oxide film is defective. In practice this means that the unprotected aluminium surface becomes roughened and less reflective with the development of numerous localised pits. Fortunately for aluminium, the pits eventually stifle and in consequence the amount of corrosion which occurs reaches a limiting or 'threshold' value. This behaviour is well established and can be safely predicted and referred to in design considerations. **A** typical corrosion-time curve, in comparison with bare and galvanised steel, is shown in Fig. 1-7. Some examples of the corrosion-time relationship for a number of aluminium alloys are given in Figs. 1-8 and 1-9.

Intercrystalline corrosion

As the term implies, intercrystalline corrosion is the process of preferential attack either at grain boundaries or within the immediately adjacent regions. It results from the segregation and/or precipitation of alloying elements along the boundaries and this has the effect of destroying electrochemical stability at these points. Most of the heat-treatable alloys have some susceptibility to inter-

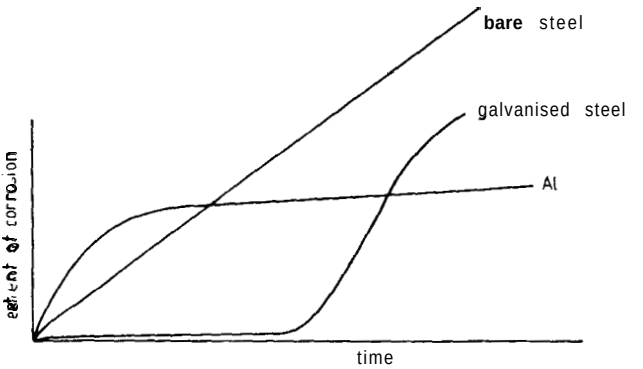


Fig. 1-7. 'Threshold' corrosion behaviour of aluminium compared with that of bare and galvanised steel

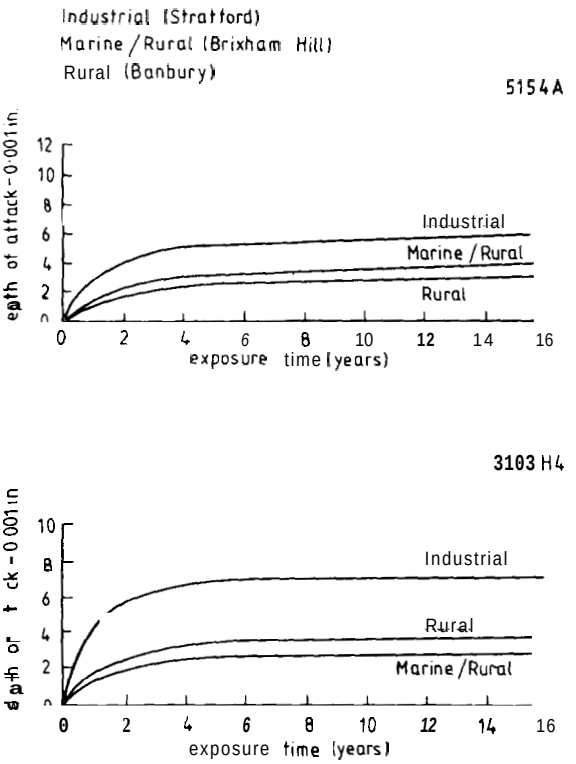


Fig. 1-8. Corrosion-time curves for the sheet alloys 5154A and 3103

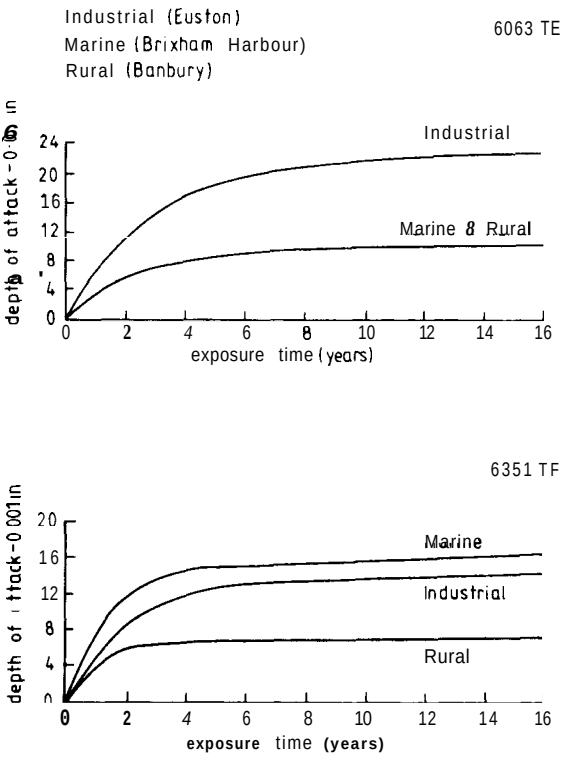


Fig. 1-9. Corrosion-time curves for the extrusion alloys 6063 and 6351

crystalline corrosion but normally this does not pose a serious practical problem. If extensive intercrystalline attack occurs, it is usually indicative of incorrect heat-treatment.'* For example, if the Al-Cu alloys are subject to delayed quenching following solution treatment, copper diffuses to the grain boundaries, and the adjacent copper-denuded regions become increasingly anodic and corrosion sensitive. An example of intercrystalline attack in an Al-4% copper alloy is shown in Fig. 1-10. Alloys containing more than about 3.5% magnesium can also become susceptible if they are in a supersaturated state.

Stress-assisted corrosion

One of the most insidious forms of attack is that of stress corrosion and in the extreme it can lead to total failure of a component. Essentially it is the propagation of intergranular cracking of the material whilst elastically loaded at

stress concentrations well below the fracture toughness of the material. Stress corrosion requires a combination of a residual or applied tensile stress, a corrosive environment particularly containing chloride ions, and a directional microstructure allowing easy crack propagation. Al-Cu, AI-Mg, Al-Zn-Mg and AI-Li alloys are all sensitive to stress corrosion cracking, though with the Al-Mg series it is only those having more than about 3% Mg that are affected. In Al-Cu and Al-Mg alloys stress corrosion resistance is affected by the balance of the anodic reaction on the grain boundaries and the cathodic reaction on the interior surface of the grains. Al-Mg alloys can become sensitised by precipitation of a βAl-Mg phase on the grain boundaries. In the case of Al-Zn-Mg alloys localised intergranular hydrogen embrittlement is also thought to play a part.[13] The basic concept is of nascent hydrogen, generated by corrosion, diffusing along the grain boundaries and causing loss of strength, until finally cracking is initiated.

Care is taken during material fabrication to minimise the risk of stress corrosion sensitivity, but materials can be sensitised by subsequent fabrication operations such as welding or heat treatments such as paint curing, or, in service, conditions involving elevated temperatures.

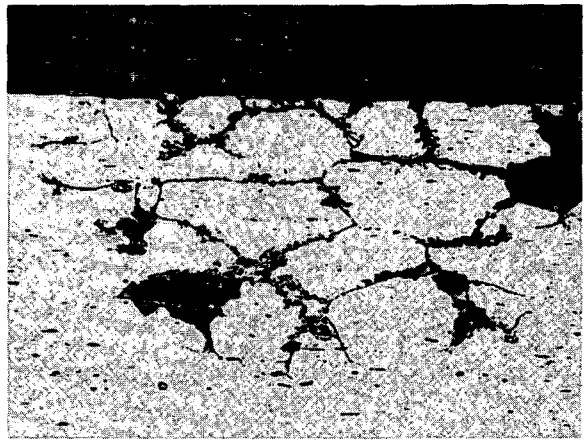


Fig. 1-10. Example of intercrystalline corrosion in AI-4% **copper** alloy

Another type of attack to which stress is thought to contribute is termed exfoliation or lamellar corrosion. Again, this is a dangerous mode since large amounts of metal can be destroyed. Fig. 1-11 illustrates the effect. During exfoliatory attack, corrosion proceeds along grain boundaries parallel to the metal surface and corrosion product accumulating in its wake creates sufficient stress to prize open the intervening material.[10] Exfoliation can be found in most of the heat-treatable alloys and also in the work-hardening Al-Mn and AI-Mg

alloys, but is most likely to occur with Al-Cu and Al-Zn-Mg-Cu alloys exposed in a marine environment. The basic causes are recognised, however, and accommodated in fabrication practices.

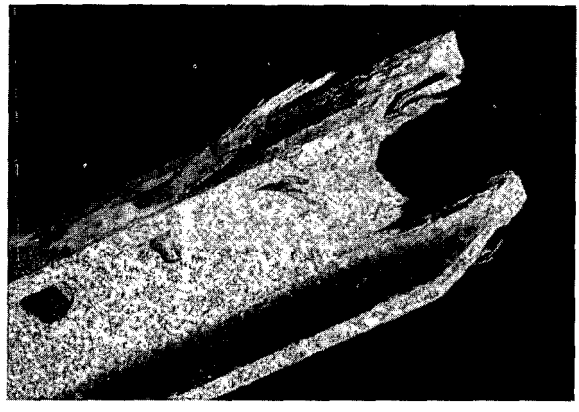


Fig. 1-11. Severe exfoliation in an extruded section of 7020 alloy (2 years life)

Filiform corrosion

Filiform corrosion has been known since the 1960's in the aircraft industry[14] and in architectural applications,[15] but problems in the 1990's, with numerous incidences of filiform corrosion on painted aluminium architectural sheet and extrusions in Northern Europe, have refocussed attention on this problem.

Filiform corrosion only occurs on coated substrates and growth proceeds in a linear manner producing a characteristic worm-like trace (Fig. 1-12). It occurs under a wide variety of organic layers on substrates given mechanical, chemical or electrolytic treatments and has been reported for most alloy families and most product forms. Filiform corrosion is initiated at a break or defect in a coating, and this enables a corrosive environment to react with the underlying aluminium substrate. Growth is predominantly in the working direction on both sheet and extrusions and filament growth rates are about 0.15 to 0.4 mm/day.

It is now widely accepted that filiform corrosion is driven by a differential aeration cell between the anodic filament head and the cathodic tail.[16] Aluminium dissolution occurs at the active anodic head of the cell, and at the passive trailing area oxygen and water are reduced to produce hydroxyl ions. When the cell electrolyte is saturated with dissolved aluminium ions, aluminium hydroxide is precipitated as pseudoboehmite. Aluminium both dissolves in the cell electrolyte and reacts directly with water to evolve hydrogen. Hydration of the dissolved aluminium ions acidifies the cell electrolyte and a pH of 1 to 2 has been measured.

Both water and oxygen must be continuously supplied to the cell or growth stops, and chloride ions are essential to provide electrical conductivity and to stimulate the initiation of corrosion. These ions migrate with the filament head electrolyte and growth stops once they have been consumed by incorporation in the corrosion product. Growth proceeds by anodic undermining of the coating and the voluminous corrosion products precipitated behind the active head provide the pressure to cause delamination and lifting of the coating.[17,18] This is shown diagrammatically in Figure 1-13.[19]

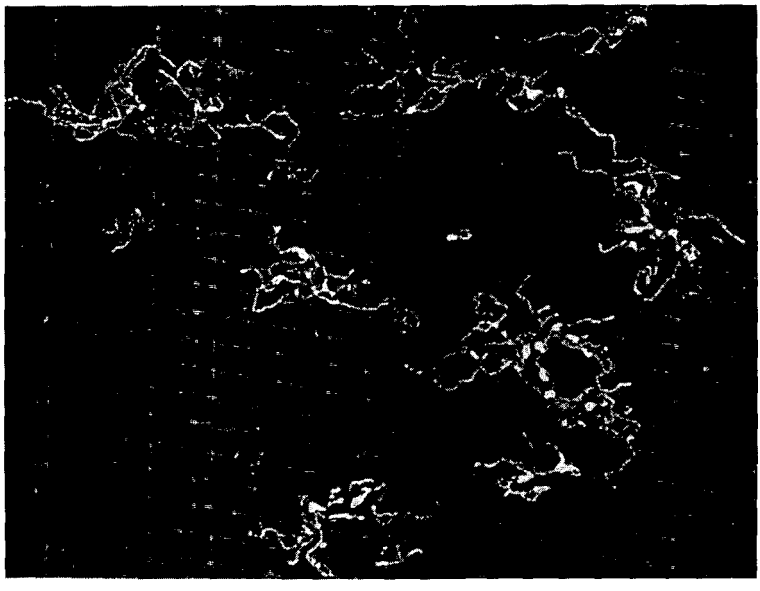


Fig. 1-12. Filiform corrosion occurring beneath a clear lacquer on aluminium

Filiform corrosion is least likely to occur on well cleaned and pretreated aluminium surfaces, particularly those pretreated with chromate conversion coatings, and indeed there is some suggestion that it is the move away from such pretreatments for environmental reasons that has caused the current problems. However a great deal of work is underway to establish good alternatives to chromate pretreatments and this will be considered again in the chapters on Chemical Conversion Coatings (Chapter 5) and Organic Finishing (Chapter 14).

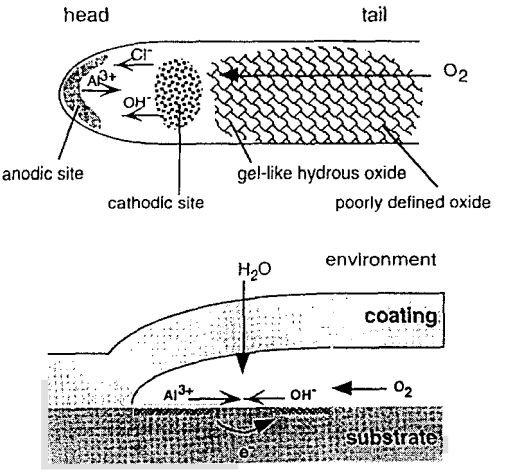


Fig. 1-13. Propagation of filiform corrosion according to the anodic undermining mechanism on aluminium substrates[19]

Crevice and poultice corrosion

If aluminium is placed in slightly loose contact with itself or other materials, such that a crevice is established between the two respective surfaces, a corrosion cell may be established. The resultant attack occurs at the base of the crevice, the mouth being unaffected. Early views of the mechanism of crevice corrosion involved a differential aeration cell with a higher oxygen content at the mouth compared to the crevice, but it is now known that the process is more complex, and that the driving force for attack is the continuing development of acidity at the crevice tip.[20,21]

Concentrations of oxygen or aluminium ions which differ from the inside of the wet crevice to the outside surface, can set up local anodic pits fed by a large external cathode. When current can pass from the activated crevice to the cathode, a galvanic cell is established, and this can also occur under dirt films or accumulated chloride rich poultices (so-called 'poultice' corrosion). The aluminium hydroxy chloride complexes in the pit are thermodynamically unstable, but they form gels that are kinetically stable, and it is the acidity from the gel that activates the crevice. If the crevice or the cathode surface dries out the corrosion will stop. However the most rapid and damaging form of corrosion occurs when a crevice is between dissimilar metals which are galvanically coupled. Recent views of crevice corrosion have been summarised by Betts and Boulton[22] and De Force and Pickering.[23] Crevice corrosion is quite independent of alloy type and it will occur even with alloys which otherwise are highly resistant to corrosion.

Poultice corrosion, where poultices, either of porous material or of material which naturally absorbs or retains moisture, are created on the metal surface, has already been mentioned. It is essentially a form of crevice corrosion with serious corrosion occurring at the poultice/metal interface where moisture is retained (Fig. 1-14).



Fig. 1-14. Poultice corrosion on an extruded 6063 alloy section (12 months life)

Bi-metallic or galvanic corrosion

Attack by bi-metallic contacts can be as damaging as stress corrosion, since, once initiated, it continues to propagate. In general terms the two main contributory factors are the severity of the environment, and the electrochemical separation between the respective metals as given in the Galvanic Series. The more aggressive the environment and the larger the potential difference, then the greater is the attack likely to be. The effect occurs when two dissimilar metals are in contact, the more noble being cathodically protected by the less noble metal, which becomes a sacrificial anode. If the area of the anodic metal is small compared to that of the cathodic metal, corrosion will be accelerated, whereas if the ratio of areas is reversed the overall corrosion rate is less. This, for example, is the principle behind the sacrificial zinc coating of steel. The situation occurs most commonly when dissimilar metals are used in fastener combinations e.g. a steel bolt through aluminium sheet, or a copper fitting attached to an aluminium tube. The galvanic effect can be prevented if an electrical insulator is placed between the two metals. In some cases this can be as simple as a paint coating, but in others separation by a plastic tape or gasket is required.

All aluminium alloys can suffer from bi-metallic corrosion and, for practical purposes, a general guide to the contact effect of a number of dissimilar metals is given in Table 1-3.

TABLE 1-3

General guide to galvanic influence of various metals on aluminium

Metal	*Comment*
Cadmium	Slight effect
Chromium	Small to negligible
Copper and copper alloys	Severe
Graphite	Severe
Lead	Negligible except *in* severe marine environments
Stainless steel	Negligible except in severe marine environments
Steel and Iron	Slight except in severe environments
Tin	Negligible except in salt solutions
Titanium	Negligible except in severe marine environments
Galvanised steel	No effect until zinc coating is destroyed

Impingement and cavitation

It is perhaps academic to separate these two types of corrosion because they usually initiate from the same basic factors.[24] In both there is a strong mechanical component associated with the movement of fluids relative to the metal surface. Above certain velocities of movement, the liquid may exert sufficient force to physically remove the protective oxide film; for aluminium this occurs at velocities above about 6 m/sec (20 ft/sec). Additionally, entrapped air bubbles within the liquid may implode on contact with the metal surface and the energy released has a similar effect on the film. Implosion of bubbles is usually described as cavitation. Once the protective film has been removed, local corrosion of the surface can initiate. Although susceptibility to impingement and cavitation has some dependency on the hardness of the material, aluminium alloys are not regarded as having adequate resistance for many practical applications, where liquid flow rates are high.

An example of impingement attack due to fast flowing water is given in Fig. 1-15. Examples of pitting and of bi-metallic corrosion are also illustrated by this component.

Chemical environments

Chemical environments are usually defined as those involving definable chemical species, including food-stuffs, and aluminium is used in contact with many of these. Possibly the main difference between chemical and natural environments is that of pH. Chemical environments are usually more alkaline or more acid, and this may affect the particular corrosion mode. For example,

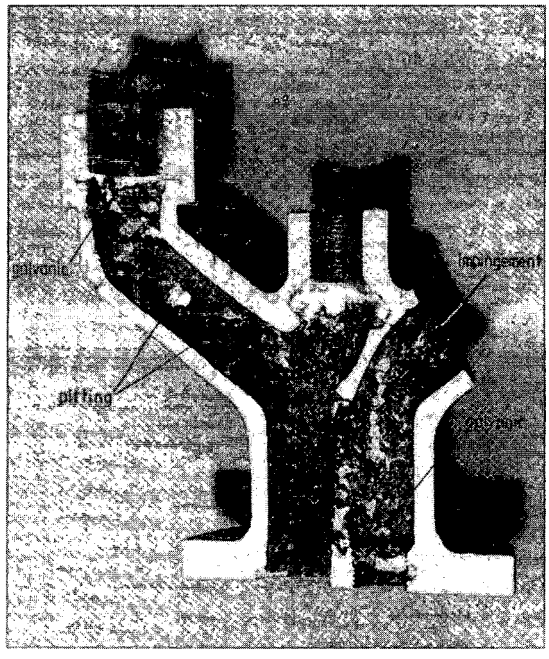


Fig. 1-15. Impingement, galvanic and pitting corrosion occurring on an aluminium component. The galvanic corrosion was caused by threaded brass inserts

due to the amphoteric nature of aluminium, the oxide film is soluble at pH values below about 3 and above about 9. In consequence, the corrosion mode is usually one of general attack rather than one of the localised types.

Considerable published information is available[25,26,27,28] on the corrosion behaviour of aluminium with a large number of foods and chemicals.

4. PROTECTION OF ALUMINIUM

For many applications aluminium requires no protection and everyday examples of its excellent resistance can be seen as roofing, siding, lorry bodies, rail cars, ships' superstructures etc. This high resistance is due to the tenacious air-formed oxide film which develops at its surface, and the ability of the film to re-form when damaged. However, to ensure maximum corrosion resistance under the more stringent environmental uses, when some of the previously mentioned types of corrosion may occur, the following factors are important:

(1) Correct choice of alloy in relation to service condition, with special regard to purity in composition and strict material control.

(2) Careful control during fabrication.

(3) Correct design in service to avoid such features as crevices or encatchments for moisture, and galvanic effects.

(4) Use of the best protective system.

Protection may take the form of cathodic protection systems, sealants, inhibitors, metal spraying and applied coatings or finishes.

Cathodic systems

In a corrosive situation, the regions on a metal surface which suffer attack are termed anodes, whilst those which are unaffected are called cathodes. Advantage is taken of this relationship in cathodic protection systems by making the original anodic regions become cathodic. This may be achieved in three ways; by cladding with a more anodic material, by the use of sacrificial anodes, or by applying currents to the component so that it becomes cathodic with respect to other metals in the system.

Cladding was extensively used to protect AI-Cu alloy sheet used on aircraft during the war. As previously mentioned, copper markedly lowers the corrosion resistance of aluminium, and this effect can be offset by coating such alloys with pure aluminium. The 'galvanic' protection afforded by the pure aluminium is augmented by its own high intrinsic resistance.

Similar protection is also obtained from Al-1%Zn alloys, but their use is limited to aluminium alloys less noble than the AI-Cu series. For example Al-1%Zn cladding has been used to protect irrigation pipes made from the AI-Mn alloys; its effectiveness in protecting Al-Mg-Si alloys and AI-Mg alloys is also reported.

Possibly the most recognisable example of protection by sacrificial anodic material is that of zinc on steel. The term 'galvanised' zinc is used in this case because the principles of protection are those of galvanic corrosion. When exposed to a corrosive environment the zinc is dissolved in preference to the steel; alternatively the phenomenon may be regarded as that of steel galvanising the corrosion of zinc for self protection. Aluminium can also be protected in a similar manner and certain aluminium alloy anodes are available for this purpose. These are based on the Al-Zn and the Al-Hg systems. To improve the protective efficiency of the Al-Zn alloy anodes, small amounts of either tin, indium or strontium are added. The use of aluminium sacrificial anodes for protecting aluminium is confined to sea water or high conductivity brine applications; in

fresh waters where conductivity is low, the 'throwing' power of the anode, i.e. the distance over which it will protect, is severely limited.

Because of the restriction in throwing power associated with electrolyte conductivity, a large number of anodes would be required to protect aluminium used, for example, as a pipeline buried in a high resistivity soil. However, this problem may be overcome by applying a d.c. current to an electrode fixed to the pipe; this system is known as 'impressed current' protection. The advantage of the system is that the amount of protective current can be varied as required and regulated from an external source. The mechanism of protection is similar to that of the sacrificial anode.

Metal spraying

Aluminium can be protected by sprayed metal coatings, which behave anodically in a similar way to cladding. Pure zinc is often used but tests have shown that pure aluminium will effectively protect Al-Cu alloys whilst Al-1%Zn sprays are effective with Al-Mg-Si alloys and with the high strength Al-Zn-Mg-Cu alloys. Adhesion of sprays is quite good, providing that the aluminium surface has been roughened by grit blasting, but the mechanical strength and elongation of sprayed deposits are generally poor.

Sealants

Sealants and greases are the usual materials employed to prevent crevice corrosion in those instances where it is impossible to avoid them. For example, in aluminium overhead conductor lines where several aluminium wires are placed around a steel core (ASCR), a chromate grease is inserted between each wire to prevent crevice attack and galvanic corrosion from the steel. Sealants are usually mixtures of organic and inorganic salts and they function either by their high impermeability to moisture, or, as in the case of chromate-containing ones, by the continuous leaching of an inhibitor-type ion. Materials that have been found suitable for sealing crevices and joints are listed in Table 1-4 in decreasing order of durability, together with notes on their application and performance.

Inhibitors

The function of inhibitors is important in many protective finishing processes; for example, they are incorporated in paint primers as well as in cleaning solutions and chemical conversion treatments, where they stabilise the reaction between the solution and the metal and prevent rapid and irregular corrosion at the expense of film formation. They are also used in such specialised applications as water coolers, fuel tanks, etc.

TABLE 1-4

Sealants for crevices and joints

Sealant Type	*Mode of use*	*Reninrks*
Polysulphide	Gun applied	Where a life in excess of twenty years is required in an aggressive acid or neutral environment; particularly useful on tall buildings and in shipbuilding.
Polybutene 'Neoprene' Natural rubber	Tapes. Can be brush or gun applied if required.	Lives of up to twenty years. Easier to use than polysulphides but material cost is up to 100% higher.
Butyl rubber	Tapes	Used for maximum life in alkaline environment, or in general building, when the ease of application is more important than the long life and high recovery properties of polysulphide and polybutene. The resistance to acid environments is only fair.
Polyurethanes	Tapes	For maximum reliability over comparatively short times, say five years. Excellent where only limited movement is expected. Polyurethanes become brittle with time.
Greased cotton or synthetic fibre	Tapes	Cheap, around 25% of cost of polysulphides, easy to apply. Difficulties arise at holes. The grease used for impregnation must be carefully chosen to suit the service conditions.

Where the immediate corrosion products of a metal are sparingly soluble, corrosive attack by an electrolyte may often be inhibited. Inhibitors, therefore, function by producing insoluble reaction products, or alternatively, by being themselves strongly adsorbed on the metal surface. They are either anodic or cathodic, according to their specific function.

Inhibitors employed with aluminium function anodically and cathodically, and both soluble and insoluble compounds are employed, the latter being used mainly in paint primers. Important examples are the chromates of zinc, barium and strontium. Other inhibitors commonly used include soluble chromates or dichromates, which exercise a protective influence in neutral salt solutions and certain acids, where they increase anode polarization. Borates, phosphates and nitrates are frequently used in ethylene glycol anti-freeze solutions, while solutions containing methyl alcohol often contain chlorates and nitrites also. Lactates, acetates, borates and chromates have been suggested for use with aluminium containers for commercial alcohols, while sodium silicate (water glass) and fluosilicates are effective in alkaline solutions and are widely used to inhibit cleaning solutions. Studies have shown that ferrocyanides[29] and amide?" are also effective against alkaline attack. In mixed metal systems which also contain copper, sodium mercaptobenzothiazole has been found to be an effective inhibitor.[24]

Organic colloids are also frequently used to inhibit attack by alkalis, and agar-agar or gum arabic may reduce the corrosion rate of a 10% sodium hydroxide solution by up to 80%. Nitrogen-containing organic compounds, such as triethylamine and tri-n-butylamine,[31] are useful in inhibiting attack by acid. Acridine and phenyl quinoline, a related compound, prevent attack by 3N hydrochloric acid.

Protective finishes

Whilst aluminium can satisfactorily be used without finishing treatments in many applications, the potential problems of corrosion, which have been described, are usually reduced or eliminated by the use of appropriate finishing processes. In addition, the desire to maintain the original appearance of the aluminium, or to impart colour or other decoration to the surface, necessitates the use of finishing treatments, and it is the ability of aluminium to be finished in so many ways that allows such a wide range of applications. The choice of finish and alloy to be used will depend on many factors, including the service environment, and appearance desired, the suitability of the alloy for the particular finishing process, the processing cost, and any special requirements such as abrasion resistance, formability, electrical resistance etc.

The finishes available include the following:

Chemical Conversion Coatings – thin oxide, phosphate or chromate films, used for light service conditions and as a basis for application of paint and other organic coatings.

Anodic Oxidation Coatings – electrochemically produced oxide coatings with a wide range of thicknesses, corrosion protection, colour, hardness, optical and electrical properties – generally used where maximum protection is required.

Organic Finishing – paint, lacquer and resin finishes in a very wide range of types, giving great flexibility in finish, colour, corrosion resistance and functional properties.

Vitreous Enamel Finishes – a limited range of coloured finishes for special applications such as holloware and building.

Electroplated Finishes – with suitable surface preparation a full range of decorative and functional electroplated coatings can be applied to aluminium.

These finishes are the main subject of this book, and they are discussed fully in the subsequent chapters.

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CHAPTER 2

Mechanical Surface Treatments and Finishes

1. GENERAL NOTES

The appearance and serviceability of an aluminium product depend on the mechanical or chemical surface treatments that precede the actual finish. The extent to which they are respectively used depends on the initial state of the surface, the method of manufacture of the article concerned, and the finish required. Mechanical surface treatments are dealt with in this chapter; chemical treatments are detailed in the following chapters. The mechanical etching of aluminium, a new industrial process which combines mechanical treatment with chemical etching, is described in Chapter 4.

Mechanical treatments may be used for a variety of purposes, as follows:–

1. The elimination of scratches, pits or other superficial blemishes and the provision of a smooth or lustrous surface. This is achieved by various grinding and polishing operations which remove the high spots of a rough surface, either by a cutting action of the abrasive or by flowing the metal with the formation of a thin amorphous layer on the surface. With small articles, this is often carried out economically by treating the work in quantity in polishing barrels, or in vibratory machines.

   Mechanically polished surfaces are either left unprotected, as in aluminium kitchen ware, or may be lacquered, or anodized for improved corrosion resistance. Mechanically polished surfaces may be scratch-brushed to provide a 'satin' finish, which subsequently may be anodized or lacquered, but usually satin finishing is carried out on virgin metal without polishing.

Mechanical polishing is also used prior to electroplating. In the production of aluminium reflectors, high-purity metal is first polished mechanically to as high a finish as possible, prior to electropolishing.

2. The preparation of rough light metal castings for polishing, anodizing, organic finishes, etc. Blasting with sand, grit, or shot is used to provide a clean, rough surface, suitable for the direct application of paints and sprayed metal which adhere to such 'keyed' surfaces. Blasting may also be used in 'highlighting' surfaces or as a preliminary to scratch brushing. Alternatively, fine sand-blasted surfaces may have an attractive matt appearance which may then be lacquered or anodized for protection. If blasting is used before polishing, care must be taken not to harden the surface.

   Blasting provides a chemically clean surface. If care is taken to avoid finger-marking or otherwise staining the surface, subsequent cleaning may not be necessary prior to organic finishing. Shotblasting may also have a beneficial effect on the corrosion resistance and mechanical properties of the work by removing superficial cracks, hardening the metal surface and adding a compressively stressed layer to the surface.

3. The production of designs and textures on the surface. Fluting, hammering, pattern rolling, high-lighting, etc., produce designs on the metal which may be subsequently lacquered or anodized, or partly or wholly painted or enamelled, according to the required finish.

The sequence of operations preceding a surface finish can vary widely for different types of articles and for the different finishing processes (Fig. 2-1). The actual mechanical operations carried out in the different sequences are fairly standard and are described in the following sections.

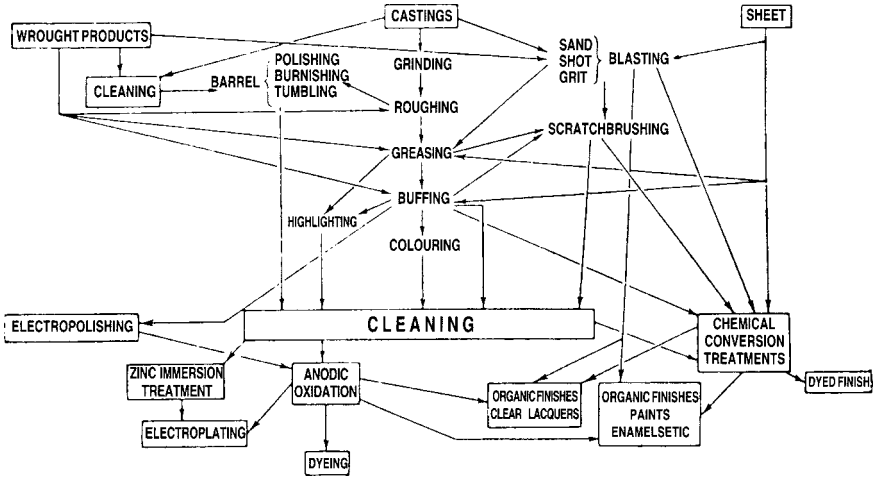


Fig 2-1 Flow sheet of finishing operations

2. BLASTTREATMENT

Abrasive blasting with shot or grit is used only to a limited extent in the aluminium industry to clean or apply a decorative finish to surfaces. The process is particularly suitable for producing a good key for painting. It is best carried out with materials such as fused alumina and glass beads. Steel abrasives are not favoured, as residues of ferrous materials may induce corrosion.

The abrasive may be projected onto the surface from a rotating wheel, or by using compressed air. **A** wide variety of specialised equipment is available for the purpose, ranging from cabinets with a window and arm-sleeves through which the operator manipulates the work, to barrel-type machines in which the components to be treated are rotated under the blast, and continuous, automatic or semi-automatic equipment. Attractive satin finishes can be obtained by vapour blasting in which a fine abrasive suspended in water is used to produce a satin finish; this can subsequently be given an anodic treatment. Combinations of blast treatment and polishing can give decorative and artistic finishes on domestic appliances and architectural fittings that usually are then anodized.

Mechanical effects

Abrasive blasting has an important value in producing mechanically advantageous effects on aluminium alloys that are subject to stress or fatigue, as in the aerospace industry. Shot peening work-hardens the metal surface, whilst the impact prevents the spread of cracks which might be initiated from local surface notches and imperfections on such items as crank-bases, pistons, and supporting members in aircraft landing gear. The treatment imparts compressive stresses to the surface, and can in some cases, double the fatigue life of components subject to alternating stresses.

The material used can affect the colour of the finish. Light grey appearances are obtained by blasting with silica sand (the use of which is not recommended on account of the health hazard) whilst carbides produce a dark grey surface. The actual surface texture is a function of the air pressure (impact velocity of the blasting medium), the nozzle size, grit dimensions, and the distance and angle of the nozzle from the work. These are determined largely by experience or by trial and error. Lower air pressures, large nozzle sizes and fine abrasives tend to produce finer finishes.

Blast treatments generally produce a chemically clean surface, so that further cleaning may not be required before anodizing, provided there is no delay between operations and care is taken to avoid finger marking or other contamination.

3. WHEEL POLISHING AND GRINDING

Mechanical polishing operations may be divided into five stages, all or some of which will need to be applied. Depending on the nature of the job, these may be economically carried out either manually or automatically.

Automatic polishing machines are available for polishing tubes and sheet and can be designed for many wrought or cast shapes and finished products. There is generally little difference in the actual operation whether carried out by hand or by machine, though it is not easy to achieve mirror finishes by automatic polishing alone. Careful inspection is essential before preliminary automatic roughing operations, and good-quality metal is an initial requirement. Deep scratches or pits, if present, will not be eliminated by machines set to polish only to a uniform overall pressure. It may thus be desirable to supplement automatic machines with manual polishing, especially for high-quality work. Automatic machines are non-selective in general and will impart the same degree of polishing regardless of individual spasmodic imperfections.

The preliminary state of the article is of importance when it is to be polished for subsequent anodic treatment or electroplating. Certain casting alloys are difficult to produce free from pores and may be unsuitable for electroplating. When porosity is only on the surface, however, this can be wholly eradicated by mechanical treatment which removes the defective upper layer and flows the metal, closing the pores. In the repair of castings, holes are sometimes drilled out and tapped for the insertion of threaded plugs of the same material. They are subsequently peened to ensure permanent location and ground off. Care must be taken with such castings to avoid differential etching and no delay should be permitted between operations which may cause local corrosion.

Differences in alloy composition may show up differences in texture on mechanical polishing, both when different alloys are present in the same article or where there are differences in production of similar alloys. This is of practical importance, but applies mainly in the case of large flat surfaces which are to be mirror finished. On the other hand, alloys which are in a hard condition either by virtue of their composition or because of heat treatment, cold working, etc., are more difficult to polish than pure aluminium or softer alloys. Alloys containing a high proportion of silicon, for example, take a bright finish less readily than simple aluminium-magnesium alloys.

According to Benson' sheet alloys 1100, 3003 and 5005 and extrusion alloy 6063 are particularly suitable for mechanical polishing while for a particularly high specular finish 5357 and 5457 sheet and 5357 and 6463 extrusions are recommended.

The theory and practice of polishing have been reviewed in detail in a book by W Burkart and K. Schmotz[2]. The exact mechanisms of polishing have not been established with certainty. According to one view, the function of both grinding and polishing is to remove metal stock in progressively finer stages

until a high lustre is achieved. An alternative view contends that in the final stages of polishing, metal is displaced from the peaks into the valleys producing the much debated 'Beilby' layer of amorphous or very finely crystalline metal, but by a mechanism of plastic deformation rather than the viscous flow which Beilby envisaged. Electron microscope studies have demonstrated that the top layers of a polished surface are crushed or disordered into a very finely crystalline state: it has also been demonstrated that local temperatures as high as 500-1000°C can occur during grinding and polishing.

Samuels[3] has discussed in very succinct terms the effects of mechanical finishing processes on metal surfaces. He distinguishes between the outermost fragmented layer where the base crystals are broken up into very fine sub-grains by severe plastic deformation, and the much thicker underlying layer of minor deformation where the strain decreases with increasing depth.

Little work of this type has been carried out on aluminium, but Vacher[4] has measured the depth of the plastically deformed layers produced in grinding commercially pure aluminium (Table 2-1). Although the detail remains to be filled in where the polishing of aluminium is concerned, the essential nature of the polishing process is understood in general terms.

TABLE 2-1

Depth of the deformed layer in polycrystalline commercially pure aluminium detected by X-ray diffraction methods[4]

Surface Treatment	*Apparent depth of deformation (niicrons)*
Polished on 600-grit alumina	5
Abraded on 3/0-grade emery paper	50
Abraded on No.0-grade emery paper	26
Abraded on No.1G-grade emery paper	33
Abraded on No.100 alumina, cloth backed belt	95

An attempt to fill in some of this detail was made[5] by studying the effects of type of grease, kind of abrasive, buffing pressure, speed, cloth and initial condition of the surface on the results obtained on polishing aluminium. The condition of the polished surface was greatly influenced by the materials and methods used. Table 2-2 shows some examples of typical aluminium oxide grit sizes used in specific polishing applications on aluminium.

TABLE 2-2

Typical aluminium oxide grit sizes used in specific applications

Aluminium Product	*1st stage'*	*2nd stage*	*3rd stage*
Diecast	–	180 grit	240 grit
Sandcast (Internal surface)	40-60	180 grit	
Sandcast (External surface)	90	150 grit	240 grit
Machined for deburring	50-120	180 grit	
Sheet	120**	180 grit	240 grit''
Bumpers	180 (localised)	240 grit''	
Structural components	180		240 grit''

* First stage may not be necessary where multi-stage banding is envisaged, depending on surface roughness.

** Grease or lubricant normally used.

The polished surface may have different properties from the bulk metal, such as a higher corrosion resistance which is sometimes noticed. However, as Steer and Samuels[6] have shown, the flow layers and fragmentation produced by polishing are generally undesirable and may lead to a great deal of trouble during subsequent plating or finishing. For example, by incorporating radio-active carbon-14 into the carboxyl group, investigations[7] have confirmed surface reactions between stearic acid in polishing compound and the aluminium surface.

In an interesting study of the effect of polishing on the surface of the metal, von Krusenstjern and Hentschel[8] measured the depth to which polishing compound penetrates the surface, by analysing successive layers removed by an alternate anodizing and stripping technique.

Fig. 2-2 shows that the depth of penetration varies considerably with the alloy composition and, in general, noticeable amounts of iron from a rouge composition were still found at depths of 3-5 microns (0.12-0.2 mil). On the other hand, varying the polishing speed from a usual 8000 surface feet per minute (40 m/sec) or increasing the pressure on the polishing wheel to the point at which the surface is overheated, has little or no effect on the depth to which foreign matter from the polishing compound penetrates the aluminium surface.

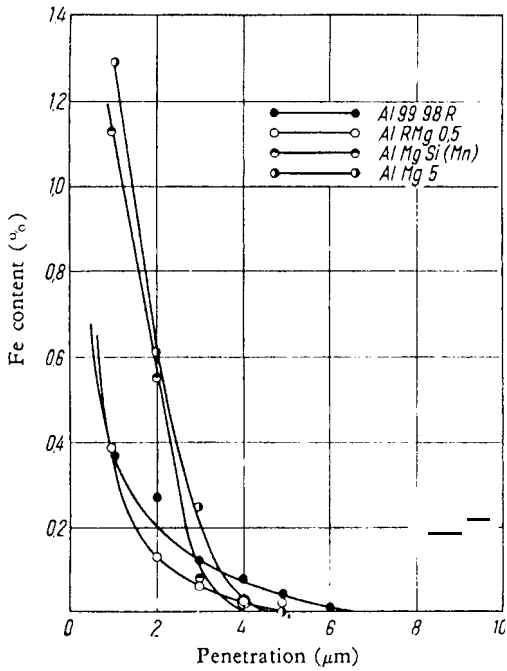


Fig. 2-2. Effect of alloy composition on the depth of penetration of iron into **the** surface during polishing **with** rouge[8]

Mechanical polishing procedures

The five stages of mechanical polishing are often described by the following terms:

1. Grinding
2. Rough Polishing (or “Roughing” or “Coarse Banding”)
3. Grease Mopping (or “Greasing” or “Fine Banding”)
4. Buffing, Mopping or Polishing
5. Finishing, (or “Colouring”)

These terms may not be very logical or descriptive but they have been widely used in industry for many years. Nomenclature can vary considerably from one country to another, and these terms can mean different things in different industries and different companies. In particular, the mechanical polishing term “Colouring” can be misleading as it means altering the shade of metallic grey from dark grey to light grey.

1. Grinding

Very uneven or deeply scratched surfaces, particularly rough sand castings and flash removal etc., frequently require a grinding operation in which wheels are specially treated, e.g., by filling with wax, to prevent loading of the abrasive surface with aluminium particles, and to avoid 'rough glazing'. The abrasive employed is generally silicon carbide of 20-60 grit. Alternatively, alumina is sometimes used in the form of a bonded abrasive wheel.

The peripheral speed of the wheel is low and should in any case be inside the range 1,500-4,000 feet per minute (460-1220 m/min). Care must be taken to avoid overheating and dragging of the surface, but dry grinding is usually preferable to using lubricants.

Silicon carbide of 80-100 grit is most suitable for grinding hard anodized aluminium[g].

2. Rough Polishing (or "Roughing" or "Coarse Banding")

This operation is carried out on all sand castings and many gravity die castings as well as on wrought shapes. It is carried out with set-up wheels, 1.5-4 inches (approx. 40-100 mm) thick, whose diameter may vary from 6-20 inches (0.15-0.5 m). The peripheral speed is usually 5,000-6,000 ft per minute (1524-1829 m/min), though some operators successfully employ speeds of up to 10,000 ft per minute (3048 m/min). On rough castings, grades of emery from No. 60 up to No. 100 may have to be used successively, or 60-120 mesh fused aluminium oxide grit may be employed. The wheels may be lubricated with tallow, with or without the addition of animal or vegetable fats, to avoid overheating. Care must be taken, however, not to drive the lubricant into the metal, as it might contaminate the surface by sweating at later stages.

For curved surfaces and intricate shapes, flexibility is very important and felt wheels dressed with emery may be replaced by cloth buffs dressed with adhesive and abrasive such as emery or "Aloxite" (the trade name of a fused alumina). Roughing may be carried out also with wheels made of canvas, wood faced with leather, or felt. Alternatively, flexible aluminium oxide paper discs may be used. The wheel material must be chosen in each case with some regard to the nature of the work.

Instead of emery or Aloxite wheels, backstand polishing is now almost always employed. This type of machine, which has come into widespread use in recent years, employs an endless belt coated with abrasive on one face and running over two pulleys. The operator works at the front pulley (called the contact wheel). Compared with the polishing wheel, this system combines the use of a larger abrasive surface with ease of production and economy in changing and dressing of wheels.

Henley[10] proposed a polishing band 9 ft long by 4 inches wide (approx. 3 m by 100 mm), i.e. with a polishing area of 3 sq ft (0.28 m^2), and stated that superiority in heat dissipation over emery bobbing gave less risk of overheating and eliminated time-consuming dressing of the wheel. Increasingly, the modern trend is to use resin rather than animal glue to bond fused alumina to cloth belts. Greaseless abrasive compounds are preferable to grease-containing mixtures particularly where the surface need not be cleaned before lacquering. The grit size employed is 80, 100, 120, 180 or 240 and lubricants include tallow, animal fats, vegetable fats and machine oil or pastes composed of paraffin and turpentine. 'Dry' polishing of aluminium is to be avoided.

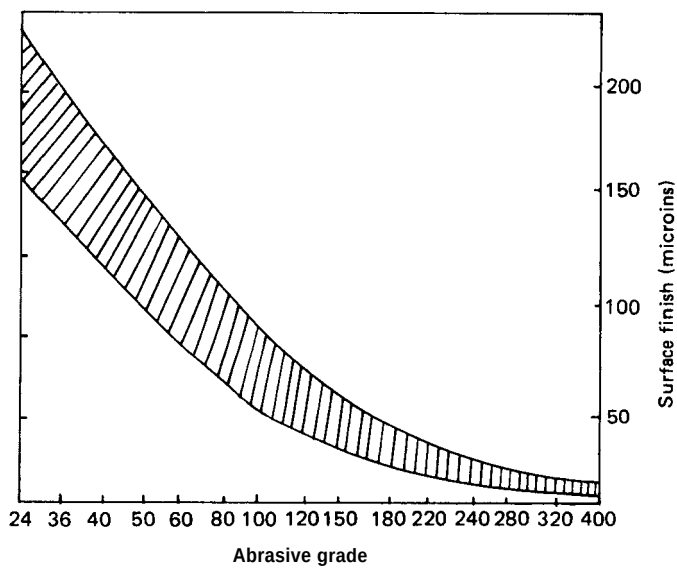


Fig. 2-3. Surface finishes which can be obtained with varioiis grades of abrasive belts

The surface finishes which can be obtained with various grades of abrasive belts are shown in Fig. 2-3.

3. Grease Mopping (or "Greasing" or "Fine Banding")

The third wheel stage, grease mopping, employs finer abrasives and softer wheels. Felt, open air-cooled, stitched, bias cut, cotton wheels, or stitched disc cotton mops, faced with 100-240 mesh emery or Aloxite may be used, and the material

should be chosen for the hardness required. Lubricants are always used in this operation and may include tallow, oil, beeswax or various compositions. Peripheral speeds are similar to, or slightly higher than, those employed in roughing operations and care must be taken again to avoid overheating, as this is detrimental both to the work and the wheels. Grease-mopping may be the first stage in the polishing of many die castings and automatic machine products.

The grease-mopping stage is nowadays more often carried out on backstand abrasive band polishing machines, similar to those used for the rough polishing but using finer grits and more flexible contact wheels

A grease-mopped surface that has been overheated is sometimes given a light etch in dilute sodium hydroxide solution followed by a nitric acid dip, after which the work is rinsed in warm water and dried preparatory to buffing.

4. *Buffing, Mopping or Polishing*

The operation known as buffing, mopping or polishing is designed to eliminate abrasive marks and produce a smooth, lustrous surface. Buffing more than any other polishing operation on aluminium depends on the skill and experience of the operator. Thread count and stiffness of the mop material, composition, wheel speed and the pressure applied are all important and must be suited to each operation. Sheet and many wrought products that need no roughing or grease mopping may be buffed as a first operation.

Mops may be constructed from loose or stitched calico and are usually composed of discs sewn together spirally near the centre or right up to the circumference. The cloths may vary in thread count from 60 by 60 to 84 by 92, with the higher thread count giving a harder wearing buff. Mop hardness is regulated also by means of cloth disc separators between the large discs making up the buffing wheel or by stitching or by cloth treatment and impregnations. Bias cut cloth mops are popular for this operation.

Wheel speeds of 7,000-8,500 ft per minute (2150-2560 m/min) are generally employed. Care must be taken when buffing aluminium that particles of metal do not build up on the polishing wheel, as these may cause gouging of the surface. The embedding of abrasive particles into the metal must also be prevented, especially when the work is to be electroplated or electropolished or given a dyed anodic finish.

Many types of polishing composition are on the market and may differ widely in type and grain size of abrasive as well as in grease or binder. Where work is to be anodized it is important to avoid the use of compositions containing iron oxide, such as rouge, as even a trace of iron may lead to patchy or cloudy anodic coatings.

A German development which has gained some success has been the use of silicones in polishing compositions'' and these have been stated to reduce the polishing time and to increase the reflectivity of the surface as well as to aid removal of polishing composition in vapour degreasing.

Particularly in the final polishing operation, the grain size of the abrasive employed is of importance. If too coarse, the crests tend to be cut rather than flowed[12] with the result that a bloom may appear on the work.

It is useful to remember that increase in wheel speed increases effective mop hardness. A hard mop cuts rather than flows the metal and therefore softer buffing at lower speeds is required for annealed aluminium rather than for metal in the hard condition. On polishing lathes where the spindle speed cannot be changed, variations in the polishing speed are obtained by altering the wheel diameter. The temperature, too, is affected by the polishing speed. A temperature of 200°C is easily reached on the surface, while locally it may rise to 500-1,000°C at contact points. A high temperature if held too long leads to excessive deformation and lattice distortion and this may be particularly in evidence after anodizing.

When polishing castings, the porosity is important. Adequate grinding is essential to avoid dragging the pores during buffing and the surface should be polished in both directions.

Special care must be taken with surfaces that are to be electropolished. Dragging of the surface during buffing may result in pitting during electropolishing, and low wheel speeds and good construction of the buff are essential. Care is also necessary not to cut through the clad layer when high-purity aluminium clad material is buffed. Cut spots will appear dark and of low reflectivity, and such articles will usually have to be scrapped. Local overheating from too high a buff pressure causes dull patches not easily removed by "colour"-buffing. When this trouble is experienced, a softer buff and a fast-cutting compound should be employed to minimise the necessary buff pressure.

After buffing, ordinary work was generally cleaned in some organic degreasing compound, such as trichloroethylene, but aqueous cleaners are replacing solvent based cleaners where possible. Reflector surfaces, constructed of high-purity aluminium or clad aluminium, are often treated in dilute sodium hydroxide solution to dissolve out embedded particles prior to "colour" buffing. For this treatment, the article is immersed for 30-60 seconds in dilute sodium hydroxide at 50-60°C. Alternatively, a chromic acid/ sulphuric acid pickle may be used.

5. Finishing (or "Colouring")

Finishing or "colouring" is the final operation after buffing. Its purpose is to bring out the full brightness and reflectivity of the metal. No metal is removed by this operation. A soft cloth or flannel mop is employed. The polishing composition may be a very fine grained calcined alumina. Sometimes an amount of Vienna lime is also applied during or after this operation. "Colour"-buffing is applied to all surfaces where a mirror finish is required.

It is apparent that many of the polishing operations overlap and the terminology in common usage is frequently ambiguous. The directions given are mainly in

the nature of a guide and the number of operations and their nature should be determined for each article depending on shape, hardness, method of fabrication, nature of surface and finish required. The wheel stages in some typical polishing operations are listed in Table 2-3

TABLE 2-3

Typical polishing sequences

Material	*Sequence of operations*	*Material*	*Sequence of operations*
Sand castings	(Grinding)* Rough Polishing Grease Mopping Polishing Finishing	Sheet, wrought materials	Polishing Finishing
		Forgings, Tubes, Extrusions	(Grease Mopping)* Polishing Finishing
Gravity die-castings	(Rough Polishing)* (Grease Mopping)* Polishing Finishing	Automatic machine products	Grease Mopping
Pressure die-castings	(Grease Mopping)* Polishing Finishing	Small articles of all kinds	Polishing Finishing Barrel tumbling & burnishing

* Operations in parentheses may be omitted

Reflectivity

The reflectivity of mechanically polished aluminium is high compared with most other metals and usually increases with the purity of the metal. The maximum brightness characteristic of the metal is not normally obtained by mechanical polishing only, partly because of inclusion of abrasive and polishing composition in the surface, and partly because of the fine scratches and damaged surface layer of the metal itself. These lead to a cloudy finish which becomes more on anodizing.

Henley[13] reported that cloudiness could be avoided by etching the work in 2% caustic soda solution at 65°C after grease mopping until the cloudy patches were indistinguishable, followed by a rinse in cold water and a short dip in 20% (vol) nitric acid. The work was then rinsed in clean cold and hot water and dried ready for light mopping with a tripoli compound followed by a finishing composition on a calico mop. In some cases only the last stage was necessary.

Nowadays a non-etching cleaner would be used followed by a proprietary etch (containing gluconate to avoid precipitation of aluminium), especially as grease mopping would leave a thin film of grease.

When a mechanically polished and anodized surface is cloudy, careful stripping and re-anodizing markedly improves the finish. In practice some anodizers use an anodizing — stripping — reanodizing sequence as a matter of course. The work is anodized for 5 minutes, stripped for up to 1 minute in a boiling solution containing:

phosphoric acid (d. 1.75) 3.5% (wt)
chromic acid 2%

in a stainless steel tank, followed by re-anodizing.

A particular instance of this anodizing, stripping and re-anodizing technique to produce a perfect super-purity aluminium reflector has been described by Dale[14]. Reflectors of 99.99% aluminium were lapped with both 4-8 μm and 0-2 μm diamond abrasive, separated by a chemical metal-removal stage, after which the reflectors were cleaned, immersed in the boiling solution of phosphoric and chromic acids as noted above, rinsed, anodized in 6% (vol) sulphuric acid at 6 amp/ft^2, 14-16 V, 17-19°C for 20 minutes, rinsed, stripped, re-anodized, sealed in boiling distilled water and de-smudged in 40% (vol) nitric acid before rinsing and drying.

Super-purity (99.99%) aluminium may be used for reflectors, jewellery and high quality holloware where the finish produced by mechanical polishing is not considered adequate, and in such applications it is almost invariably the practice to follow mechanical polishing by electro-brightening or electropolishing. Electrolytic or chemical polishing procedures are also used for commercial purity aluminium and its alloys with the aim of reducing or eliminating mechanical polishing operations. This subject is discussed fully in the next chapter.

Matt and satin finishes

Decorative non-reflective surfaces, varying from a coarse sand-blasted finish to a satin finish, are obtained by various treatments.

Fine set-up wheels or grease wheels may produce a finely-lined surface which may be cleaned and lacquered or anodized. This process may be improved by applying a suitable grade of emery or garnet paper while the article is rotating. Alternatively, flat surfaces may be treated with sand, emery, aloxite or garnet on a flat-bed finishing or sanding machine, after which the work may be given a short treatment in an electropolishing bath or cleaned and anodized or lacquered.

The most important mechanical methods by which a matt surface may be obtained are, however, scratch brushing, using calico mops with greaseless compositions, sandblasting, or finishing with abrasive filled non-woven nylon materials. Various finishes may be obtained by these methods depending on the operating factors and the initial state of the surface. Surfaces so treated are

attractive and may be used for many purposes. Dalla Barba et al[15] have developed a process consisting of shot blasting followed by alkaline etching to give a matt surface prior to anodizing. Consumption of caustic soda is reduced by 75% thus reducing water treatment and sludge formation. The process also removes the common defects of extrusions – streaks and scratches.

Etching to produce matt surfaces is discussed in Chapter 4.

Scratch brushing

Both coarse- and fine-matt finishes may be obtained by scratch brushing, depending on the operating factors. The process is carried out by means of a wire brush applied either manually or preferably driven on a hand lathe or automatic machine. Very large work that is impossible or inconvenient to lift, may be scratch brushed by means of a brush worked on a flexible drive. **A** great deal of the work formerly carried out with wire brushes is line-textured by means of wheels or rolls consisting of non-woven nylon fibres in which grains of silicon carbide or aluminium oxide are dispersed.

There has been (and still is) considerable development of these non-woven abrasive-filled nylons. It is now possible to use them for satinising, polishing, de-burring and grinding operations. Nylon webs are being developed with greater tensile strength and are converted into a wide variety of mops, buffs, convoluted wheels and rollers. The hardness can vary from soft mops to wheels resembling a grindstone and the use of these non-woven abrasive-filled nylons will continue to increase, replacing the older methods of abrasive-dressed mops and wire wheels.

These non-woven nylons impregnated with abrasive grains are available in a very wide range of densities, sizes and impregnations. These wheels require less operator skill than do the older methods, and the abrasive surface is continually renewed so there is less glazing and clogging of the wheel surface. They can also be used with water sprays to reduce overheating and help prevent the clogging of the surface.

The metal surface prior to scratch brushing can be given a medium sand-blast or a preliminary roughing and greasing operation, and, for fine satin finishes, castings may first be buffed with a mop using greaseless composition. The surface must be free from dirt and grease, and is preferably cleaned in the degreaser. Nylon abrasive-filled webs are often used after the roughing or the grease mopping operation.

The diameter of the wheel is usually 6-10 inches (150-250 mm) and the peripheral wheel speed varies with the nature of the work. Coarse finishes on wrought articles are obtained by speeds of 5,000 ft per minute (1500 m/min), while with castings, where there is a greater danger of tearing the surface, the speed is reduced to 2,200-2,600 ft per minute (650-800 m/min),

or even lower when a very fine satin finish is sought. Nylon web wheels are usually run at about 3000 ft per minute (900m/min).

The wire brush may be of stainless steel, nickel or nickel-silver and may be either straight or crimped. The wire diameter, depending on the work and nature of the finish, varies between 0.002 and 0.020 inch (0.05 and 0.5 mm), the finest wire being used for satin finishes on greased or buffed surfaces. With some metal brushes, notably those of nickel-silver, brushing must not be too prolonged or a rough surface may result due to cold welding of the material with the aluminium[16]. Fibre brushes sometimes replace wire brushes in finishing operations. Brushes have to be cleaned frequently with pumice stone or soft brick to avoid dragging by metallic or aluminium-oxide particles. For the same purpose, care must be taken not to exert too heavy a pressure in scratch brushing—a light application is sufficient.

The angle of application of the work to the brush must be uniform, but can be varied according to the desired finish. Sometimes, contrasting designs are obtained by varying the direction. Scratch brushing may be carried out either dry or with a jet of water playing on the brush.

As a modification of the scratch brushing process, a spin finish may be given to hollow work by revolving it against an oily cloth dipped in abrasive or an abrasive emery cloth, and finishing with stainless steel wool, similarly treated, and a cleaning cloth.

Some scratch-brushed surfaces, if not lacquered or anodized without delay, are liable to attack when exposed to a corrosive medium. This is caused by the breakdown of the natural oxide film and the local electrochemical corrosion that takes place where metal particles, particularly brass, cathodic to aluminium, have become embedded in the surface from the wire. To prevent local attack of this kind, the scratch brushed metal should be cleaned by immersion in a nitric acid dip.

4. FUNCTIONAL ABRADING AND POLISHING PROCESSES

Polishing is a process using abrasives or abrasive compounds that adhere loosely to a flexible backing such as a polishing mop. Abrading operations usually follow grinding, and precede buffing operations. In general, abrading will permit a more aggressive action than polishing, and has a greater capability to modify the shape of the component and has a higher definition of scratch pattern. Polishing achieves finer finishes, has greater flexibility, and a tendency to follow the contour of a component.

Abrading and polishing processes are used for refining edges and surfaces of castings, forgings, machined and stamped components, and moulded and fabricated parts. They make attractive, decorative surface appearances, and

produce a surface suitable for subsequent plating, anodizing or painting. Functional requirements as well as aesthetic specifications must be considered. Components with improved edge and surface finishes are generally safer, more durable and more efficient. Many products must have sharp edges removed to avoid cutting the user, or associated components.

Iinprovement of edge and corner radiusing and of surface finishing go far to remove stress raisers from which fatigue cracks are most likely to propagate. Mechanisms have reduced friction characteristics if the edge and surface finishes are improved, which result in greater efficiency and normally require less dynamic energy to function at design limits. Radiused edges also make automatic assembly of components easier and more efficient. Abrading and polishing equipment and materials have now improved sufficiently to enable these techniques to be used for flexible machining applications. Automatic abrading processes can be utilised for substantial metal removal purposes, whilst maintaining close tolerances and improving surface finish. Polishing operations can be employed for edge and comer radiusing, and can generate extremely fine surfaces, in some cases matching honing and lapping; they can also maintain the very close tolerances associated with modern machining technology.

Equipment for polishing is similar to that used for abrading operations for manual, semi-automatic, or fully-automatic applications. Abrading equipment normally requires greater precision and rigidity than polishing machinery because the polishing process is more flexible, whilst the abrading process is more frequently used to modify the shape of parts and to machine them to specific tolerances. Consequently, abrasive equipment will require more precise component fixturing and care in the set-up of the equipment than does polishing equipment. The prime mover in the advance of metal improvement techniques has been the international aerospace and aeronautical industry[17].

Fully automated equipment that very closely follows manual deburring methods has been developed and is in use. Typically, but not necessarily extensively, the more modern abrasive media such as nylon, extruded and impregnated with either silicon carbide or alumina oxide abrasives, are formed into brushing sections and are used automatically.

The machines are designed to remove burrs and to produce controlled radii on components after numerical controlled milling; one, two or more polishing heads with nylon bristles are mounted over static flat bed work tables on a traversing frame which runs on tracks on either side of the bed. As well as longitudinal lateral motions, the brushes can oscillate automatically for 250 mm, rotate vertically through 340" and also have a reverse rotation capability. A 30" 'tail-wag' facility is also built-in.

Alongside the development of the more sophisticated methods of finishing by 'polishing' originated in the aerospace industries, growth in cosmetic polishing for the holloware industry has continued. In the non-developed countries there has been an increase in the production of aluminium holloware. With the availability of primary aluminium from many sources, large production units

have been set up in countries which are not historically associated with high class finishes. Outputs in the order of 600-700 holloware components per hour have led to the development of relatively simple, relatively inexpensive, high output machines which need little maintenance and expertise in setting.

The advent of the long mop, typically 7 ft (2.1 m) wide or 12 ft (3.6 m) wide, using bias cut cotton sections with liquid tripolis or liquid calcined and fused alumina compounds, has enabled outputs of such components at the rate of 600-1,000 per hour, at low piece part and labour costs. In addition, the necessity of abrasive operations prior to polishing has, to a great extent, been obviated.

Notwithstanding the advances in polishing techniques, the basic premise that the surface produced as a function of polishing time and polishing pressure remains. The newer methods postulate that increasing the surface availability of the mopping area, whilst reducing the speed, has the advantage of giving a longer polishing time, cooler operations, and hence a lesser destruction of the polishing medium. Also, the lower revolutions per minute and the larger diameter bias cut cloth buffs enable the component to be buried into the wide buff surface which in turn reduces the need for precise settings of buff and component. This method of polishing is referred to as "mush" polishing. Similar systems are used for the finishing of aluminium door furniture and window fittings.

Indexing polishing equipment is used quite universally where the need for finishing aluminium components with various areas requiring deburring, radiusing and surface finishing is present, and can be used for such parts as aluminium fasteners, pump components, and other functional aluminium parts as well as for pure cosmetic finishing on a wide range of aluminium components. The benefit of the indexing system is the ability to remove specific burrs from areas both internal and external to the part itself, and to polish specific part areas. As many as 10 separate operations are possible at each of the stations, and with present 'pick-and-place' or robot systems, parts can be automatically loaded and unloaded during the process cycle on other components obviating operator involvement. With this method of automatic polishing, harder, faster revolving buffs are used and so the article is not "buried" so far into the buff as with mush polishing. This method is often referred to as point contact polishing and so requires greater accuracy on buff and component settings.

5. BARREL AND VIBRATORY SYSTEMS

Both abrasive belts and polishing mops are capable of producing well deburred, finely finished, aluminium components if carried out correctly. They do, however, have some disadvantages:

1. They can be costly in terms of materials used and also in the labour content of the operation. They are essentially processes where components are treated

singly. There are a few exceptions where production throughputs can justify the cost of automatic systems.
2. There is the fatigue factor to be considered which comes as a result of the intensity of hand labour and the nature of the process.
3. There may be the necessity to include cleaning processes to remove unwanted polishing or abrasive solids from the components.

Because of these factors, and others, industry has looked for more acceptable ways of carrying out these finish operations on engineered components, which would give an effective means of finishing components in batches rather than individually and involve minimal labour and material costs.

Barrel polishing

Barrel polishing is carried out in circular or inclined polygonal barrels made of wood, plastics, steel, or rubber or plastic-lined steel. The polygonal shape gives a good cutting action by allowing the parts to be polished to fall and abrade one another. Higher speeds of around 60 m/minute are used for lighter articles, heavier parts being processed at about 30 m/minute linear velocity.

An initial scouring action can be employed, in which case the components are mixed with water and abrasive media such as alumina or granite chippings; synthetic media can also be employed. The articles should be degreased when necessary. The barrels are run about two-thirds full. In the case of heavier articles, excessively high speeds should be avoided, as this can lead to locking of the parts so that no polishing action occurs at all.

In the final polishing operation the components are put into a barrel which is almost half filled, taking care to avoid damage due to impingement. Soap or synthetic detergent is added, and also trisodium phosphate as a brightener. Other additions include rosin-free wood pieces, and limestone chips.

Best industrial practice is to use barrels solely for aluminium components. The pH of the liquid in the barrel must be monitored and maintained at about pH8 to minimise chemical reaction with the aluminium. As hydrogen may be evolved, barrels used for aluminium components must be vented.

Vibratory polishing

The barrelling machine, however, has many problems. It is a closed process which makes it difficult to check parts during operation. It requires a wet deck area to receive discharged water in large quantities, and needs overhead hoist equipment to load and reload media and components. It also involves long process times of 6-12 hours.

By further development, the rotational motion of the barrelling machine became the vibratory motion of the open 'U' section tub of the vibratory machine. This not only eliminates the above-mentioned problems but also makes it possible ultimately to develop circular vibratory systems with the inbuilt facility to separate and discharge the components from the machine by the operation of a simple flap and screen assembly. Process times are also shortened as a result of the constant vibrating action of specially developed media rather than the intermittent cascade of the barrel. These are nowadays often metered into the process tubs on a constant loss basis, bringing cleaner processing, especially to components manufactured in aluminium for high technology products.

As a result of these developments the finishing processes have also been incorporated into automatic production lines.

The most important advantages are:

1. Low cost processes
2. Low labour costs (only load and unloading required)
3. Batch finishing of components
4. Consistency of finish on batches of parts
5. Cleanliness of parts
6. Elimination of inconsistent standards due to operator fatigue

Vibratory machines are used for descaling, deburring, the removal of flash or grinding marks, and for polishing. The parts to be treated are mixed with abrasives, polishing compounds, and water, the barrels being run almost full. The compounds and solutions used are frequently proprietory, developed for specific operations and metals. Vibratory machines have been produced for airframe components. Tennant" has reviewed mechanical finishing in the aerospace industry.

Fig. 2-4 shows a vibratory system with compound recirculation.

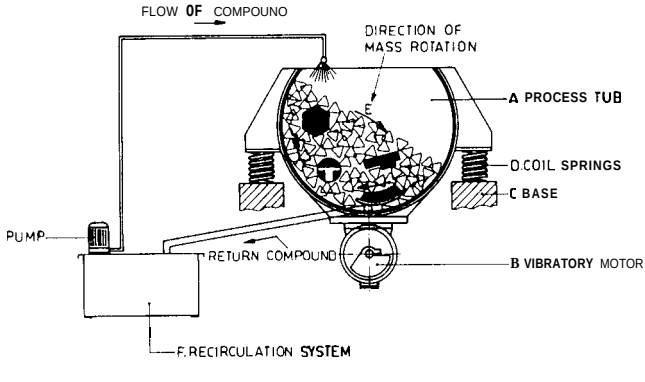


Fig. 2-4. Basic vibrator with compound recirculation system

Vibratory machines have two rotational movements, which serve to increase the pressure of the abrasive medium on the load. The barrels are cylindrical, and operate at up to 3,500 oscillations a minute, depending on their size. Automatic separation of components from media is a feature of the spiral vibratory machines in which the parts are separated and discharged continuously. Delicate parts, or those incorporating inserts, can be held in place in fixtures if necessary. The rate of processing is high, and can be completed in an hour or less, especially in the case of high energy machines which can operate as much as 30 times faster than conventional vibratory ones.

Spindle machines are quite capable of handling large articles, as they are characterised by the fact that the components are held in fixtures and lowered into a tub containing the polishing mixture. The tub rotates at 100-200 m/min. and is vibrated at the same time. Spindle type plants provide a high standard of finish quickly in 10-20 minutes, but are clearly only suitable for comparatively expensive items, as the parts have to be handled individually. A wide range of designs and features are available in the products of different manufacturers. Some typical components before and after processing are shown in Fig. 2-5.

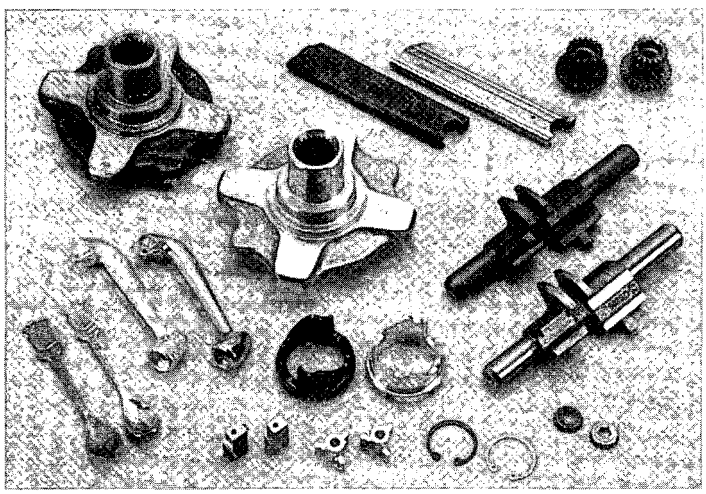


Fig. 2-5. Typical components before and after processing

Hinz[18] has given an overview of vibratory finishing where a chemical polishing solution or an etching solution is used so that removal action is enhanced by chemical reaction.

Polishing media

The polishing media play an essential part in the successful operation of vibratory and also centrifugal polishing plant. They consist of various combinations of abrasives, liquid compounds and accelerators. The functions of the media are:

a) To separate the parts and so prevent impingement damage;
b) To create the pressure mass in which the process is carried out;
c) To hold the abrasive which does the actual work;
d) To carry the chemical compounds so that they are evenly distributed throughout the mass.

The early media which have been thus far considered were natural in composition and random in shape. This itself constituted a problem, in that because of the random shape, it was often possible for chips to lodge in holes or slots in the components causing damage when being extracted. This led to the development of new types of synthetic media which were preformed into rods, cones, polygons, etc., so that all the chips were of a similar size and shape in a particular batch. The media are produced by mixing suitable abrasives in a ceramic clay, extruding the mix through dies to achieve the desired cross sectional shape, and cutting to length. The pieces are then fired in pottery type kilns. These are the most widely used type of media today (Fig. 2-6).

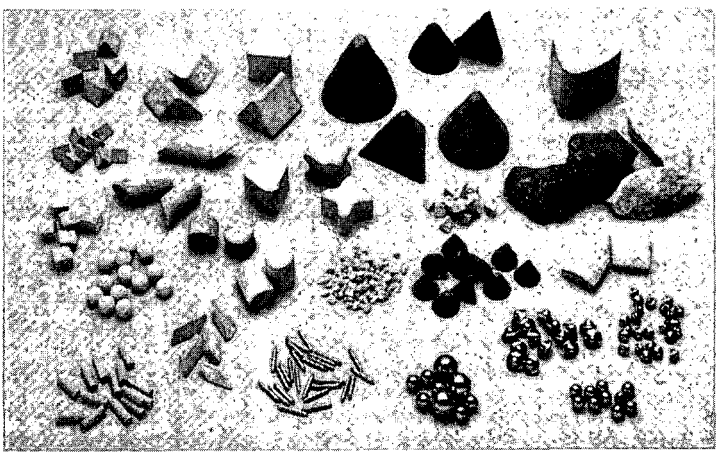


Fig. 2-6. A range of media in various materials, shapes and sizes.

They combine efficient cutting characteristics with relatively fast process times and are manufactured in a number of cutting grades and shapes to meet the

requirements of a particular application[19]. Whilst these ceramic media can be used successfully with aluminium components of all kinds they can have certain drawbacks when used to process precisely machined components in vibratory machines. This arises as a result of the vibrating media impinging on the surface of the component and creating an orange peel effect. In part, this can be reduced by lowering the amplitude of vibration which, however, has the effect of lengthening the process time.

The problem does not create any great difficulty when cutting down cast or forged components prior to machining or in the de-flashing of die castings, where, because of its density, a ceramic medium can be of assistance. Nor does the problem arise in those processes carried out in barrel or centrifugal force machines where the media action is one of sliding rather than impinging as in a vibratory machine.

For all machines the ideal medium, however, when processing aluminium components, is one of low density and softness. With the advent of plastics it has become possible to manufacture such media using a mixture of resin bonded plastic or urea-formaldehyde with suitable abrasive grits such as alumina, limestone, etc.

Normally these types of media are produced by moulding and so can be supplied in the ideal anti-lodgement shapes of cones and pyramids. This type of media has become very popular in the finishing of aluminium components and those manufactured from aluminium alloys. It can combine high degrees of surface finish with good cutting characteristics according to the size and grade chosen.

When one discusses size of media it should be remembered that small media produce fine finishes, and large media produce fast but rougher finishes. This relates to media of either a ceramic or a plastic base and in this sense can be regarded in the same way as one would consider a grinding wheel, where a wheel with a coarse open grain would be used to achieve a high metal removal rate without too much concern about the ultimate fineness of finish. For fine finishes, however, a fine grain, close bonded, wheel would be most satisfactory.

However, cutting action is not just the result of the size of media; it also depends on the type, grade and amount of abrasive in a particular chip. In simple terms a cutting chip is composed of hard abrasive grains embedded in a softer ceramic or plastic base. It is so designed that as the surface grains are eroded by the action in the machine, the soft base also wears to expose fresh, sharp grains of abrasive. The size, type and density of the abrasive determines the amount of work done on a part and the standard of finish achieved. It is obvious therefore that great care should be taken in the selection of media for specific purposes. It is also obvious that the heavier cutting grades are not generally acceptable for the finishing of aluminium components, which can be easily scratched on fine surfaces. Such heavy grades can however be used for the scurfing or cut down of unmachined aluminium castings.

One other type of media needs to be mentioned in relation to the finishing of aluminium components, i.e., the non-abrasive types of material. Generally speaking, such media are manufactured from steel, stainless steel or porcelain, and supplied in a number of shapes and sizes. Steel media are usually in the form of balls, ball cones, cropped wire, cylinders (both straight cut and angle cut) and needles. Porcelain type media usually take the form of balls or balls with a parallel annular ring. The function of this type of media is primarily for the bright finishing of aluminium components where cutting is not required, or after cutting has been done. The rolling action of such bright media can, when used with the correct compounds, produce highly polished surfaces on a wide range of aluminium components. Care should be taken, however, when processing machined parts, to ensure that the amplitude is not such as to cause impingement marks on the surface of the metal by the impact of the media. Where this can occur then it is usual to use the lower density porcelain type media.

Compounds

The three elements which are fundamental are the action of the cutting chip, the compound, and the machine. Each has its own part to play.

Compounds are added to the media in the machine in order to assist or modify its action so that the desired finish is achieved. Compounds also act as cleaning agents which keep the media in the best possible condition for effective cutting or polishing.

In general the compounds are diluted with water and fed to the tub either by recirculation or by a metering system which operates on the constant loss principle. The compound additions can perform a number of functions during the process, in that they can contain components which will degrease, clean, abrade, inhibit against corrosion or add lustre or brightness to parts which are being processed. They vary from acidic to alkaline and are generally safe in use and bio-degradable.

Various types of accelerators have also been introduced; these are particularly effective where reactive metals such as aluminium alloys are employed, and are generally acidic or alkaline in nature, with suitable inhibitors to promote a uniformly smoothing action.

Other considerations in the finishing of aluminium components

a) Work loads

It is important to consider the possibility of the impingement of hard media on the machined faces of soft metal components. Damage by impingement can also occur from contact between components during the processing cycle. It is therefore essential that the work load of components is carefully estimated. The safe way, of course, is just to put one part in the machine, but whilst this is

sometimes done with very large components, for the general run of parts which are smaller and produced in batches it is obviously not economical. General estimation of the ratio of media to parts in the process tub will vary with the shape or complexity of the parts to be processed or by the final quality of finish to be achieved. Ratios can vary between 1:1 and 10:1 in finishing machines. Normally aluminium parts would have a ratio of not less than 3:1 and the majority would be processed at 5:1 or 6:1 ratio. Each component needs to be taken on its merits, however, and if carefully chosen the ratio can produce components which are entirely free from impingement damage.

For larger components two methods of processing are possible. Firstly, the components can be fixtured, as with any other machine tool, so that the parts are held in the vibrating or rotating mass. Secondly in vibratory machines the process tubs can be compartmented so that each part to be processed is placed in its own section, making impingement of the parts impossible.

b) Process times

It is not possible to lay down hard and fast rules with regard to process times. They will obviously vary according to the amount of work to be done and the type of surface finish required.

The tendency in this type of finishing is that the media first works on the component edge which makes it an ideal de-burring system. After the burr has been removed the edge treatment continues and the process of radiusing is carried out. During this time, but at a slower metal removal rate, the surfaces are being worked on and cut down achieved. This sequence is one of the reasons why de-burring operations can be carried out on aluminium or other components without undue work being done on the machined surfaces. Where castings are to be cut down, then it is always advisable to carry out the operation where possible before machining since the cut down is the largest operation.

In general terms, in vibratory plants, cut down operations take between 1 and 1½ hours, de-burring and radiusing between ½ and 1 hour, and polishing or burnishing 15 to 30 minutes. These times would be lengthened in barrelling machines and considerably shortened in centrifugal force type machines. It should be stressed that these are not rules but guides. They can vary considerably according to a specific component and the composition of the component.

Centrifugal finishing

The centrifugal finishing machine is generally used for mechanical deburring and surface finishing. One of the prime advantages of centrifugal barrel finishing is the ability to handle fragile parts for deburring, descaling and generating radius and radii. In the aircraft and aeronautical industry the ability of the process

to impart very high compressive stress on the surface of the parts, so improving resistance to fatigue failure, is particularly valuable.

Centrifugal barrelling equipment basically comprises a number of drums mounted on the periphery of a turret. The turret rotates at a high r.p.m., in one direction whilst the drums are rotated at a somewhat slower speed in the opposite direction. The parts to be deburred and finished are loaded into each of the drums, usually using a medium, water and a compound. Turret rotation can create variable high centrifugal forces up to fifty times gravity, compacting the load within the drums into a tight mass. Rotation of the drums works actively on this tightly packed mass and the media slide against the parts being processed, removing burrs and refining surfaces.

The abrading action, whilst under high centrifugal force, results in a very short process cycle. To illustrate, a product rubbed lightly by an abrasive is not affected greatly; but the same abrasive can dramatically affect the surface condition of the product when rubbed with the pressure increased by up to fifty times. Process cycles would be usually less than 1/50 of the time needed to debur all finished parts in barrels operated under normal gravity conditions.

Most centrifugal barrel machines have variable speed turret rotations, and this allows variation of the 'G' force by lowering or increasing the turret speed, thus developing heavier deburring processes at higher 'G' force, whilst having the capability to handle more delicate parts at lower 'G' forces (Fig. 2-7).

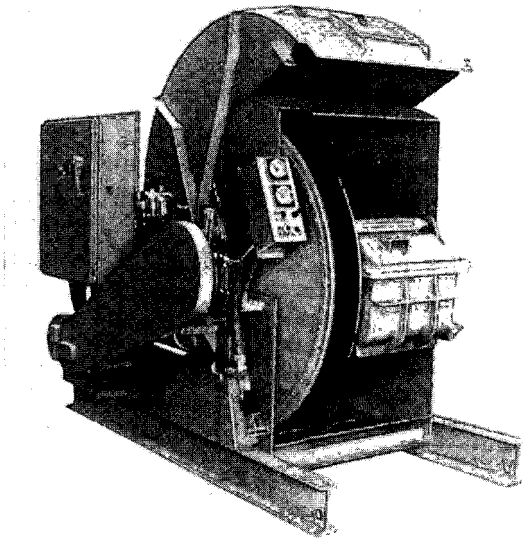


Fig. 2-7. Modern centrifugal barrel machine

A further example of the use of centrifugal force for finishing is illustrated in the wide use of centrifugal disc finishing machines. This type of high energy deburring and finishing unit incorporates a dual speed centrifugal disc, located at the bottom of a stationary urethane-lined vertical process tub; the process relies on toroidal removal of the mass (abrasive, media and parts to be processed), combined with the upward flow of the mass, activated by the disc and slowed by contact with the stationary wall. The parts are returned to the centre in a constant high energy pumping cascade, producing the necessary friction of the media on the metal part.

This principle combines the advantages of the original barrelling techniques – the split layer – with the advantages of vibrators, in that action is continuous at all times. High production rates can be achieved together with very satisfactory finishing results. With the proper selection of the most suitable compounds and media, fast deburring, heavy grinding and fine finishing can be achieved. Typical examples are aluminium castings, pump housings, etc., where a normal deburring cycle of fiteen minutes is achieved, as compared with several hours in conventional vibratory machines.

Critical to the success of centrifugal disc finishing is control of the gap between disc and side wall, which must be less than 0.010 inch (0.25mm) for equipment to be capable of handling anything but the simplest application; and the gap must be kept controlled throughout the life of the disc and the drum. Because of the substantial activity within the centrifugal disc machine, disc and drum walls are subject to heavy abrasion. For this reason the materials used for the building of conventional vibratory equipment are not normally well suited to centrifugal disc finishing machines. High wear resistant alloys are preferred which result in a disc life in excess of 5,000 hours for most applications.

Centrifugal disc equipment is normally capable of handling part sizes from ¼ to 8 inches (0.6–200 mm) in length and can achieve a higher quality of finish, holding closer tolerances than the more conventional vibrator methods, whilst process cycles are generally less than one fifth of those of vibratory finishing. Most centrifugal disc finishing machines have open tubs which facilitate ‘in-process’ inspection and control, and this equipment is well suited to batch automation.

Fig. 2-8 shows a vibratory machine with ‘in-tub’ separation of components and media. The vortex effect during operation is seen in the illustration (Fig. 2-9).

Spindle finishing may also be classified as a high energy mass finishing process. However, because parts must be fixtured, spindle finishing is less versatile than other techniques. However, for deburring regular shaped parts which are easily fixtured, spindle equipment has proved to be of substantial benefit and equipment is readily available from numerous sources. High energy, or centrifugal mass finishing techniques, have become highly sophisticated and flexible, and lend themselves to robot and fully automatic operation.

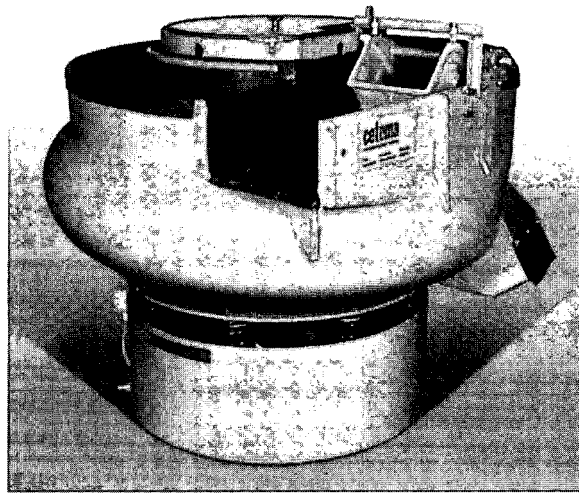


Fig. 2-8. Vibratory finishing machine with 'in-tub' separation system

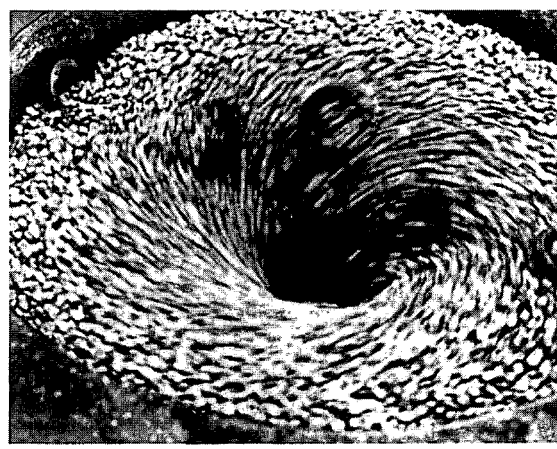


Fig. 2-9. The vortex effect during operation of the vibratory finishing machine

Another development, becoming more common in use, for the removal of internal burrs from small and large aluminium parts is the electrochemical deburring system. An electrochemical deburring machine selectively removes burrs from a component and has no effect except in the immediate vicinity of the burr. Its general application is for the removal of recessed and difficult to

reach burrs. Electrochemical deburring dissolves the burrs from a component in a controlled manner, effectively by deplating. Direct current (about 20 amps for every linear inch of edge from which the burr is to be removed) is passed between the workpiece to be deburred, which forms the anode, and the tooling, which is the cathode within the electrolytic cell. **A** gap is maintained between the tool (the cathode) and the work piece (the anode) of between 0.015 to 0.020 inches (0.38–OS mm).

The electrical circuit is completed by pumping an electrolyte or salt solution through the gap between the tool and the workpiece. Chemical action between the metal and the salt solution dissolves the burrs to form hydroxides which are collected as an insoluble brown sludge in a settling tank in the electrochemical deburring machine. One of the real benefits of this process is its ability to remove burrs without the use of strong chemicals that could change the chemical and physical characteristics of the material being deburred.

6. POLISHING BY MACHINE

There are basically two means of polishing, (1) Point contact polishing and (2) Mush polishing. Point contact is where the mop comes into contact with the work, so to cover a surface multiple heads are needed, each head polishing a little bit of the surface, as opposed to mush polishing where the whole surface is covered by "mushing" or burying it into the mop.

1. Contact polishing

For contact polishing, the machine imitates the movement of a manual polishing operation and densely packed mops are used rotating at fast speeds, usually higher than 1,200 r.p.m. Because the wheel is very hard when rotated at high speeds, the area covered is relatively small.

To increase the versatility of finishing equipment, and to maintain more precise control, hydraulic drives for conveyors or tables are often used, facilitating precise control of speeds; other developments include programme control, complete with three-dimensional fixture manipulation.

Point contact polishing requires far greater attention to machine setting, but is more economical in mop and compound usage. It is widely used in mainland Europe.

2. Mush polishing

This technique is becoming more widely accepted, and is a method by which a broad mop is used to cover much larger areas than is possible in contact buffing. Shafts can be up to 12 ft. (3.6 metres) long with polishing mop sections

mounted along the shafts, usually separated with 13-75 mm (½–3 in.) of space between each of the buff sections.

In mush polishing the mop itself flexes and envelops the contours of the component being finished. Parts travel across the face of the wheel, quite often without precise manipulation of the fixtures. In general, simple rotation or oscillation is all that is required to ensure a uniform finish on component faces. Shaft speeds for mush polishing are almost always much slower than for contact polishing. The slower speed of rotation keeps the working temperature of the mop sections lower. Productivity is generally higher than with contact polishing methods whilst uniformity and quality of finish are enhanced by the increased flexibility of the slower speed mops. Components are sometimes buried up to 2" (5 cm) into the mop surface.

Compound application

The prime purpose of the polishing wheel is to carry the compound which is usually sprayed onto the wheel by the use of air operated spray guns or airless systems. Solid bar compound application may also be used. It is applied to the wheel using a compound applicator which moves the bar to the surface of the wheel at timed intervals and by preset increments. The disadvantage of this system is that pieces are left over and regular reloading of the applicator is necessary. Liquid compounds are more often used, and basically there are three methods of application.

A. Low pressure application

Low pressure application utilises pressure tanks or pumps. Tanks are pressurized to approximately 50 p.s.i. (345 kPa) depending on the viscosity of the compound. Compound made for this type of system is fairly fluid so that it constantly seeks its own level and does not develop cavitation which might introduce air into the system.

When a pump is used, a 3:1 (density) ratio pump is placed directly into a large drum of compound. The compound is then pumped directly to the system which will include a compound line or manifold, air manifold, and electric solenoids for actuating the guns and timers. In this low pressure system, depending on the viscosity of the compound, pressures up to 825 kPa (120 p.s.i.) are used.

Due to the air cushion set up round a revolving mop, these low pressure systems are very wasteful of compound. Up to 50% of the compound can be thrown back owing to poor penetration of the air cushion.

B. High pressure systems (Airless spray systems)

High pressure systems utilising a 30: 1 pump, high pressure lines and high pressure manifolds can be used to penetrate the air cushion. Guns are fired in

the same manner as the low pressure systems utilising timers and solenoid valves. High pressure systems are most widely used where there is a multiplicity of identical machines being fed with the same compound. The gun in these systems is basically an on/off valve. Thus there is high pressure throughout the system so the compound reaching the mop depends not only on the timer on/off time but on the viscosity of the liquid compound – the thinner the compound, the more arrives at the mop.

C. High velocity spray gun systems

The big disadvantage of the high pressure system being dependent on the viscosity of the liquid compound, has been overcome by using low pressure/high pressure guns in conjunction with low pressure systems. These guns have typically a 25: 1 ratio between the air cylinder and the firing mechanism of the gun. The pressure of the liquid compound is low till it reaches the gun; the 25:1 intensifier in the gun fires the compound at high pressure onto the mop. The main advantage of this type of system is that the same measured amounts of compound are fired into the wheel at pressures up to 8,500 kPa (1500 p.s.i.). No matter what the viscosity of the compound, the same volume of compound reaches the mop from the pre-set fixed size compound chamber in the gun. All liquid compounds are thixotropic so the more they are moved, the thinner they become, so even the length of piping in an old single pressure system affected the amount of compound which reached the mop.

Normally, tripoli and calcined alumina compounds are most effective in this type of system because the rate of wear using aluminium oxide compounds can become too great. The high pressure when the compound is fired from the gun ensures nearly all the compound penetrates the air cushion and ends up on the mop.

Satin Finishing

In some cases, a non-lustrous finish will be required, and for this application, particularly for automatic operations, the advent of nylon abrasive wheels has facilitated the operation. There are basically two types. The first type, which is normally used for satin finishing, is based on a flexible, resilient, abrasive impregnated, non-woven nylon or similar impregnated material. The abrasive is dispersed evenly through the material so that wheel performance remains consistent despite wheel wear. These types of wheel in many cases can be shaped to conform to curved, irregular surfaces. They are water resistant and are produced in a large range of sizes. A wide variety of densities and grit sizes is available, and they can be used both wet and dry. Some typical abrasive grades used for various operations are shown in Table 2-4.

TABLE 2-4

Typical abrasive grades used for various operations

Heavy stock removal	24-30-36-40	Heavy metal removal and large depth of cut
Medium stock removal	50-60-90	Average stock removal and progression from coarser grades
Light stock removal	100-120-150	For operations requiring minor dimensional changes and progression from coarser grades
Finishing	180-220-240	Final finishing operations, prior to final polishing, 'in-line' finishing
Lapping	360-400-500-600	Final high finishing, usually for engineering applications

The wheels are especially useful for improving uniform scratch patterns in aluminium, but also can be quite effective in the removal of burrs and the generation of radii on sharp edges. They operate at various speeds ranging from 3-33 metres per second (600-6,500 sfm) depending on the specific wheel and application. When nylon wheels are used to finish flat sheet stock, wheel oscillation at about 200 cycles per minute, with 10 mm amplitude, is recommended to attain a uniform streak free finish. **As** with manual satin finishing, the development of the non-woven abrasive filled webs is rapidly increasing.

A second and more recent application is the extruded impregnated nylon brush wheel. The abrasive is extruded into the nylon filaments, and is made up into brushes; it can be used basically for the same application, but will not normally give such a regular finish. Their ideal application is in the removal of burrs and the generation of larger radii. The use of these abrasive filled nylon filaments is increasing as technology improves the various properties of the filament carrying the abrasive.

Polishing wheels

Polishing wheels carry the abrasive compound across the work surface and produce a cutting and colouring action. Selection of improper polishing wheels may result in the production of an unacceptable, or too expensive surface finish. Polishing wheels in general use are classified under the designations of

(a) Bias buffs;
(b) Finger buffs;
(c) Full-disc buffs;
(d) Stitched buffs.

Each type has certain characteristic advantages that have been discussed in detail by Nelson[2"] :

a) Bias buffs

In automatic polishing the use of bias buffs is normal. The cloth for the buffs is biassed by first taking a length of cloth, folding it longitudinally and sewing it into tube. The tube is then cut continuously at an angle of 45° into strips thus making all the threads at 45° to the edges of the strip. This prevents the cloth fraying.

Bias buff sections are usually composed of sections of approximately ½-1 inch (13-25 mm) wide and are made concentric to the spindle by the use of centre plates. The nature of construction and assembly is such that air circulates through the centre to cool the buffs and to prevent build up of heat in the surface of the buff in contact with the part. Resilience of the buff section is controlled by:

(a) Varying the number of plies in each section;
(b) The diameter of the centre retaining plate;
(c) The degree of pleating.

Heavy buffing operations require sections with a greater number of plies and a greater number of pleats in their construction. The gathering of the pleats at the centre of the buff maintains the aggressiveness of the buff as the wheel wears out and the surface speed decreases. Use of cloth treatments can increase the stiffness and abrasiveness of the wheel and can lengthen the time before the wheel wears down to an unusable condition.

The use of cloth treatments is increasing and can prolong buff life by as much as 50%. Compound retention is also improved. A very wide variety of treatments is available. Cloths containing SO% cotton and SO% polyester are increasingly being chosen due to their high tensile strength.

Cutting wheels are composed of cloth with approximately 86/80 threads per square inch, whilst lighter duty wheels are made up of cloth with 60/60 threads per square inch. All the materials are cut on the bias so the threads are continuous from the centre out and do not fray during use.

b) Finger buffs

These buffs are composed of individual segments of bias cut cloth, assembled on a buff hub. When polishing pressure is applied, these segments yield and flex as they follow the work contour. The freedom of movement afforded each segment provides the flexibility and pliancy required for buffing highly contoured surfaces. The density of finger buffs is varied by:

(a) Altering the number of layers stitched into each segment unit;
(b) Increasing and decreasing the number of rows of sewing on each segment;

(c) Changing the number of fingers mounted around the centre ring;
(d) Changing the diameter of the hub.

Finger buffs are normally used when other types or buffs are unable to make adequate contact with the work surface.

c) Full disc buffs

Full disc buffs are made so that each ply in the buff has a full one-piece circular layer of cloth. Loose buffs, in which the layers of the plies are assembled and held together with a single row of stitching around the arbor hole, are generally used for light cutting down or colouring operations, and other applications in which a great deal of looseness and flexibility is desirable. The density and thus hardness of the buff can be varied by the type of stitching used and the distance between the rows of stitching. Very hard buffs can be produced by selecting a stiff cloth and sewing with very little distance between the rows. A very wide range of cloths are available from soft raised cloth to starch filled hard cloth. Full disc buffs are usually confined to manual polishing.

d) Stitched buffs

Stitched buffs are constructed from new, or regained, irregularly shaped remnants and strips of cloth which are by-product cuttings from other textile articles. Pieces are laminated between and outside layers of full discs of cloth. Various designs are stitched in to tie the plies together into a completed mop section. A variety of grades and qualities of pieced buffs is available. These are manufactured from all coloured pieced material or from a mixture of unbleached, bleached and mixed weights of cloth counts of fabrics. These buffs are generally used in heavy cutting down operations or in operations that severely attack the face of the buff with a raking effect. They are the cheapest type of buff available.

Selection of compounds

The selection of polishing compounds is influenced mainly by the initial surface condition of the component, the type of polishing equipment being used, and the surface finish required[2]. The size and design of the part to be polished may also influence compound selection, particularly whilst the dwell time is low.

Buffing compound contains an abrasive and a binder consisting of a fatty acid such as stearic acid, tallow, and an amine. Many buffing compounds derive their names from the abrasives used in their formulation. Others are designated to reflect the type of metal on which they are most commonly used or the function they perform; they might include the following:–

Tripoli compound

Tripoli powder originally came from Tripoli in North Africa and was widely used for making polishing powders and abrasives. A similar deposit was found in the Seneca, Missouri, area of USA. The American deposit, a residue from the decomposition of highly silicaceous limestone, has a small particle size, greater absorption qualities, and is more suitable for polishing than the North African product.

Tripoli contains a crypto-crystalline silica, of which there is approximately *75%* crystalline silica. It has the ability to cut sharply at first and then break down in size, resulting in a finer cut and a higher colouring action. In the UK and USA, tripoli is the most common medium used for polishing aluminium because it is a natural product and cheap. Spanish tripoli is not as good as American tripoli.

Crystalline silica can cause lung damage to people exposed to it over a long period of time. Adequate ventilation and masks should be provided.

In Germany, where tripoli is not used because it contains silica, calcined aluminas are mainly used. Elsewhere there is a gradual move away from tripoli towards calcined, alumina-based products.

Cut or cutdown compounds

These usually contain tripoli, fused alumina oxide abrasives or fused calcined alumina.

Cut and colour compounds

These combine fast cutdown and colouring operations, sacrificing maximum cutting properties and the extra brilliance of separate colour buffing. Abrasive mixtures are selected to suit the particular metal being polished and the desired levels of cut and colour. They are mostly produced from calcined alumina abrasives of varying particle sizes and hardness.

Colouring or finishing compounds

The use of a very fine soft abrasive produces maximum brilliance and freedom from scratch on the polished component. Choice of mop hardness, polishing compound, peripheral speed, rate of speed, contact pressure and polishing time will vary with different components and the degree of lustre required by the operator. Very fine calcined alumina powders and highly lubricated binders are normally used.

Liquid buffing compounds for automatic or semi-automatic polishing

These contain abrasives that are suspended in a liquid binder carrier. They are available in similar or identical forms to that of bar compounds, but offer the following advantages:

(a) Reduce direct labour costs because less time is involved in applying or replacing compounds;
(b) Reduce waste of polishing compound because it can be applied in smaller quantities by automatic control and leaves no unusable waste;
(c) Provide a wider range of cutting and colouring characteristics because they can be formulated from a wider range of grease binders;
(d) Extend buff life by wetting and penetrating the buff to a greater depth, by maintaining an optimum amount of buffing compound on the surface of the buff at all times and by permitting a cooler buff operating temperature;
(e) Are essential for wider buffs;
(f) Saponify and emulsify faster than bar compounds and therefore are less likely to back transfer on the work piece, or to set too solidly in crevices or recesses, thus easing removal in subsequent cleaning operations.

Unlike bar compounds, they are not limited by the necessity of forming a bar that is physically strong to survive application shock.

Heller[22] has discussed the cleaning of buffing compound from buffed components. Cleaning procedures are detailed in Chapter 4.

Current Trends

The need to upgrade finishing operations is spurred by competitive consumer demands and government regulations regarding safety and environmental pollution. **A** major trend is towards the use of robotics and CNC technology.

With polishing mops, buffs and compounds, the move is towards the following:–

(1) calcined alumina instead of the natural abrasives tripoli, pumice and sand,
(2) non-fraying bias cut mops instead of cut disc and sewn mops,
(3) cloths impregnated with compound,
(4) cloths incorporating polyester fibre into the cotton to increase tensile strength and life,
(5) impregnated non-woven nylons.

Developments have taken place in cloth treatments using resins, solvents (to carry the resin into the cloth) and water-based impregnations.

Wrapped abrasive nylon is claimed to have a superior polishing finish over traditional wire brush methods. A patented extrusion method guarantees a stable nylon filament with a high concentration of abrasive grit on the brush surface.?'

Liquid compound applied on semi-automatic or automatic polishing machines is replacing the manual application of solid compound. The trend is now to move away from applying compound to woven mops to the use of impregnated non-woven nylons. These do not yet produce a mirror polished finish but can produce a satin finish which is becoming more acceptable because it is cheaper

and because modern expectation is for things not to shine any more. Bright finishes can be obtained by bright anodizing or bright plating.

Chemical Mechanical Polishing and Mechanical Etching of Aluminium

Several developments have been made combining chemical dissolution with mechanical abrasion.[18,24,25,26,27,28,29,30] Yu[24] has developed a chemo-mechanical method using a slurry of phosphoric acid, hydrogen peroxide, water and abrasive material for the chemical mechanical polishing of aluminium. Specialist examples include chemical mechanical polishing for the formation of ultra fine pitched interconnects.[25] Takeuchi and Tohyama[26] use a jet of electrolyte containing silica particles to smooth a zincated aluminium surface prior to electroless nickel plating. Runnels and Eyman[27] have developed pulsed-force chemical mechanical polishing. Polishing is exerted by a pulsed force directed substantially normal to the surface in combination with an abrasive motion directed across the surface to erode material from the surface.

A new ecological process, the mechanical etching of aluminium,[28,29,30] has been developed in Italy. Extruded aluminium is fed into a machine which mechanically blasts the surface and then immediately etches it in caustic soda. Details of the process and of the cost savings achieved through the reduction in caustic soda consumption are given in Chapter 4.

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CHAPTER 3

Electrolytic and Chemical Polishing

1. GENERAL NOTES

As well as the mechanical methods discussed in the previous chapter, electrolytic and chemical processes are employed in the production of smooth, bright surfaces. Although their function in industry is in many respects similar, the principle by which polishing is carried out is, however, very different. While mechanical polishing produces a flowed amorphous surface under the influence of pressure and high local temperatures, chemical and electrolytic polishing are selective dissolution processes by means of which the high points of the rough surface are dissolved faster than the depressions.

The potential advantages of these methods are obvious:

(a) Being similar in operation to anodizing and electroplating processes, they can be employed together in a single production line, with considerable reduction in plant and simplified control, while mechanical polishing may often be replaced entirely;

(b) They are suitable for bulk treatment and labour costs are appreciably lower, particularly on components not suited to automatic polishing machines;

(c) The surface is clean and gives better deposit adhesion as well as high corrosion resistance;

(d) The reflectivity and colour are often superior and there is no tendency to 'bloom'.

Industrial electrolytic and chemical polishing processes for aluminium are of two types:

(a) Processes designed to replace or reduce mechanical polishing.

These provide a smooth, bright, though not a 'mirror', finish, and are characterised by high dissolution rates (between 2.5 and 5.0 μm (0.1 and 0.2 mil) per minute). In most cases the best results are obtained on high purity aluminium or its alloys, but some processes may be employed on commercial purity based grades of aluminium, producing a correspondingly lower grade of finish.

(b) Processes employed after mechanical polishing.

These processes have a low rate of attack and are employed on aluminium reflectors and other components which require a higher specular reflectivity than is obtained by mechanical methods alone. Their use is generally restricted to high-purity based materials as reflectivity falls off sharply as the quantity of second-phase constituents present increases.

The two types of process, therefore, have different functions in the finishing cycle and will be discussed separately.

Factors involved in replacing mechanical by electrolytic or chemical polishing

A large number of electrolytic and chemical polishing processes have been developed to replace mechanical treatment, and some of these have gained widespread acceptance throughout the industry. However, the new processes give a finish which is, to some extent, different from that obtained by mechanical methods. They will not give an undistorted mirror finish on a machined surface, though the finish may have a higher reflectivity and often a much richer colour. On rounded or broken surfaces the finish is often indistinguishable from that obtained by mechanical polishing. It cannot be over-emphasised, however, that the economic savings which are possible can only be achieved by taking the scope of the process into account when designing components.

While no generally detailed comparison can be made between costs of the various processes, the following guide lines may be followed.

Mechanical polishing costs are predominantly due to direct labour, and the shape of the component is the largest single factor that determines whether automatic polishing machines are applicable, or alternatively, the number of hand operations. Furthermore, recessed parts may require the use of mops of different diameter and thickness, while edges may increase the consumption of mops and polishing composition. In electrolytic and chemical polishing, the shape of the article to be polished is mainly important in so far as it affects jigging and, in extreme cases, the need for auxiliary cathodes.

In electrolytic and chemical polishing, costs are mainly due to consumable materials which are directly proportional to the amount of metal dissolved, and

hence to the total surface area. In mechanical polishing, the significant part of the surface is treated, which may vary from a fraction to the whole of the component surface. The greatest savings are, therefore, obtained by electrolytic or chemical polishing where the ratio of significant to total area is high.

Where articles are wired or jigged for electroplating or anodizing, the handling costs involved need not be taken into account in polishing, and labour costs of electrolytic or chemical methods may fall away entirely, particularly as, due to the lower standard of pre-cleaning required, the polishing process may often take the place of one or more cleaners or swills, e.g., in an electropolishing anodizing sequence.

In practice it is sometimes desirable to pre-polish to some extent, e.g., to a 150 grade emery finish, to obtain the best type of surface. Even here, however, the electrolytic or chemical polishing process will generally be carried out at lower cost than final polishing, giving, in addition, a brighter finish than can normally be obtained.

These considerations apply both to electrolytic and chemical polishing processes. Chemical treatments require no current and are therefore often less expensive than electropolishing, as the high current requirement of the latter involves considerable capital outlay for rectifiers. However, this is offset to some extent by the greater fume and extraction problems with chemical brighteners.

Whilst chemical processes produce a finish which is often only slightly inferior to that obtained by electropolishing, it must be realised that the lower metal removal rate of the latter processes means that a higher quality metal surface is required. In many cases it is therefore not possible to use electropolishing without prior mechanical polishing. The fact that most electrolytic processes produce an oxide film which has to be removed after brightening and before anodizing may also effect the choice of process to be used.

2. ELECTROPOLISHING

Introduction

The metal to be electropolished forms the anode in an electrolytic cell. Continued dissolution of the metal occurs in such a way that irregularities on the surface are reduced or removed and the surface becomes smooth and bright.

A machined or mechanically polished surface may be considered as a series of hills and valleys. Microscopically, the surface is more complex with smaller irregularities superimposed on the macroscopic hills and valleys. To produce a truly flat surface, both the macroscopic and the microscopic irregularities must be removed. Tegart distinguished the functions of an ideal polishing process as

(a) “smoothing” by elimination of the large-scale irregularities (above a micron in size), and

(b) "brightening" by removal of the smaller irregularities (down to below the wavelength of light, about a hundredth of a micron in size, for maximum specular reflectivity).

An electropolishing process combines both these two distinct functions. As will be detailed later, smoothing is due to the formation of a relatively thick viscous layer of reaction products close to the anode. Brightening is due to the formation of a thin solid film on the surface of the anode.

Theory

The electropolishing of aluminium is an anodic oxidation process. During electropolishing, an oxide film is formed at the aluminium surface. At the same time, the outer surface of this oxide film is dissolving in the electropolishing solution. If the solubility of the oxide in the solution fell due to a change in the operating parameters such as a drop in temperature, then the oxide film thickness would increase. In other words, instead of electropolishing, the anodic process would become anodizing, the anodic production of a thick oxide film on the surface of the aluminium.

An understanding of the conditions needed for electropolishing aluminium can be obtained by comparing it with other chemical and electrochemical surface treatments for aluminium. These include:–

Etching
Anodising to form a thin barrier layer of oxide in non-solvent type solutions
Anodising to form a thick layer of oxide in solvent type solutions
Electropolishing
Chemical polishing

The controlling operating parameters include the following:–

applied voltage
temperature
solubility of aluminium oxide in the solution
oxidising power of the solution
These factors are interrelated.

Two types of process, chemical and electrolytic, in which aluminium is subjected to oxidation reactions form the basis of some of the principal finishing processes for aluminium and are discussed in detail later. In these processes, the purpose is to grow an oxide film of substantial thickness which will prevent access of the atmosphere to the metal and stop further corrosion. This is achieved by the use of solutions containing acids which have a slow dissolving action on the film and

under whose influence the latter is rendered sufficiently porous to allow further access of the film-forming medium to the metal. In anodic oxidation, if the dissolution rate is very small, e.g., as produced in boric acid or ammonium phosphate electrolytes, the film soon stops growing and at high voltages it is possible to form dielectric films for use in, e.g., condensers. When the dissolution rate is not as small, as in sulphuric acid solutions used in commercial anodizing processes, the thickness of the oxide film increases with time of anodizing. It is not possible to increase the anodic oxide thickness indefinitely because, ultimately, it is limited when the rate of growth of the oxide at the aluminium interface is balanced by the rate of dissolution at the oxide-solution interface.

At constant voltage there is, therefore, a maximum up to which increase in dissolution rate increases the limiting film thickness which is reached when rate of film growth has decreased to balance the rate of dissolution, and above which film dissolution is more rapid than the rate of growth. Under such conditions, solid films of a limited thickness can be formed and electropolishing may be possible. As will be seen, the actual dissolution rate and the film thickness at which electropolishing takes place may vary widely. In some electrolytes, polishing takes place through films of sufficient thickness to yield considerable protection against corrosion, or alternatively, the solid film may be only a few molecules thick. For example, electropolishing aluminium in the Brytal process (sodium carbonate and trisodium phosphate), and the Alzak process (fluoborate solutions, etc.), produces an Al_2O_3 film of sufficient thickness to give interference colours and a substantial measure of protection. In other processes, notably in concentrated acid solutions, the presence of solid films which was for a long time in some doubt has now been well established and goes a long way to answer problems unsolved by earlier theories based on diffusion layers.

The fact that the metal is covered by a solid film during several different electropolishing and chemical polishing processes was demonstrated by Hoar *et al.*[2,3] by a mercury wetting test. The existence of a solid film during the electropolishing of aluminium has also been demonstrated by Raub and Baba[4] who employed capacitance measurements to determine its magnitude. By electron microscopy it was also shown that this film had a porous structure like normal anodic oxide coatings, with the pore size and density depending on the conditions of electrolysis. When the current was interrupted the film proceeded to dissolve and the capacity increased again.

Fujinara[5] also studied the formation of surface films during the course of electropolishing 99.9% aluminium in various electrolytes, and showed that the film consisted of a barrier layer of 0.2-2.0 μm and a porous layer up to 0.5 μm, the thickness of each being proportionate to the d.c. voltage. It is not surprising therefore that the current wave form should exercise an influence on electropolishing and Steiner,[6] who studied this, reported both beneficial and detrimental effects of a fluctuating current. It is well known that the Brytal process will not operate effectively with single phase rectified current. Hoar, Mears and Rothwell[7] have postulated that the oxide is of a 'contaminated' type containing foreign anions

through which the cations may pass to produce anodic brightening. In the presence of chloride or other aggressive ions the passivity is locally destroyed by field stimulated entry of anions into the film at the less regular points which leads to breakdown and pitting. A higher field strength assists the re-establishment of the solid film and the return to brightening conditions.

As is to be expected, therefore, the film which is formed under electropolishing conditions is not qualitatively different from that produced in industrial anodizing processes. Lichtenberger-Bajza[8,9,10] and Holló[11] report that, depending on the basis metal, this film is 0.1-0.2 μm thick after electropolishing in phosphoric acid-butyl alcohol solution, the thicker films being formed on the purer metal. Thickness is not affected by polishing *time* and the film is based on a barrier-type structure.

Lichtenberger-Bajza[8,10] who applied the Hunter method (see page 333) for determining the thickness of barrier-type anodic oxide coatings, found thicknesses of 0.5-5.0 μm formed during electropolishing aluminium in phosphoric-sulphuric-chromic, phosphoric-chromic and sulphuric-hydrofluoric acids as well as in phosphoric acid-butyl alcohol electrolytes. As in industrial anodizing processes, the barrier layer thickness increases with the use of higher current densities, while when the phosphoric acid concentration is raised, a higher current density is required to form the same thickness of barrier layer.

Again, as in anodic oxide films formed in anodizing electrolytes, the film formed during electropolishing consists of hexagonal cells and both the cell and the pore diameters grow with increasing potential. At a voltage of 30-35 volts the cells have a diameter of approximately 10 ym and a pore diameter of 6 μm[9].

The barrier layer thickness formed in phosphoric acid–butyl alcohol solution does not exceed 0.5 μm on pure and super-purity aluminium and is less than 0.1 μm thick on Al-Cu-Mg alloy.

Still in conformity with films formed in industrial anodizing electrolytes, a porous film can be distinguished above the barrier layer on electropolished aluminium. Chemical analysis of the film formed on 99.99% aluminium shows it to contain 79.9% Al_2O_3 and 7.3% $AlPO_4$ as well as 0.064% Fe and 0.31% Si.[9]

Current-voltage relationship

The typical relationship between the current and the anode potential which is observed in electropolishing is shown in Fig. 3-1 drawn as in original publications on electropolishing. It is shown re-drawn in Fig. 3-2 with voltage on the vertical axis and current on the horizontal axis as is the convention in modern potentiostatic polarisation work. The latter enables ready comparison of electropolishing with etching, passivation and oxygen evolution as the potential is successively raised.

As seen, as the voltage is increased, there are four stages:–

(1) between A and B, the current increases proportionally to the applied voltage; etching of the aluminium occurs in this region,

(2) at B, the current is unstable and fluctuates, sometimes with an observable definite periodicity due to the periodic growth and destruction of a thin oxide film on the surface of the anode,'.'

(3) from B to C, further increase in applied voltage is accompanied by little or no change in current density; electropolishing occurs in this region at constant current density (sometimes known as the limiting current density or critical current density); the quality of polish increases with increasing voltage up to C,

(4) further increase of the potential above C leads to a rise in current density associated with gas evolution; gassing defects develop on the surface in this region; at much higher voltages, vigorous oxygen evolution results in an etched and polished surface.

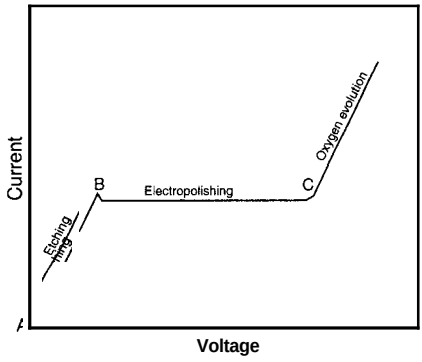


Fig. 3-1 Typical electropolishing curve as drawn in original publications on electropolishing

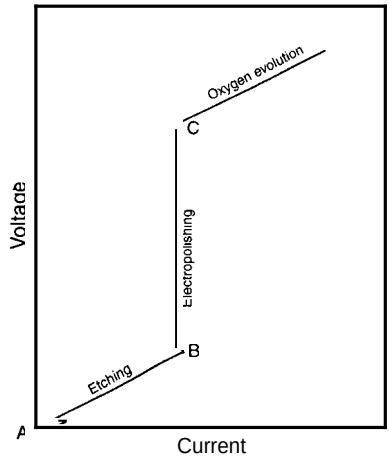


Fig. 3-2 Typical electropolishing curve with voltage on vertical **axis** as conventionally drawn in modern potentiostatic polarisation work

According to Huber, three reactions occur at corresponding stages on the diagram

$$(1)\quad Al \rightarrow Al^{3+} + 3e$$

$$(2)\quad 2Al + 6OH^{-} \rightarrow Al_2O_3 + 3H_2O + 6e^{-}$$

$$(3)\quad 4OH^{-} \rightarrow O_2 + 2H_2O + 4e^{-}$$

In the first stage, represented by A-B, metal dissolution is determined by concentration and activation polarization; the process is that of the normal anodic

etch in which atoms are dissolved from the surface according to their free energy. As the anode potential reaches that of the oxide electrode, the anode is covered with an oxide film which prevents reaction (1). Reaction (2) takes place between B and C and is controlled by the rate of film dissolution. Both the film dissolution and the current density are limited by the rate of diffusion, that is, they are independent of the voltage. At point *C* the anode potential is sufficient for oxygen evolution.

Anodic polarization in a range of electro-brightening solutions, including the Brytal, Battelle and Alzak processes, has been studied by Gabe.[13] He obtained polarization curves in these electrolytes over a range of operation temperatures and concluded that a distinction can be made between electropolishing and electro-brightening on the basis of activation energies for **dissolution and** transition temperatures (Table 3-1). Catonne[14] also discussed the electropolishing of aluminium using data from potentiostatic and potentiodynamic polarisation curves.

TABLE 3-1

Activation energy data for electropolishing aluminium[13]

Solution type	*Activation energy, kJ/mol*		*Transition temp. °C*	*Polishing cd at recommended temp. mA/sq.cm*
	Low temp.	*High temp.*		
Brytal	38.9	96.3*	76	35-60
Sulphuric-chromic	*16.6*	12.5*	77	1-2
Sulphuric-phosphoric	64.0	28.8*	*58*	30-40
Battelle	*13.6*	26.3*	43	90-110
Alzak	28.0*	68.6	10	15-30
20% Perchloric-methanol	20.5*	20-30		

* optimum polishing condition

Suppression of etching

The presence of the oxide film is of great importance, as it explains the suppression of crystallographic etching. This is attributed to dissolution according to their proximity to pores and to faults in the oxide film. With continuous film growth and dissolution, these points of access are constantly changing and metal atoms are therefore attacked more or less at random. The efficiency with which etching is suppressed will vary with the thickness and porosity and electrical properties of the film, as well as with the metal composition and grain-size.

The smoothing mechanism

The basic smoothing action in electropolishing is due to relative attack on asperities and may be associated with several factors:

(1) As described by Edwards,[15] there is a general tendency to smoothing of a metal surface, even in reactions where metal is dissolved uniformly.

(2) Under conditions where film dissolution is controlled by diffusion of the metal ions away from the surface, differences in concentration gradients between the anolyte in the valleys and at the crests of the surface have a profound influence on the relative film dissolution at these points. This mechanism has been quantitatively expressed by Elmore.[16]

(3) The thickness of the oxide film itself will vary, at least initially, between the crests and valleys. Thus, according to Evans and Whitwham[17] and some later authors, conditions for passivation are reached sooner in the valleys due to accumulation of dissolution products. This is counteracted almost immediately by the consequent increase of current density on the crests. The thickness of the oxide film is governed by its dissolution rate, which depends on the rate of diffusion, differences in concentration gradients and the local current density.

(4) An important part may in some cases be played by gas bubbles. Thus, according to Faust,[18] a gas film is formed as well as a viscous liquid film, and the former accounts for the micro-polishing effect as well as for the high electrical resistance across the liquid-metal interface (in the absence of a solid oxide film). When the gas film predominates, the smoothing action increases at the expense of brilliance, and *vice versa.*

Odier[19] and Jacquet,[20] who worked with the Brytal process and the Alzak hydrofluoric acid/sulphuric acid process, found marked variation of the polishing efficiency with the position of the surface relative to the direction of escape of gas bubbles. Gas bubbles may also affect the quality of the finish adversely by causing parallel streaks. This occurs when streams of bubbles are allowed to follow the same course on the lower surface of the metal.

Neufeld and Southall[21] have studied the influence of gas evolution on pitting with electropolishing of steels, and they conclude that this does not represent a breakdown of polishing, but is in effect superimposed on a still-polishing surface. In the first stage of pitting a pattern of gas evolution is set up which may be random and centred at many points, or it may occur at fewer, favourable sites. The pattern initially established is continued into the second stage, when pits grow due to the formation of a stream of gas bubbles from the same point. Thus the initial surface conditions strongly influence electropolishing behaviour.

Gassing defects have been studied with aluminium by Clifford and Arrowsmith,[22] particularly with chemical polishing processes, but for electropolishing they concluded that the main cause of gassing defects was live immersion of the aluminium without pretreatment. The defects took the form of a central flat plateau surrounded by an annular groove (sometimes described as a 'castle and moat' effect) and again they were associated with surface irregularities such as large intermetallics, or gross inclusions from the prior mechanical polishing operation (Fig. 3-3).



Fig. 3-3. Gassing defects on electropolished aluminium"

Morphology *of* Electropolished Aluminium

For a surface to have mirror bright specular reflectivity, the size of surface irregularities must be below the wavelength of light. Atomic force microscopy, capable of atomic scale resolution, has been used to examine the morphology of electropolished aluminium.[23] Two distinctly different surface morphologies of waves and mounds (Fig. 3-4) were observed for different electropolishing conditions and transitional structures were observed for intermediate conditions.

Both the surface wave period and amplitude appeared to increase with increasing electropolishing voltage. Prior to electropolishing, the range of surface height measurements was over 50 nm. Electropolishing reduced this height range to less than 5 nm after polishing. These results demonstrated that a better understanding of the chemical and electrochemical conditions that determine surface roughness

during polishing will enable better control and more reproducible production of surfaces that are flat on the sub-micrometer and nanometer level. Such applications include the manufacture of memory discs for computer and data processing systems[24] and the nanofabrication of quantum dot arrays[11] by depositing metal in the pores of anodized aluminium where the electropolishing determines the flatness of the two-dimensional array, the pore spacing and uniformity.

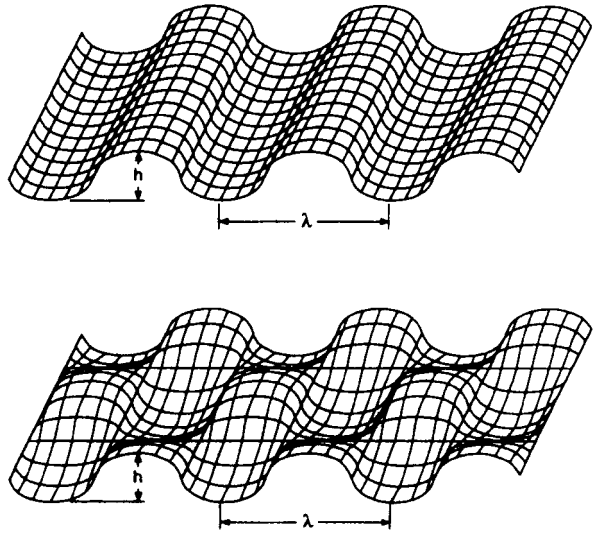


Fig. 3-4. Schematic illustration of the one and two-dimensional nature of surface wave and mound morphologies of electropolished aluminium. The height (h) ranges from 0-5 nm and the peak spacing (A) ranges from 50-150 nm depending on the polishing conditions[11]

Electrobrightening processes

There is only a moderate smoothing action in electrobrightening processes, the objective being to smooth comparatively shallow surface deformations. The action is, therefore, neither intense nor speedy. Current densities are low and do not usually exceed 3-5 A/dm^2 (30-50 amp/sq ft), while the amount of metal removed is normally of the order of 2-12 μm (0.08-0.5 mil). The time of treatment may extend to 20-30 minutes. It is usually desirable to precede with some mild buffing operation.

Electropolishing processes

The objective with electropolishing processes is to deal with abrasion and scratches on the surface. The electrochemical action is, therefore, more intense

and necessitates higher current densities of the order of 10-35 A/dm^2 (100-350 amp/sq ft). More metal is thus removed – perhaps two or three times that removed in electrobrightening, and in a much reduced time, usually in a few minutes.

In practice two types of solution with widely different applications may be distinguished: (a) the reflector processes which are designed as finishing treatments after mechanical polishing; and (b) the concentrated acid processes, the primary function of which is to replace mechanical methods of surface preparation.

3. COMMERCIAL ELECTROPOLISHING PROCESSES

Brytal process

The Brytal process has retained its unique position of being the only commercially successful electrolytic brightener to employ an alkaline electrolyte. The process is particularly suitable for the treatment of super-purity aluminium (99.99%). Its use has declined because of the development of 99.8% base purity alloys suitable for chemical brightening in phosphoric acid base brighteners, the availability of grades of stainless steel tanks to accommodate these brighteners, and also the increased use of aluminium coated plastic mouldings for reflectors. However, primarily the Brytal process has survived because with no other method of treatment has it thus far been possible to obtain mirror finishes on large flat areas, or to achieve quite the quality of finish and level of brightness which this process gives.

Pullen[25] first described the Brytal process and recommended the bath composition and operating conditions, shown in Table 3-2 below, which have altered very little since.

TABLE 3-2

Brytal electropolishing process

	working range	*optimum*
Sodium carbonate (anhyd.)	12-20% (wt)	15% (wt)
Trisodium phosphate	2.5-7.5%	5%
Temperature	75-90°C	80-82°C
Voltage	7-16 volts	9-12 volts

Harris[26] investigated the effects of composition and operating conditions on the degree of brightening obtained (Fig. 3-5). The present recommended level of 20% sodium carbonate and 6% trisodium phosphate allows more latitude in operating conditions than the former 15%/5% composition. Hug[27] also referred to the use of a composition of 30% carbonate and 6.5% phosphate.

The bath should be prepared from good quality chemicals and distilled or deionised water and used at 85-90°C. During the first day of use temperature is sometimes lowered to 80°C and the phosphate content restricted to about 4%.

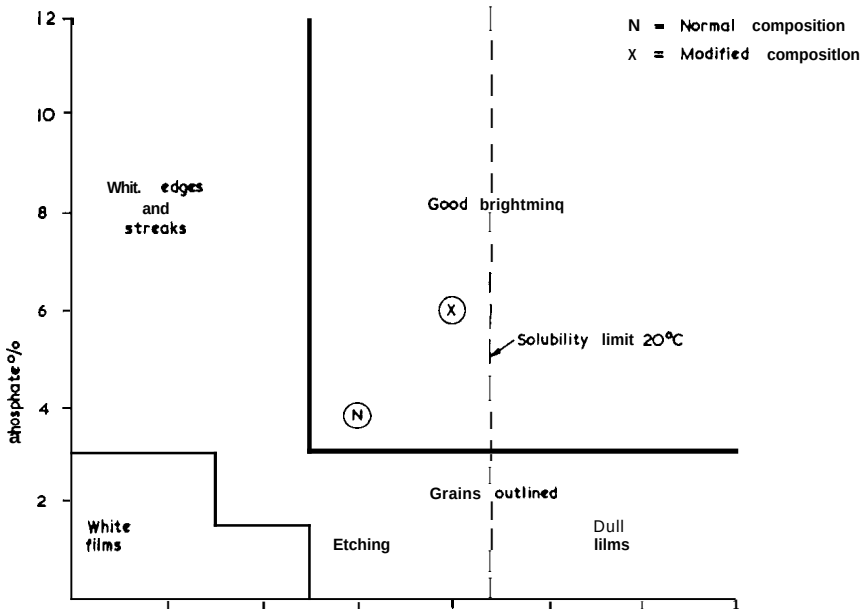


Fig. 3-5. Effect of bath composition on Brytal treatment of super-purity aluminium

There is a great deal of art as well as science involved in successful operation of the Brytal process. The work should be firmly jigged and arranged so that the significant faces are, as far as possible, inclined at about 15° to the vertical and facing downwards. The solution should be quiescent, with agitation and heating switched off before inserting the work. It is first allowed to etch for 30-60 seconds with the current off before applying the full pre-set voltage from a generator or hexaphase rectifier with less than 5% ripple. At this moment there is an initial current surge of 3.5-5 A/dm^2 (33-47 amp/ft^2) or higher which lasts for about

4 seconds before rapidly falling to about a half of this value when the gassing at the anode stops and the work begins to polish. It is *of* considerable advantage to use a moving anode which causes the work to oscillate, rotate or rock at 10-20 cycles a minute over an amplitude of 20-30 cm (8-12 inches), and in this case the operating voltage should be raised by about 6 volts to give a higher current density and a quicker acting bath, as indicated in Table 3-3.

TABLE 3-3

Current densities and voltages during Brytal treatment

	Current density (A/dm²)		*Voltage*	
Metal	*initial*	*final*	*steady*	*moving anode*
Super purity	3.6	1.6	12	18-20
99.8%	4.0	2.0	12	18-20
S.P. base alloys	5.0	2.0	15	20-22

Work should be carefully polished by mechanical means before treatment, and when this has been properly done about 10-15 minutes in the Brytal bath is adequate, but treatment times of 30-40 minutes are common.

A typical recommended tank design is shown in Fig. 3-6 where the cathodes are placed at the tank ends remote from the work, and baffle plates dipping below the solution level are included to reduce convection effects. Agitation coils or heaters are situated 10-20 cm (4-8 inches) above the tank bottom to avoid disturbing any sediment. The accumulation of this deposit, which has to be removed from time to time, is the biggest problem, and continuous filtration is possible.

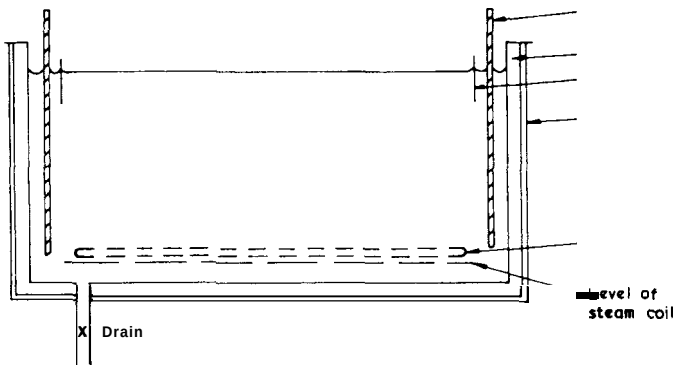


Fig. 3-6. Longitudinal section of Brytal tank

The following is a typical analysis of Brytal bath sediment after drying at 100°C:

	%
SiO_2	2.0
Al_2O_3	23.7
CaO	0.9
Na_2O	25.0
P_2O_5	26.3
Ignition loss at 1000°C	22.1
	100.0
CO_2	1.8

About 50 kg of dry sediment might be expected to accumulate in a 4000 litre tank (125 lb in a 1000 gallon tank) in the course of a day's use.

The polishing action of the bath depends on both a solid oxide film about 0.5 μm thick which forms on the surface and also a viscous complex phosphate layer present in the solution. After treatment this oxide film remains, but is usually invisible until it is wiped, when the iridescent interference colours appear. This film must be removed before anodizing and this is done in a boiling solution of 7% phosphoric acid/4% chromic acid. It is also possible to remove it after anodizing by scrubbing with a mild abrasive, or in 50% nitric acid, but anodizing can be tricky to perform with the 20 volt barrier layer present as this must be broken down before anodizing current will flow.

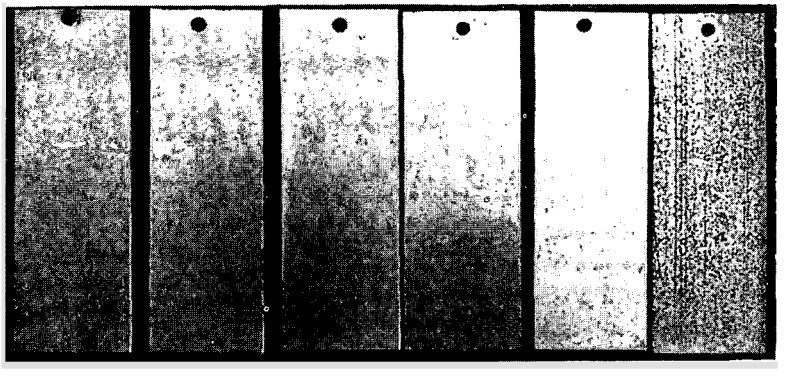


Fig. 3-7. Effect of chloride in Brytal electrolyte

The carbonate content of the solution does not alter other than by drag-out during use, and the principal maintenance required is a periodic addition of trisodium phosphate to maintain the concentration at between 4.5 and 6.5%, and water to replace evaporation losses. The latter can easily be the biggest item and this can be substantially reduced by floating plastic spheres or plates on the surface. The main deleterious impurity is chloride which can lead to very pronounced pitting if it exceeds 0.1%. Fig. 3-7 shows the degree of pitting produced by various levels of chloride in the Brytal bath.[26]

A number of defects can occur during Brytal treatment and Table 3-4 below lists the main faults that have been observed.

TABLE 3-4

Common faults in Brytal treatment

Fault	*Cause*
General dullness	1. Low phosphate concentration 2. Low voltage or current density
Brilliant heavily grooved surface	1. Voltage and current density too high
Dull patches	1. 'Burning' during polishing
General or local etching	1. Preliminary etch too long 2. Poor contact to anode 3. Overloaded bath 4. Metal purity too low
Profiling: bright but uneven	1. Overloaded bath 2. Incomplete stripping or etching before pretreatment 3. Voltage fluctuations during treatment
White or brown streaks: may not be visible until after anodizing	1. Excessive movement of electrolyte or work 2. Gas flow from cathodes or closely adjacent articles 3. Etching of film during removal from bath
Hairline scratches	1. Scratches left by loose threads on polishing mops
Bubble marks with tails on upper surface	1. Adherent gas bubbles
More numerous bubble marks	1. Low electrolyte concentration 2. Accumulation of sediment
Numerous minute pits or pimples on upper surfaces	1. Accumulation of fine sediment
Deeply etched pits	1. Excessive chloride in bath, or 2. Chloride-contaminated grease on surface of work

The Brytal process is eminently suitable for the treatment of super-purity aluminium (99.99%) and the Mg or MgSi alloys BTRI, BTR2 and BTR6 which are based on this purity (see Table 3-16 on page 139). **A** mirror finish can be obtained on these alloys which retains both its total and specular reflectivity even when anodic coatings up to 20 μm or more are applied.

In Russia, the Brytal process has been used on 99.8 and 99.9% purity metal,[28] but developments by Harris[29] claim to allow commercial purity material to be treated. This is achieved by operating a modified bath at a lower pH than usual, preferably 9.5-10.5 (normally 11.0-11.6), and making sure that reaction products are continuously removed from the surface of the work, e.g., by vigorous air agitation. The ratio of total carbonate content to total phosphate content in the electrolyte is preferably between 1.25 and 3, and the actual contents are 170-220 g/l CO_3 and 60-125 g/l PO_4, respectively. The preferred operating temperature is about 90°C and typical voltages 10-15 V.

Another interesting modification of the Brytal process is mentioned by Elssner who found that the reflectivity of alloys based on commercial grades of aluminium could be improved by the addition of aluminium phosphate'" or 5-10 g/l of an alkali metal sulphate," halide or acetate. In the presence of the latter, the current does not fall off as in the standard process, but at 8 volts will keep more or less constant at 6-8 A/dm^2 (60-80 amp/sq ft). **A** typical composition of a solution containing aluminium phosphate contains:

	g/l
trisodium phosphate (pure)	150
aluminium phosphate	20
sodium hydroxide	10

Before this treatment, the work is etched at 80°C (174°F) in a solution containing trisodium phosphate, sodium carbonate and aluminium salts.

In another variation[32] it is claimed that alkaline solutions of tartrates with the addition of approximately 0.2% aluminium powder will produce reflectivities of 90% at room temperature on 99.99% aluminium. A further advantage claimed is that the coating is not sensitive to hard water precipitates.

Reflectivity values which have been obtained with the Brytal process are given in Table 3-5. The drop in specular reflectivity with coating thickness in the case of 99.8% metal is a basic character of that purity. With any lower purities it becomes even more pronounced and it is difficult to see any object in attempting to use the Brytal process on these.

Brytal treated super-purity metal has been widely used for high class holloware, reflectors for light and heat, jewellery, buttons, badges (frequently dyed to simulate gold or brass), motor car trim and much other decorative work. Its particular usefulness is in the very high reflectivity through the visible spectrum and into the infra-red (as shown in Fig. 3-8); in the permanence of this finish at temperatures where other materials decline rapidly in this property (as demonstrated in

Fig. 3-9); and lastly in the most effective resistance to corrosive atmospheres (as shown by the results of exposure tests in Fig. 3-10, which were obtained on a factory roof in 1939 at a site where conditions were extremely aggressive).

For these reasons, Brytal treated super-purity metal has been chosen for the reflector cavities in laser equipment, where the reflecting surface is second to polished silver by only a short margin, but the surface is proof against tarnishing and can readily be cleaned when required without any damage or deterioration.

TABLE 3-5

Reflectivity of Brytal treated and anodized metal

Anodic film thickness (μm)	*0*	2	*5*	10	20
99.99% — Total Reflectivity*	90	90	89	89	88
99.8% — Total Reflectivity*	90	89	88	87	84
99.99% — Specular Reflectivity**	90	87	87	86	84
99.8% — Specular Reflectivity**	88	68	63	58	47

* BS 6161: Part 11: 1985

** BS 6161: Part 12: 1987 Method E

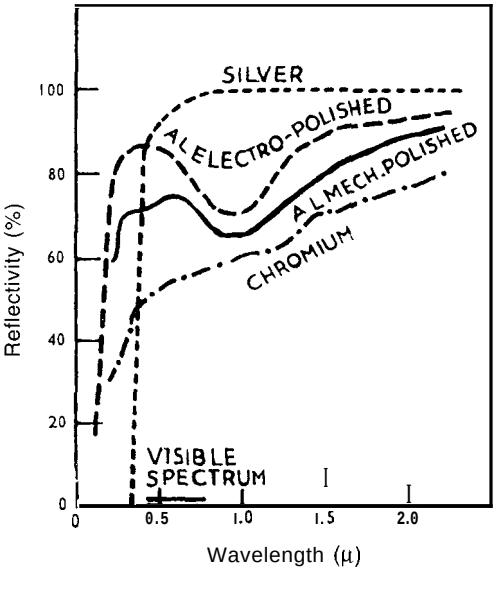


Fig. 3-8. Reflectivity of electropolished and mechanically polished super-purity (99.99%) aluminium, silver and chromium at different wavelengths

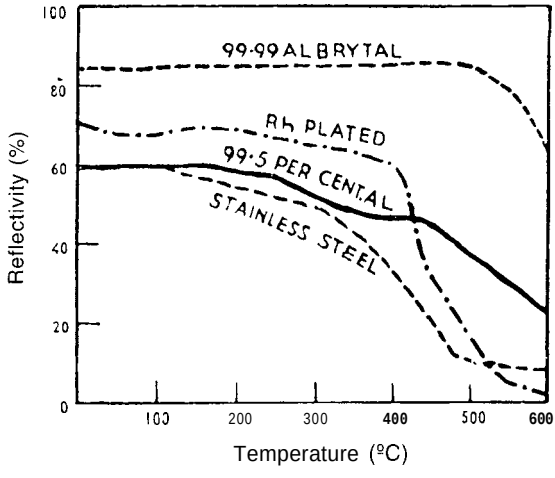


Fig. 3-9. Effect of temperature on reflectivity

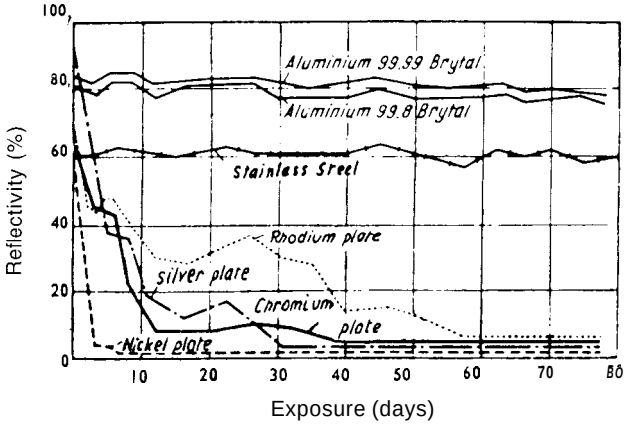


Fig. 3-10. Effect of atmospheric exposure on reflectivity

Alzak process

The Alzak process is designed for reflector finishing and has apparently gained no applications outside this field. Two types of bath have been used, employing either fluoborate electrolytes" or, less commonly, hydrofluoric acid with the addition of sulphuric, chromic or hydrosilicic acid.[34]

The standard fluoborate method employed a 2.5% solution of fluoboric acid which could be made up by mixing 40 gm of boric acid with 100gm hydrofluoric acid (48%) and allowing to cool. This mixture, which contained 37.5% fluoboric acid (HBF_4) with an excess of 7.5% boric acid, was then diluted by 20:1 to reach the working concentration; ammonium fluoride could be added to improve the conductivity. The electrolyte was operated for 5-10 minutes at 15-30 volts at approximately 30°C (85°F), the current density being 1-2 A/dm^2 (10-20 amp/sq ft).

Reflectors brightened by the Alzak process were normally anodized by the sulphuric acid process, e.g., in 7-12% (vol.) sulphuric acid at 25°C and 16-22 volts for 10 minutes, followed by sealing in boiling water for 10 minutes.

The Alzak treatment produced reflectivity values (Fig. 3-11) similar to those produced by the Brytal process for super-purity material.

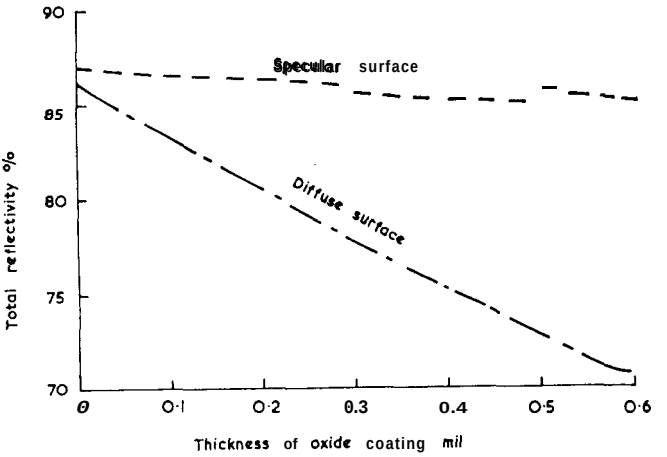


Fig. 3-11. Effect of coating thickness on reflectivity of Alzak treated super-purity material

On commercial-purity aluminium, the fluoborate treatment is claimed to produce 80% total reflectivity (values obtained by the Taylor reflectometer). Mechanical prepolishing is of great importance," and considerable care must be taken to prevent 'dragging' or inclusions in the metal. Where diffuse reflectors are required, a chemical etch (see Chapter 4) may be employed.

As in the Brytal process, a smudge film may remain on the surface after anodizing and sealing. This could be removed by light polishing or before anodizing by the chemical method given for the Brytal process. Alternatively, solutions containing approximately 1.5% sodium bicarbonate and 2% sodium carbonate have been employed at 70-95°C for 0.25-3 minutes[36] as well as a 1% phosphoric acid-0.5% chromic acid mixture at 96°C for 30 seconds.

Phosphoric acid electropolishing processes

These processes are generally characterised by faster dissolution rates than the alkaline or fluoride-type baths. They have a more marked macro-smoothing action, though they are inferior in the production of reflector surfaces of high

specular reflectivity. Their main function is, therefore, to replace mechanical polishing on commercial aluminium or its alloys, e.g., prior to anodizing.

The best-known process of this type was developed by the Battelle Memorial Institute[''] and is based on a phosphoric acid-sulphuric acid solution. frequently with the addition of chromic acid. Phosphoric acid electrolytes employed with organic additions such as glycerols, glycols, etc., as well as phosphoric-sulphuric-nitric acid solutions are also in use. While, in the U.S.A., this process has been largely replaced by chemical polishing, some electropolishing in this type of bath is still used in Europe.

Modern Battelle electropolishing process

The range of compositions and operating conditions of the modern Battelle solution[38] are given in Table 3-6.

TABLE 3-6

Modern Battelle electropolishing process

	Operating range	*Typical solutions* I	II
Sulphuric acid	4-45% (wt.)	4.7% (wt)	14% (wt.)
Phosphoric acid	40-80%	75%	57%
Chromic acid	0.2-saturation	6.5%	9%
Combined dissolved Al^{3+} and Cr^{3+}	0-6%	<4.5%	—
Water	Balance	Balance	20%
Viscosity (at 180°F)	9-I3 c.p.	10-I1.5 c.p.	—
Voltage	7-I5 volts	7-I2 volts	—
Current density	2.7-100 A/dm^2	6.4-16 A/dm^2	I7 A/dm^2
amp/sq ft	25-950	60-I50	160
Temperature	70-95°C	80-82°C	80°C
	160-200°F	175-180°F	175°F

Phosphoric acid-based solutions are mechanically agitated (contrary to the Brytal process), but stirring must not be too violent or a non-uniform finish and, in extreme cases, the growth of pyramidal projections on the surface may result.''

Chromic acid improves the specular reflectivity obtained by the process but also affects it adversely by producing trivalent chromium. Its presence passivates the metal while the current is switched off, and avoids etching.

In the absence of sulphuric acid a bright finish results, but pitting can occur even at high temperatures and voltages. Sulphuric acid has a marked influence on the cell resistance. Considerably lower voltages are required in the mixed acid baths and, in general, the higher the sulphuric acid to phosphoric acid ratio, the higher the current density.

Viscosity too is important and its optimum value is in inverse proportion to the current density. The viscosity may be reduced either by increasing the temperature or by diluting the electrolyte.

The solution life is limited to an approximately equal extent by the concentrations of aluminium and trivalent chromium. The latter, which is formed by reduction at the cathode, may be kept low by employing a porous ceramic cathode container filled with an 85% phosphoric acid solution. This prevents access of chromic acid to the cathode, but inevitably increases the cell resistance and requires the use of higher voltages. As the aluminium content rises, higher current and voltages are required and the viscosity is reduced by water addition and temperature increase. Figs. 3-12 and 3-13 show the relationship of the operating conditions to each other and to the solution life.

A steep rise of specific gravity and viscosity accompanies rise in aluminium content, while the current density at constant voltage decreases rapidly above approximately 10 centipoises (see Fig. 3-12). Fig. 3-13 shows that the maximum permissible aluminium content falls off sharply with sulphuric acid contents of above approximately 5-7%.

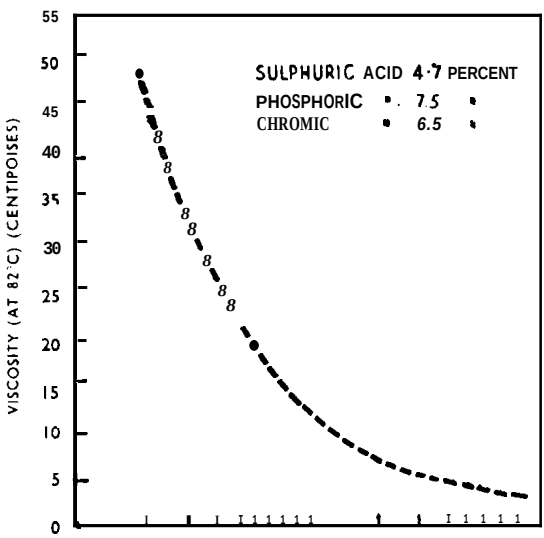


Fig. 3-12. Relationship between the viscosity required to electropolish and the current density at 12.5 volts (1 amp/sq. ft. = 0.108 A/dm^2)

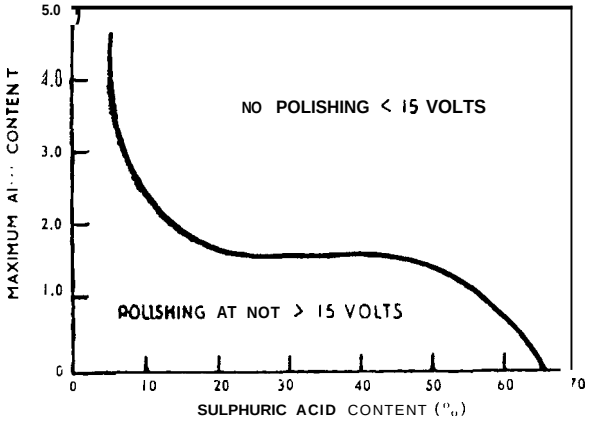


Fig. 3-13. Effect of sulphuric acid content on life of solution (Total acid content is constant)



Fig. 3-14. Icing defect on electropolished aluminium[40]

Another danger of the increase in viscosity and specific gravity caused by increasing aluminium content is the possibility of producing 'icing' or 'barnacling' defects on the surface of the work (Fig. 3-14). This phenomenon has been studied by Arrowsmith *et al*[40] and they showed that the defects occur on areas of the aluminium surface where electropolishing is prevented by the formation of an anodic film. The crystallographic shape of the defects is due to precipitation of aluminium phosphate on the surface followed by anodizing, but the phosphate subsequently dissolves at the outer surface as the anodic oxide forms at the aluminium/aluminium oxide interface.

Icing defects occur when the electrolyte composition and polishing conditions are close to the transition from electropolishing to anodizing, usually at high electrolyte specific gravity, and they are usually eliminated by adding water to the bath to bring the specific gravity down.

This process has been used to electropolish alloys of the aluminium-magnesium (e.g. 1.2% Mg) type, as well as Duralumin-type alloys. Two other alloys which are reported to have been polished contained copper 1.9%, magnesium 0.6% and silicon 1.0%, and magnesium 2.5% and chromium 0.25%. The silicon content should, however, not exceed 1% and for this reason, and because of risks associated with treating porous material, this process is not normally used on castings.

Before electropolishing, it is usual to vapour degrease the **work** followed by an alkaline cleaner. Occasionally a light anodic etch is given, e.g., in hot chromic acid/sulphuric acid solution. Discarded chromium-plating solutions of the low chromic acid-type (150-200 g/l) are suitable.

Adequate rinsing after electropolishing is essential to avoid stains. For the same reason, transfer to the electropolishing bath should be as quick as possible.

Where necessary after electropolishing, surface films can be removed in a 10% sodium hydroxide solution at 50°C for a few seconds. Alternatively, the following solutions may be used:

	phosphoric acid (d. 1.70)	35 ml/l
	chromic acid	20 g/l
	at 90-95°C for ***5*** minutes	
or	sodium carbonate	20 g/l
	sodium chromate	15 g/l
	at 70-95°C for 1-3 minutes	

Other phosphoric acid processes

Two other solutions utilise (a) the addition of compounds to preserve viscosity, e.g., glycerol, and (b) the addition of small proportions of nitric acid. The first type of solution is part of the Alzak range of processes. Besides glycerol, '' glycols or their ethers of viscosities below 110 cs[42] are used and sulphuric acid may be added. They have been used at 65-82°C (150-180°F) with up to 35 volts and 35-40 amp/sq ft (3.5-4 A/dm^2).

Electropolishing of aluminium in France developed along similar lines to the Battelle-type process[43,44] and solutions in industrial use contain phosphoric acid/sulphuric acid mixtures with sometimes nitric acid additions. The function of the latter is essentially similar to that of the chromic acid in the American process. Two solution compositions are given in Table 3-7.

TABLE 3-7

Other phosphoric acid electropolishing solutions

	A	*B*
Phosphoric acid (d. 1.71)	10%	15%
Sulphuric acid (d. 1.84)	60%	70%
Nitric acid (d. 1.33)	1%	–
Water	29%	15%
Current density	15-25 A/dm^2	15 A/dm^2
amp/sq ft	140-240	140
Temperature	95°C	85°C
Time	20 min.	20 min.

The electrolyte is agitated by means of anode rod movement at the rate of approximately 2-8 cm (1-3 inches) per second. Air agitation is not suitable. If a milky film is formed on the surface, this may be removed, prior to anodizing, in caustic soda solution.

In Russia, two solutions among several which have been reported as in widespread use contain:

	Z	ZZ
phosphoric acid (d. 1.7)	80% (vol.)	43% (wt.)
sulphuric acid	–	43
chromic acid	–	3
ethylene glycol	20%	–
water	–	11

and are used at:

current density (A/dm^2)	12-15	21
(amp/sq ft)	120-140	200
temperature ("C)	90-100	76-78
(°F)	195-212	169-172

Of these, bath I is used in the production of bright-anodized commercial-purity aluminium, e.g., gold-anodized watch cases, while bath II is used for electro-polishing Duralumin. **A** bath containing phosphoric acid (d. 1.7) 42% (vol), sulphuric acid 8%, ethylene glycol monoethyl ether 33%, water 17%, used at 30-50 amp/sq ft (3-5 A/dm^2) and 75°C, has been mentioned by Porter.[45]

Aluflex process

A German electropolishing process which became quite popular and was also used to some extent in Britain was based on a sulphuric-chromic acid electrolyte and was known as the Aluflex or Riedel-Aluflex process.[46,47] The bath is not suitable for super-purity or high purity aluminium and its alloys. The conditions of use given in the relevant patent are:

	Range	*Preferred*
Sulphuric acid	1200-1750 g/l	1450 g/l (80%v/v)
Chromic acid	20-30 g/l	25 g/l
Temperature	50-100°C	80-90°C
Voltage	8-24 volts	13-20 volts
Current density	25-80 A/dm^2	25-50 A/dm^2
	230-750 A/ft^2	230-450 A/ft^2

In practice the steady current conditions are less than those indicated above. **As** in the case of Brytal treatment there is an initial current surge of up to 40 A/dm^2 of rather longer duration before it settles down to 13-15 A/dm^2 after about 1 minute of operation.[45] The metal removal rate is rather high at about 25 μm in two minutes. An oscillating anode is normally employed. The cathodic current density should be restricted to 20 A/dm^2 and the lead cathodes are screened in porous pots containing sulphuric acid to avoid rapid cathodic reduction of the chromic acid. Organic addition agents such as ethylene glycol may also be present in the bath.[45]

This bath has disadvantages, notably the use of a lead tank, porous ceramic pots, moving anode, strong and toxic acids, high temperatures and high current density, but it is fast acting and the results obtainable on 99.8% base aluminium alloys are probably as good as with any other process.

Perchloric acid baths

These were developed by Jacquet based on the method employed for metallographic applications. The industrial process, which works at room temperature, 20°C, employs current densities of approximately 1 A/dm^2 (10 amp/sq ft) requiring 26 volts, and one such solution contains:

Perchloric acid (d. 1.55)	34.5% (vol)
Acetic anhydride	65.5%

Like the Brytal process, this method is a brightening rather than a macro-polishing treatment and gives excellent results on previously mopped surfaces. Due to the high solution cost *and the serious risk of explosion if the temperature exceeds 25°C* it has not been widely used. Tegart' has detailed the precautions which must be taken when using perchloric acid solutions. Gabe[13] considered the

use of perchloric acid / methanol solutions which have the advantage of being used cold rather than hot, are not highly concentrated like the sulphuric acid based solutions, no desmudging is necessary and they give excelleiit polishes.

Perchlorates (except potassium perchlorate) are fairly soluble in acetic acid, and in an interesting variation of perchloric acid electropolishing Heyes and Fischer[48] have suggested the use of a saturated solution of a perchlorate in acetic acid. The bath is claimed to be easy to operate and economic since when the precipitated metallic acetates reach a given concentration (about 15 g/l for ferrous metals) they can be removed by filtration and the bath regenerated by additions of fresh acetic acid.

Another anhydrous bath, a formamide solution, has been investigated in Japan for electropolishing aluminium[49] and good results are claimed to have been achieved in a solution containing 1-2 mole/l ammonium perchlorate NH_4ClO_4 in formamide, $HCONH_2$, at 20-50°C with platinum cathodes.

Summary of phosphoric/sulphuric acid processes

1. Société Procol & J.F.G.Herenguel. Brit. Pat. 638,321. Phosphoric/sulphuric mixtures as noted in Table 3-7.
2. Battelle Memorial Institute. Brit. Pat. 645,543 (1948). U.S. Pat.2,550,5 14. Phosphoric/sulphuric/chromic acid mixtures as noted in Table 3-6.
3. P.A. Charlesworth. U.S. Pat. 2,594,124 (1946). Uses an electrolyte containing 50-80% by weight of sulphuric and phosphoric acids such that the ratio of sulphuric to phosphoric is greater than 5:3; additions of 0.3-5% of aniline are made.
4. P.A. Charlesworth, Electropol Ltd. Brit. Pat. 706,473 (1949). **A** method of chemical control by adding sulphuric acid to precipitate dissolved metals as insoluble salts.
5. Ever Ready Co. Brit. Pat. 704,953 (1951). The acid electrolyte contains 1-15% of an aliphatic polyhydric alcohol or an ether alcohol soluble in phosphoric acid and water. An example is phosphoric acid 66%, sulphuric acid 15%, water 16%, ethylene glycol monoethyl ether 3% used at 15 A/dm^2 and 70-90°C for 30-60 seconds.
6. Ever Ready Co. Brit. Pat. 714,078 (1952). This covers the use of a phosphoric acid ester of a polyhydric alcohol added to the sulphuric/phosphoric electrolyte. An example is 1-5% sodium glycerophosphate.
7. Vereinigte Deutsche Metallwerke A.G. German Pat. 825,937 (1951). The additions covered are arylsulphonic acids. An example is phosphoric acid 5-35%, sulphuric acid 40-60%, benzenesulphonic acid 5-25%, balance water used at 65-100°C. Phosphoric acid may be omitted from this process.
8. Kyowa Hakko Kogyo. Brit. Pat. 1,070,190 (1964). The electrolyte may be a sulphuric/phosphoric mixture or sulphuric acid only to which is added gluconic acid, a gluconate, picoline, quinoline or ethylene glycol. The temperature is greater than 40°C and the current density over 5 A/dm^2.

9. Kurita Kogyo. Japanese Pat. 2772 (1964). The composition covered is phosphoric acid 15-20%, sulphuric acid 75-80%, water 5%.
10. Kurashiki Liki Rayon Co. Japanese Pat. 7132 (1964). Either phosphoric acid or a phosphoric/sulphuric mixture is used with a polyvinyl alcohol added.
11. Kyowa Hakko Kogyo Co. Brit. Pat. 1,077,559 (1965). The solution is sulphuric acid used with or without phosphoric acid and having in addition either glycine, beta-aniline or gluconic acid with or without nicotinic acid or nicotinamide, and ethylene glycol may also be present.
12. Kyowa Hakko Kogyo Co. Brit. Pat. 1,077,974 (1965). Electropolishing in phosphoric/sulphuric acid mixtures with an acid amide, amino acid, cyclic alcohol, isonicotinic ester, e.g. aspartic or gluconic acid, lysine or glutamine, inositol, or methyl isonicotinate. The phosphoric/ sulphuric ratio is 1:1.25-1.35 (vol) and the process is operated at over 40°C, 7 volts and over 5 A/dm^2.
13. G.P. Maitak, L.G. Andreeva. Russian Pat. 209,935 (1966). Anodic polishing in concentrated phosphoric acid or mixtures of phosphoric acid with sulphuric acid is improved by using alternating current of 500-10,000 Hz.
14. F. Garching, Poligrat, U.S.Pat. 4,740,280 (1988). A phosphoric/sulphuric acid solution to which is added 10-20 g/l phosphonic acid and 20-30 g/l of a chelating agent based on phosphonic acids and if desired 0.5-2% of a stabiliser of the latter. Preferred chelating agent is morpholino-methane-diphosphonic acid and the stabliser may be nitrilotriacetic acid or sodium glucoheptonate.
15. A.L.Askin, P.B.Schultz and D.L.Serafin, Aluminum Company of America, U.S.Pat. 5,616,231 (1997). Electrobrightening in phosphoric/sulphuric acid solution with suspended mineral particles. Pumice, activated carbon and silica are effective. A similar effect is obtained with a visible precipitate from adding 100-130 g/l sodium carbonate.

Summary of phosphoric acid processes without sulphuric acid

16. Westfalische Leichtmetallwerke GmbH. German Pat. 903,297 (1943). This is an addition to an earlier patent, DRP 763,900, which specified a mixture of chromic and phosphoric acids; part or all of the chromic acid is replaced with silicic acid. For example 1 litre of phosphoric acid, silicic acid 50g, chromic acid 30g; or 1 litre phosphoric acid with 50g silicic acid. Both solutions are used at 20-50°C and 20 A/dm^2.
17. Alais, Froges et Camargue and J. Patrie. Brit. Pat. 659,893 (1948). This is a phosphoric/nitric acid or a phosphoric/nitric/chromic acid electropolishing solution. In the first, the composition limits are phosphoric acid 13-34%, nitric acid 30-45%, balance water: and in the second, phosphoric acid 8-24%, nitric acid 34-45%, chromic acid 3-10%, balance water. Treatment is carried out at 3-7 volts, 10-50 A/dm^2 and at 20°C or below.

18. Alais, Froges et Camargue. French Pat. 941,238 (1949). An electrolyte suitable for aluminium or alloys contains phosphoric acid 750ml, water 250ml, oxalic acid 300g, boric acid 150g and litharge 1g. Treatment is carried out with agitation at 60°C and a current density of 30 A/dm^2.
19. Vereinigte Aluminium Werke AG. German Pat. 876,183 (1949); Brit. Pat. 679,078. This is a phosphoric acid brightening bath containing hydrogen peroxide or a substance, e.g. ammonium persulphate, which yields hydrogen peroxide when added to phosphoric acid. Used for chemical and also electropolishing with either a.c. or d.c. An example is phosphoric acid 1 litre, 30% H_2O_2 50ml used at room temperature and 1.5 A/dm^2 at 11 volts. Al-Cu-Mg alloys can be treated at 4 volts, 10-12 A/dm^2 and 70-80°C.
20. Y. Shiraishi. Japanese Pat. 4909 (1953). A composition of phosphoric acid 100ml, chromic acid 10g is used at 50°C and 5-8 A/dm^2.
21. M. Hayasaka. Japanese Pat. 2411 (1954). The electropolishing solution contains phosphoric acid 2 volumes, acetic acid 1 volume and is used at 15°C for 5 minutes at 3.5 A/dm^2.
22. High Duty Alloys Ltd. Brit. Pat. 619,336 (1949). The polishing bath contains 80% phosphoric acid and 10% n-butyl or amyl alcohol. It is used at 50-60°C and 5-30 A/dm^2. An almost identical process has been referred to in Germany as the D.R.L. process.[50]
23. D.E. Couch and A. Brenner. U.S. Pat. 2,740,755 (1953). The electrolyte employed in this process is 60-100% phosphorous acid, used at 5-100 A/dm^2.
24. Ever Ready Co. Brit. Pat. 746,772 (1954). This is a phosphoric acid electrolyte containing up to 10% of organic reagents. An example is orthophosphoric acid 77%, diethyleneglycol 7%, diethyleneglycol monethyl ether 3%, water 13% by weight. It may also contain about 2 g/l of aluminium phosphate. After chemical etching for 30-60 seconds the voltage is applied to give 12 A/dm^2 at 75-85°C.
25. Food Machinery & Chemical Corp. U.S. Pat. 2,736,640 (1954). The electropolishing bath contains phosphoric acid, hydrogen peroxide and from 1-3% of graphitic carbon.
26. Kurashiki Liki Rayon Co. Japanese Pat. 7132 (1964). Phosphoric acid with polyvinyl alcohol is used for electropolishing. Sulphuric acid may also be present.
27. A similar process to the above has been described by E. Bajza[51] using phosphoric acid 80% and polybasic alcohol. Electropolishing is carried out at 50-60°C and 14-32 volts for 5-10 minutes.
28. Shokosha K.K., Japan. Japanese Pat. J76035380 (1972). Phosphoric acid with 2% ferric sulphate and 1% sulphuric acid added. Electropolishing is carried out at 60-80°C with lead cathode.
29. Oxy Metal Industries. U.S. Pat. 3,970,529 (1975). Phosphoric acid with 5-70% (vol) polyalkylene ether. Temperature 65-95°C, current density 3-15 A/dm^2 and voltage 15-100 V.

Nitric acid containing processes

Very few processes for electropolishing aluminium have included nitric acid in more than small amounts. Alais, Froges et Camargue and J. Patrie. Brit. Pat. 659,893 has been referred to in the previous section (No. 17) and the nitric acid content of 30- 45% is unusually high.

In recent times the phosphoric acid/sulphuric acid/nitric acid brighteners of the Phosbrite 159 type (see chemical polishing) have occasionally been used electrolytically. The recommended current density is 10-20 A/dm^2, the temperature 70-80°C and time 0.5-3 min. **A** benefit of the lower operating temperature is less evolution of nitrogen oxide fumes.

Sulphuric acid based electrobrighteners

Sulphuric acid based electrolytes give results which are less bright than do those containing phosphoric acid, except when chromic acid is a component.

30. Société Procol. Brit. Pat. 638,321 (1947). This contained sulphuric acid 70%, phosphoric acid 15%, water 15% and was used at 85°C and 10-15 A/dm^2.
31. F. Hine. Japanese Pat. 178,514 (1949). The electrolyte composition is sulphuric acid 50 ml, citric acid 35g, water 45ml. This is used with alternating current at 50-70° C using counterelectrodes of steel, iron, nickel, carbon or lead but preferably the last. It is more suitable for low purity aluminium and alloys than for high purity metal.[52]
32. H. Burkhardt. German Pat. 825,937 (1951). The electrolyte is sulphuric 55-75%, benzenesulphonic acid 5-25% used at 65-100°C. Phosphoric acid may also be present.
33. Kyowa Hakko Kogyo. Japanese Pat. 7131 (1964). This uses sulphuric acid 30-80% with gluconic acid or a gluconate. Brit. Pat. 1,070,190 by Kyowa referred to above (No. 8) is very similar, and may operate without phosphoric acid.
34. Kyowa Hakko Kogyo. U.S. Pat. 3,365,380(1968). This uses sulphuric acid 30-80% together with a substance which adheres to the surface such as gluconic acid, gluconates, agar, starch, cellulose, maltose, polyvinyl alcohol, benzoates, tannic acid or stearic acid. It is said to produce a pearl-like appearance when used at 30-90°C and 5-25 volts.
35. Kurita Kogyo. Japanese Pat. 2772 (1964). **As** noted above (No. 9) sulphuric acid 75-80% is the principal component of this sulphuric/phosphoric electrolyte.
36. Nippon Soda K.K. Japanese Pat. JAJ 544826 (1977). Electrolyte consisting of 20-50 parts H_2SO_4, 20-50 parts polyethylene glycol (to increase viscosity), 20-50 parts water and 0.1-5 parts surfactant. Treatment at 60-80°C for ½-5 min.

Sulphuric/chromic acid electrobrighteners

37. N. Damien. Brit. Pat. 654,435 (1948). This contains sulphuric acid 50-75%, water 25-50% and sodium dichromate 15-30 g/l. The treatment time is very short and the current density high. This process has been used commercially on reflectors in France.
38. R.A. Erdmann. French Pat. 973,536 (1951). This specifies two or more of the acids nitric, chromic or sulphuric and is used at 18-30°C, 6-8 volts and 1 A/dm^2 for 20-45 minutes.
39. K. Guggenberger and Fromson Orban Co. Inc. U.S. Pat. 2,751,342. The electrolyte contains sulphuric acid and chromic acid from 3 g/l up to saturation.
40. Yuko Aluminium Manufacturing Co. Japanese Pat. 859 (1956). The electrolyte contains sulphuric acid 500 ml, $NaAlO_2$ 40 g, and CrO_3 20 g. It is used for 30 seconds to 1 minute at 60°C and 10 A/dm^2,16 volts.
41. S.B. Lepskaya *et al.* Russian Pat. 160,070 (1961). The electrolyte contains sulphuric acid 800-900 g/l, chromic acid 50-60 g/l, and potassium alum 5-10 g/l. It is operated at 50-80°C with 20-50 A/dm^2 and a polishing time of 3-8 minutes.
42. Langbein-Pfanhauser Werke A.G. Brit. Pat. 743,692 (1963; Germany 12.5.1953). The electrolyte contains chromic acid 25-30 g/l, sulphuric acid 1200-1750 g/l (preferably 1450 g/l = 80% by volume). It is used for electropolishing at 80-90°C, 13-20 volts, and a current density of 25-50 A/dm^2 for up to 6 minutes. The lead cathodes are surrounded by a liquid-tight acid-proof diaphragm. This is the Aluflex process.

Summary *of* alkaline electropolishing processes

43. British Aluminium Co. and N.D. Pullen. Brit. Pat. 449,162 (1935). The Brytal process containing sodium carbonate/sodium phosphate has been described in detail above.
44. S. Tajima,[53] 1947. Aluminium can be successfully electropolished in a solution containing caustic potash 2.5 g, caustic soda 1.4-5g, lactocasein 0.02g. water 50 ml. The bath is used at 80°C, 30-70 volts and 100-300 A/dm^2. The method is suitable for purities of over 99.6% and is not applicable to alloys containing copper, nickel or iron.
45. Alais, Froges et Camargue. Brit. Pat. 521,290 (1937). The alkaline electrolyte can be caustic soda or sodium sulphide used at near maximum concentration at about 30°C, or in the dilute state (2% solution) associated with a neutral salt of an alkali metal (e.g. sodium sulphate) at nearly maximum concentration and about 60°C.
46. AGMA AG. Swiss Pat. 256,850 (1948). A typical electrolyte contains sodium carbonate 20%, sodium fluosilicate 7%, trisodium phosphate 2%. It is used at 85°C, 13 volts and 2 A/dm^2. Pure aluminium or alloys can be treated.

47, Société de Produits Chimiques des Terres Rares. Brit. Pat. 655,699 (1948). The electrobrightening stage comprises caustic soda 100g, aluminium 10g dissolved in caustic soda, phosphoric acid 50g, water to 1 litre. It is used at 80°C, 12 volts and 6 A/dm^2. French Pat. 966,790 (1950) is almost identical, the composition being given as sodium or potassium phosphate/sodium or potassium aluminate with PO, 2-10%, and AlO_2 0.5-5%.

48. L. Prigoniker. Brit. Pat. 655,514 (1949). This process uses alternating current at high current density but low voltage. The electrolyte is principally an alkali cyanide 90-110 g/l, which may also contain as retardant sodium thiocyanate or sodium sulphate, and an organic colloid. An example is sodium cyanide 100 g/l, sodium thiocyanate 15 g/l, gelatine 5 g/l. The bath is used between 50 and 100°C, at 15 volts and 20-30 A/dm^2.

49. K. Takada. Japanese Pat. 2818 (1956). A low grade aluminium or Duralumin can be electropolished in caustic soda 3%, sodium silicate 10%, and sodium hexametaphosphate 5%, used at 40°C, 20 volts and 20 A/dm^2.

50. H. Burkhardt. German Pat. 1,212,816 (1966). This is an alkaline electropolishing bath containing alkali metal hydroxide, zinc and alkali metal carbonate 5-35% by weight with a zinc:alkali metal hydroxide ratio of 1:2.

51. Kyowa Hakko Kogyo. U.S. Pat. 3,232,855 (1966). A pearl-like finish is obtained on aluminium by electropolishing in a solution containing 0.1 mol/kg of alkali metal gluconate, and at least 1.7 mol/kg alkali metal hydroxide in water used at 3-100 A/dm^2.

52. Shokosha Co. Japanese Pat. JAJ8076093 (1978). Electrolyte containing 15-300 g/l Na_3PO_4 and 1-30 g/l KOH or $Mg(OH)_2$ with small amount of organic acid present. Temperature 30-60°C and current density 1-30 A/dm^2.

53. P.G.Harris, British Aluminium Co.Ltd., Brit. Pat. 1,569,101(1980) and U.S.Pat. 4,247,378 (1981). This is an extension of the Brytal process to allow the electropolishing of alloys down to 99.5% purity as described in detail above.

4. CHEMICAL POLISHING

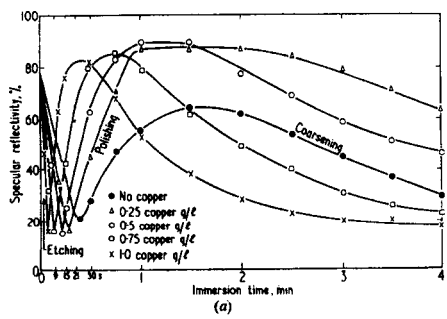
Chemical polishing processes are of more recent origin than electropolishing and have replaced them to a considerable extent. Their primary attraction is the comparatively much smaller outlay in plant required, not only for electrical power, but also for tanks and fixtures. As no electric current or anode rod movement is employed, work can often be treated in baskets or on simple fixtures.

Mechanism of chemical polishing

Basically, the mechanism of the polishing action is similar to that described for electropolishing, except for the use of current which is here replaced by chemical oxidizing agents. The driving force in chemical polishing is the electrochemical potential difference between anodic and cathodic sites on the surface.

The specular reflectivity of bright rolled aluminium falls markedly when anodized unless it is chemically polished or electropolished shortly before anodizing. A similar fall occurs in the initial stages of chemical polishing but it is followed by a rise in specular reflectivity, which can be to a value of 90% (the highest physically possible for aluminium) if the chemical polishing conditions are correct.[54] The same behaviour is found with electropolishing. The specular reflectivity remains high when electropolished or chemically polished aluminium is anodized, (though there is a slight fall with increasing time in the anodizing bath due to slow dissolution and slight roughening of the outer surface of the anodic film). Commercial bright anodizing therefore usually includes chemical polishing before anodizing.

Culpan and Arrowsmith[54] measured the change in specular reflectivity during the chemical polishing of aluminium and electron microscopy was used to observe the corresponding change in surface topography. Chemical polishing started with a sharp fall in reflectivity due to etching followed by a rise in reflectivity as polishing proceeded (Fig. 3-15(a) and Fig. 3-15(b)), reached a maximum and then dropped off.



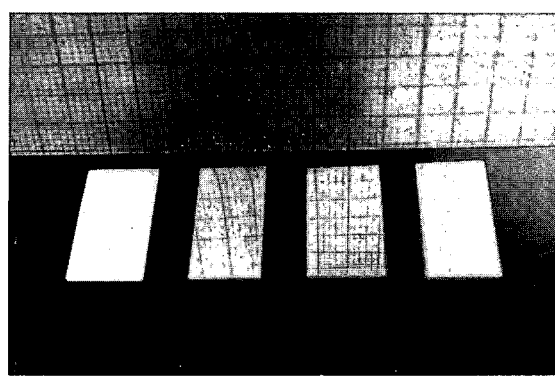


Fig. 3-15(a) above and (b) below
Variation in specular reflectivity with immersion time in chemical polishing solutions with between 0 and 1.0 g/l copper added.
(a) Etching, polishing and coarsening stages
(b) Reflectivity of aluminium chemically polished in solution containing 0.5 g/l copper; time in solution. *left to right,* 10 s, 30 s, 50 s, 3 min.

At the start, randomly distributed etch pits grew and merged together laterally until the initial surface had been removed. The original oxide was replaced by a compact solid film through which chemical polishing proceeded. Hoar[55] suggested that this film was oxide containing significant amounts of the anion from the polishing solution. The etching stage is necessary to replace the original oxide with a thin solid film which has the characteristics required for polishing.

The existence of the etching stage has long been known to commercial operators who observed it in the first half minute of chemical polishing and who ascribed it to the activity of the rolled or buffed surface. Oxide, rolling oil, and detritus rolled into the surface were considered to be the reason for the initial etching stage, which was followed by polishing once the Beilby layer had been removed. This was confirmed by Arrowsmith and Sliwinski[56] who found that the time taken for the removal of the initial oxide depended on its thickness.

Culpan and Arrowsmith[54] studied the role of copper in a phosphoric acid/ sulphuric acid/nitric acid brightening solution, and concluded that the presence of copper is necessary for maximum brightening to take place. They find that the chemical polishing process is divided into three stages, etching, polishing and coarsening. Maximum brightness is obtained after the development of the polishing structure and before coarsening. If insufficient copper is deposited on the surface, the etching stage is not completely replaced by the polishing structure before the onset of coarsening. Above the optimum amount of copper, large agglomerated particles of copper build up on the surface and produce high current densities in local areas, and the onset of coarsening is very rapid. They therefore see the role of copper as the promotion of solid film formation on the metal surface, and this is indicated by the fact that copper containing solutions give a lower rate of metal removal than copper free solutions.

These theories presuppose the presence of heavy metals in the chemical polishing solution, but this is by no means always the case. In the absence of a cathodic metal, the part of cathode may be played by the grain as distinct from the grain boundary at the start of the reaction, though at least as the reaction advances, the cathodic area may well be the oxide film itself.

Meyer and Brown[57] found that the addition of an oxidising agent, namely nitric acid, can decrease the solution rate of aluminium in phosphoric acid, and its role in the phosphoric acid based solution can be that of aiding solid film formation. Clifford and Arrowsmith[22] suggest that nitric acid has a further role, associated with copper deposition, and that at the optimum nitric acid concentration, the copper particles deposited on the surface are small and uniformly distributed. When the nitric acid level is too low, the distribution of copper particles is no longer uniform and coarse pits are associated with the large particles. When the nitric acid level is too high, the initial etching stage of the brightening process gives an orange peeled, grainy appearance and this is not superseded by normal polishing.

The rate of metal removal on high-punty aluminium (99.99%) on chemically polishing in an alkaline solution, in the phosphoric-nitric acid-base Alupol solution and in the nitric acid-ammonium bifluoride-base E.W. solution. is shown in Table 3-8.

TABLE 3-8

Metal removal, corrosion current density and gas evolution in chemical and electrolytic polishing of high-purity aluminium
(after Fischer and Koch[58])

Process	*Polishing time*	*Metal removed mg/cm²*	*Corrosion current density A/dm²*	*Gas evolved (cc./sec./dm²)*					
				NO_2	N_2O	N_2	NH_3	H_2	O_2
Alkaline Alupol process	20 sec	10-20	500-1000		47		17	traces	
Acid Alupol process	3 min	approx. 5	approx. 30	0.6	6	1.8		traces	approx. 0.6
E.W. process	15 sec	7-15	500-1000	traces	traces			13	12
V.A.W. electropolishing process	10 min	3-10	5-20						traces
		mil/in²	*amp./sq ft*	*(cc./sec./sq ft)*					
				NO_2	N_2O	N_2	NH_3	H_2	O_2
Alkaline Alupol process	20 sec	10-20	5000-10,000		470		170	traces	
Acid Alupol process	3 rnin	5	approx. 300	6	60	18		traces	approx. 6
E.W. process	15 sec	7-15	5000-10,000	traces	traces			130	120
V.A.W. electropolishing process	10 min	3-10	50-200						traces

According to Fischer and Koch,[58] the mechanism of the chemical polishing reaction depends on two processes:

(1) *The anodic process:* dissolution of the aluminium of the local cell at current densities high enough to form the necessary porous solid film, and

(2) *The cathodic reaction:* reduction of the oxidizing depolarizing agents at the cathodic areas, e.g., in the electrodeposition of copper.

In addition to these processes, oxygen evolution may occur at the anodic areas while deposition of copper and hydrogen may take place at the cathodic areas, the secondary processes taking place either simultaneously or alternately with the primary process.

The anodic reaction can be written as: $Al \rightarrow Al^{3+} + 3e^-$

When nitric acid is a constituent of the chemical polishing solution, the following can occur:-

(a) Nitric acid may react with a metal in the undissociated state $OH.NO_2$. This is the reaction found with noble metals, e.g., copper,[59] and results in the formation of the oxide of the metal and oxides of nitrogen. The cathodic reaction may then be the reduction of $OH.NO_2$ to the hydroxyl (or oxygen) ion plus nitrous acid and subsequently nitrogen oxides. The net result of the reaction would be expressed as:

$$2\,Al + 3OH.NO_2 \rightarrow Al_2O_3 + 3HNO_2$$

(b) Nitric acid reacts with the metal in the dissociated form $H^+ + NO_3^-$. This is the reaction most commonly found when nitric acid is in contact with less noble metals, such as aluminium, in which the destruction of hydrogen ions occurs preferentially as the cathodic reaction.

According to the gas analysis in Table 3-8, it therefore seems probable that in polishing aluminium in the phosphoric-nitric acid type solution, the nitric acid is reduced according to (a), and this is also in agreement with the depression of the dissolution rate on adding nitric acid to phosphoric acid. In fact concentrated nitric acid forms a very thin stable passivation film on aluminium, the thickness of which goes through a maximum. The magnitude of this maximum depends on the method of preparing the surface (see Fig. 3-16)[60] after which it reaches a steady value. Hamlin[61] considered the chemical reaction for the formation of the passivating oxide on the aluminium could be written as follows:-

$$14Al + 10HNO_3 \rightarrow 7\,Al_2O_3 + 4N_2 + 2NO_2 + 5H_2O$$

As the oxide forms at the surface of the metal, it is simultaneously dissolved at the oxide/solution interface by phosphoric acid:-

$$Al_2O_3 + 6\,H_3PO_4 \quad + \quad 2Al(H_2PO_4)_3 + 3\,H_2O$$

Chatterjee[62, 63, 64] studied phosphoric/sulphuric/nitric acid solutions and found that the solution which gave a maximum brightening of the surface during chemical polishing exhibited a lower exchange current density for the hydrogen evolution reaction, a lower corrosion current, a higher hydrogen overpotential and a more noble corrosion potential than those obtained from either the consituent acids or their other mixtures as would be expected from the formation of a thin passivation film. By considering the solvent power, chemical action and electrochemical properties of these solutions, Chatterjee[64] developed a phosphoric acid free brightening solution which contained ammonium vanadate to impart similar high viscosity to that of phosphoric acid based solutions.

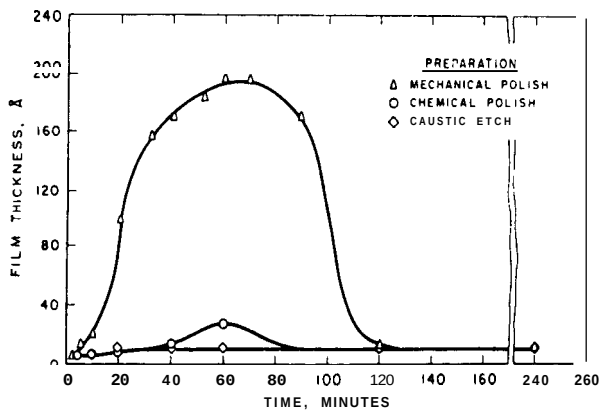


Fig. 3-16. Film growth on high purity aluminium in concentrated nitric acid[60]

The absence of reduction products of nitric acid in the E.W. solution suggests there may be a different reaction in that solution. However, Arrowsmith and Cunningham,[65] in their study of E.W. type solutions, show that the mechanism of polishing is similar to that in **phosphoric-sulphuric-nitric** acid solutions but they point out that control is more critical. They made electrochemical measurements of potential during chemical polishing (Fig. 3-17) and these showed the importance of nitric acid in producing an oxide film on the surface so that polishing could occur. Too little nitric acid gives general etching of the surface and too much acid gives pitting. As the aluminium content of the bath rises ($Al(NH_4F_2)_3$ is precipitated

so additions of ammonium bifluoride are made to maintain the correct HNO_3:NH_4HF_2 ratio. The role of lead in this solution, either as an impurity or as added lead nitrate, is similar to that of copper in other brightening solutions; it is deposited on surface intermetallics and influences the cathodic evolution of hydrogen.

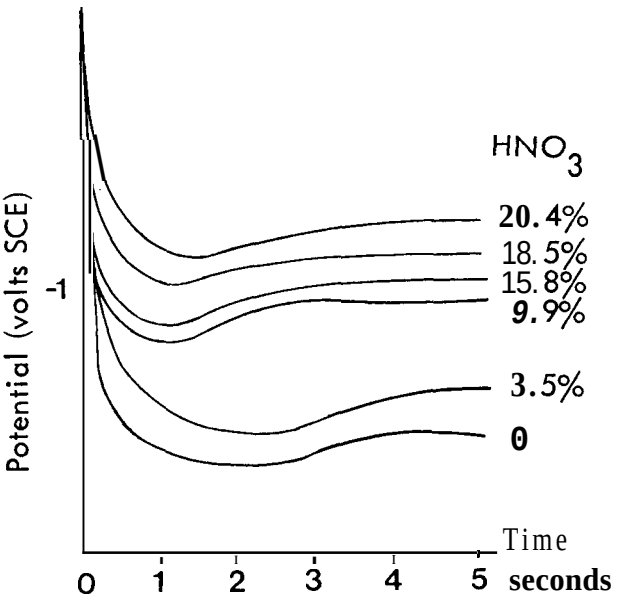


Fig. 3-17. Typical potential-time curves showing influence of increasing HNO_3 added to 8% NH_4HF_2/1% dextrin/0.04% $Pb(NO_3)_2$[65]

A second type of chemical brightening process is characterised by low dissolution rates in more dilute solutions. Examples on aluminium are the hydrogen peroxide-based solutions described below, while the dilute Kaiser and General Motors solutions using nitric acid and chromic acid as oxidizing agent may be other examples. In this instance, no smoothing takes place as is understood in the case of the phosphoric acid based solutions, and brightening is due to the formation of the solid film itself.

This is considered to be due to the fact that the conditions for oxide formation are reached somewhat sooner in recesses than on the projections, thus allowing more metal to be dissolved from the latter before the film is formed, while the more rapid growth of oxide where the field is higher can itself lead to smoothing of asperities.[66] In this way it has been found possible to brighten aluminium by repeatedly anodizing and dissolving the coating.[67] The electropolishing process described by Evans and Whitwham[17] rests on the same principles.

In the case of the chemical brightening processes in this group, alternate growth and dissolution of the solid film is due to periodic passivity, which is probably due to changes in the pH of the solution in the immediate vicinity of the surface. In such cases, the growth of a solid film is promoted by the rise in pH due to the cathodic reactions, the destruction of hydrogen ions or the formation of hydroxyl ions, which coincides with a larger metal ion concentration near the surface. Formation of the passivating film then decreases the hydroxyl ion concentration while, during the passive period, diffusion will also help to restore the original pH at which the oxide is dissolved and the cycle repeated. In comparatively dilute solutions of hydrogen peroxide the potential of aluminium is raised to electropositive values by the formation of a protective film. This film is destroyed in the presence of chloride, but is otherwise stable in acid solution. However, the film is broken down above pH 5,[68] above which the reaction of hydrogen peroxide with the metal changes.[59]

In the case of acid hydrogen peroxide solutions, this mechanism is aided by the fact that hydrogen peroxide is an oxidizing agent only at low pH, while in more alkaline solutions it is catalytically decomposed with the formation of oxygen gas. Periodic oxygen evolution has been noted by Marshall in such solutions on iron,[''] and this gas evolution probably marks the period during which the film is formed, until decreasing pH causes both reactivation of the metal and the reconversion of the hydrogen peroxide as oxidizing agent.

5. INDUSTRIAL CHEMICAL POLISHING PROCESSES

A. Phosphoric acid-based processes

Most of the solutions employed in industry for the chemical polishing of aluminium are based on phosphoric acid. Concentrated ortho-phosphoric acid at a temperature above 80°C will attack aluminium vigorously with the release of hydrogen to produce a surface which is very bright, and without revealing the grain structure of the metal, but the finish is usually quite diffuse. When a proportion of nitric acid is added to this the mode of attack is at once modified to produce a more specular surface by virtue of the regulating action of an oxide coating which forms on the metal.

Specular surfaces are generally produced in mixtures of phosphoric and nitric acids to which numerous other additions can be made to secure a greater levelling action or to confer some other benefit. The presence of a heavy metal (Cu, Ni, Fe, Co, Ag, Cd, etc.) in the form of nitrate or sulphate is of varying value, and weak acids such as acetic, boric, citric and molybdic acids are beneficial.

Sulphuric acid is also added but its function is as much for the sake of economy as for any inherent contribution that it makes since it will effectively replace a

proportion of the expensive phosphoric acid. The various other additives proposed are listed in the following pages.

Some brightening solutions have been based on phosphoric and sulphuric acids only without any nitric acid. They provide a less specular surface — more in the nature of a bright etch; these have been very widely used and continue to find application for decorative effects.

Phosphoric-sulphuric acid processes

Sulphuric acid may be added to phosphoric acid solutions and such mixtures are used at 100-140°C (212-284°F); the higher the sulphuric acid content the higher the optimum temperature. While the solution requires agitation and fume extraction, phosphoric acid and phosphoric-sulphuric acid mixtures give a bright finish on aluminium; the reaction is not accompanied by oxide formation and the smoothing efficiency is limited to coarser surface textures, i.e., etching is only very partially suppressed. A white film consisting of a phosphate of aluminium remains on the metal after treatment, and is removed in a solution containing:

chromic acid	30 g/l
sulphuric acid ***or***	
phosphoric acid	30 g/l

operated at 60-80°C (140-175°F).

The mechanism of formation of this film is uncertain but it is probably due to local saturation of reaction products at the solution interface. This theory is favoured by the observation that repeated dipping and draining has a beneficial effect on the finish, as well as by the partial suppression of etching obtained.

The following solutions based principally on phosphoric acid with additions of either sulphuric acid or sulphates, have been proposed.

1. United Anodising Co. Ltd., Brit. Pat. 625,834 (1946); also U.S. Pat.2,650,156. This was originally known as the Alpol process and uses either equal proportions of phosphoric and sulphuric acid or 75% phosphoric and *25%* sulphuric acid at a temperature of 100°C.
2. L'Aluminium Français., French Pat. 1,000,938 (1952). This employs phosphoric acid containing 10-100 g/l of an alkali metal persulphate; silver sulphate and glycerol may also be present.
3. Reynolds Metals Corp., Brit. Pat. 958,499 (1960). The composition limits are between 15% phosphoric/85% sulphuric acid and 30% phosphoric/ 70% sulphuric acid with the total acid concentration between 88.4 % and 90.5%. The temperature of use is from 95-105°C and a silver salt may also be present.
4. E.L.F.A. French Pat., 1,517,658 (1961). Aluminium or aluminium alloy is brightened in a solution containing phosphoric acid with additions of both sulphuric and chromic acids, used at 70-130°C. This is one of the very few mixtures using chromic acid although they are very common for electropolishing.

5. Albright and Wilson., Brit. Pat. 1,088,287 (1964). The solution contains phosphoric acid, up to 50% sulphuric acid, copper nitrate from 0.5-20%, up to 5% NH_4^+ ions and less than 25% water. Up to 5% each of HCl, H_3BO_3, $FeSO_4$, Ti or V compounds, oxalic or tartaric acid and carboxymethylcellulose may be added. The process may also be accompanied by electropolishing at 10-20 volts.
6. Rasa Industries Co., Japanese Pat. JAJ 7924899 (1975). Phosphoric acid-sulphuric acid brightener with 0.005-5% (wt) amino acid together with Cr, Ni or Ag salts.
7. Nihon M. and T. Co., Japanese Pat. JAJ 8034866 (1976). 50-80% (vol) phosphoric acid and 50-20% (vol) sulphuric acid with 0.001-0.01% (wt) of betaine compounds and 0.05-5% (wt) of polysulphide compounds.
8. Sumitomo Chemical Co., Japanese Pat. JAJ 5368626 (1976). Double polishing treatment with first treatment in a phosphoric acid-sulphuric acid solution (preferably with 7% (wt) of acetic acid present) and second solution containing an acid such as phosphoric acid, sulphuric acid or acetic acid and 0.005-0.5% (wt) of permanganate (pH 2.1, 20-50°C for 10-60 secs).

Phosphoric-nitric acid processes

The addition of nitric acid to phosphoric acid solutions improves the quality of the finish. That passivation occurs is well demonstrated. At suitable concentrations and temperatures, etching may be almost entirely suppressed and these processes may be used as finishing treatments for mechanically polished surfaces.

In the absence of other constituents, the composition given in Table 3-9 may be used.[70, 71]

TABLE 3-9

Phosphoric-nitric acid solutions

	Optimum range	*Typical solution*
Phosphoric acid	73-83% (vol)	80.5% (vol)
Nitric acid	2-5%	3.5%
Water	14-23%	16%
Temperature	approx. 90°C	as indicated

The solution given is suitable for use on commercial aluminium, and on wrought alloys containing magnesium[57] and manganese (5251). A total reflectivity figure of 87% in white light has been given for pure aluminium; the reflectivity of alloys is slightly lower. The treatment time varies between 15 seconds and 5 minutes. This solution, under the name R5, is in wide use in the U.S.A. today.

Copper is frequently added to this solution to improve the finish, e.g., Mohler[72] found that specular reflectivity was improved from 40% to 70% on 2024 alloy and from 40% to 55% on 7075 alloy when 0.01% (wt) copper was added to a phosphoric-nitric acid bath used for polishing these high-strength alloys.

Workers at the Monsanto Chemical Co. in the U.S.A. recommend[73, 74] a solution containing 3% (wt) nitric acid and 0.01-0.02% (wt) copper (see Fig. 3-18).

An interesting feature of this diagram is that the high quality region is relatively small and that a certain amount of aluminium must be present in order to avoid etching (below the high quality area). According to these authors the lowest chemical costs consistent with high quality work are obtained in a solution containing:

	% wt
nitric acid	2.8-3.2 (= ~ 4.9-5.6 % vol)
water	17-23
aluminium phosphate	10-12
phosphoric acid	64-70
copper	0.01-0.02

Compositions to the right of the 'high quality' area in Fig. 3-18 cause precipitation of aluminium phosphate (ice) on the work.[40] At the top, i.e. above 12% $AlPO_4$, the rate of attack decreases and the finish falls off, being unacceptable above about 14% $AIPO_4$, although the solution can be regenerated by addition of sulphuric acid or by surface active agents. However, the viscosity of the bath rises with the increased aluminium content and stains may be caused which are due to its poor draining and rinsing properties. At the left of the 'high quality' area too much water is present to obtain a good finish. In general, high water content may to some extent be offset by using higher temperatures and nitric acid concentrations.

As the aluminium phosphate concentration depends upon the drag-out rate, every bath will, in practice, often find its own stable concentration level which can be increased by, e.g., extending the drain time, in order to reduce solution costs provided it remains below the critical limit of about 12%. If the $AlPO_4$ content of the bath is too high it may be corrected in practice by decreasing the drain time, i.e. increasing the drag-out volume. On the other hand, changes in water content of the phosphoric-nitric acid bath depend partly on water taken in by drag-in from rinses, and water produced by the polishing reaction (the dissolution of 450g aluminium produces about 550g water), and partly on evaporation losses.

The following brightening baths based principally on phosphoric and nitric acids have been proposed. (The enumeration continues from the list of phosphoric-sulphuric acid processes on p. 105).

9. Aluminum Company of America., U.S. Pat. 2,650,157 (1947); Brit. Pat. 659,747 (1948). This solution and its composition has been referred to above. It is the basis of the very successful R5 process and also Phosbrite 159. Sulphuric acid may be present optionally and the commercial products contain other additives also.

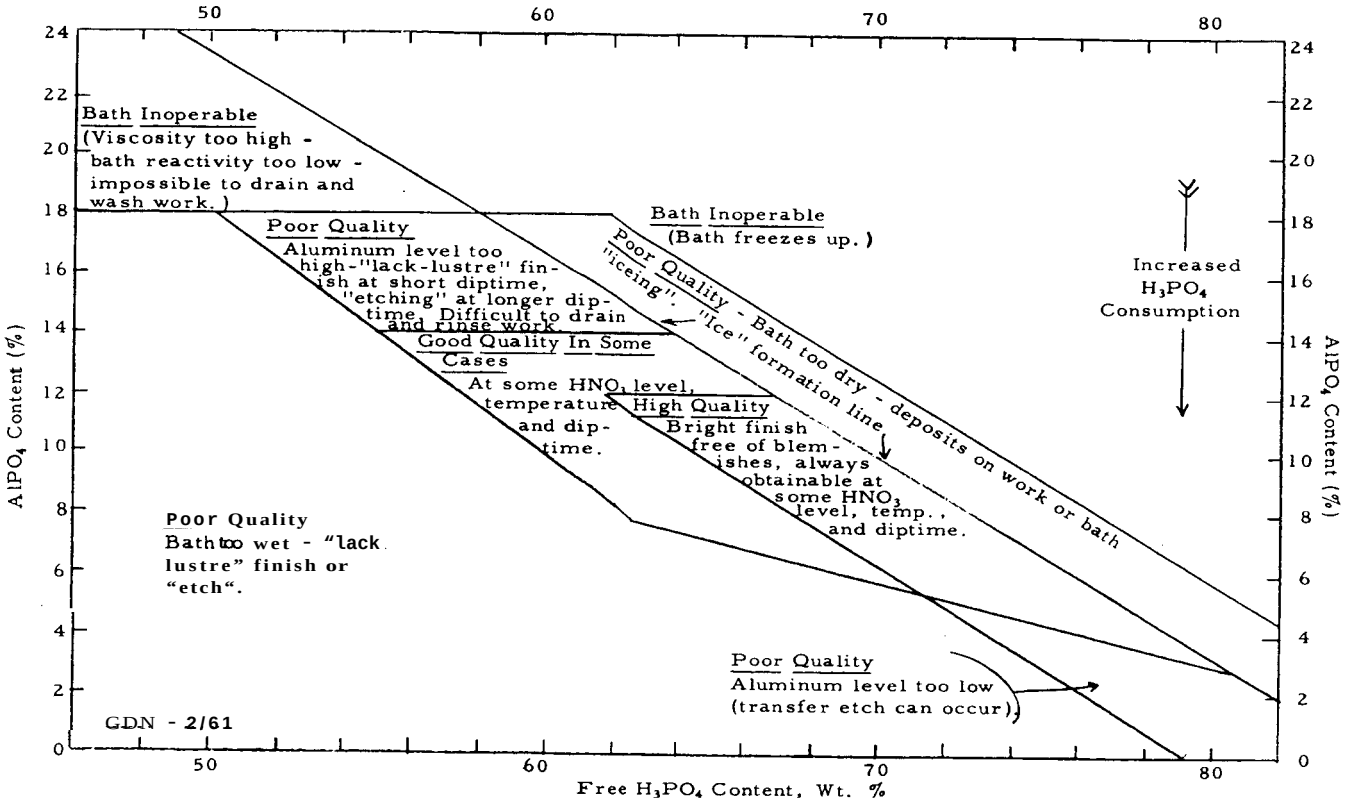
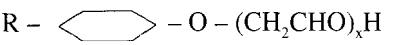


Fig. 3-18. Effect of composition of a phosphoric-nitric acid polishing bath on the finish. Bath operated at 88-99°C and containing 2.8-3.2% wt. nitric acid and 0.01-0.02% copper[73]

10. K. Hayasaka., Japanese Pat. 320 (1950). This contains from 40-98% phosphoric acid and from 2-40% nitric acid.
11. K. Hayasaka., Japanese Pat. 3863 (1950). Similar to the foregoing but the nitric acid level is given as 0.5-5%, water 1-5%, and in addition it contains 1-10% $AlH_6(PO_4)_3$. It is used at 50-150°C.
12. Aluminium Laboratories., U.S. Pat. 2,678,875 (1950); Brit. Pat. 717,580 (1951). The phosphoric/nitric brightening bath contains 5-50 g/l silicic acid.
13. Colonial Alloys Inc., U.S. Pat. 2,729,551 (1948; publd. 1956). This claims a phosphoric/nitric acid brightener with water, a typical example being 70% phosphoric acid, 15% nitric acid and 15% water.
14. A.Teubler, Vereinigte Leichtmetallwerke., Brit. Pat. 758,481 (1954). This process covers the addition of citric acid. An example is 10 g.mol/litre phosphoric acid, 4-9 g.mol/litre nitric acid and 0.01-0.25 g.mol/ litre citric acid used at 60-120°C.
15. Hitachi Manufacturing Co., Japanese Pat. 2962 (1956). The nitrate is present only as aluminium or potassium nitrate, in addition to copper as either sulphate or nitrate. An example is phosphoric acid 100 ml, $Al(NO_3)_3$ or KNO, 5-20g, $CuSO_4$ or $Cu(NO_3)_2$ 0.5-Ig.
16. Conversion Chemical Corp., German Pat. 1,237,874 (1959). This covers the use of 75-87% phosphoric acid, 2-5% nitric acid, balance water to which is added 0.05-3% of 2,4,6-triamino*sym*triazine or urea or dicyanamide.
17. Monsanto Chemical Co., U.S. Pat. 3,094,489 (1959). This patent covers additions of ammonia or ammonium hydroxide to a phosphorichitric acid solution.
18. Monsanto Chemical Co., U.S. Pat. 3,202,612 (1960). In addition to containing copper and ammonia, an organic acid is included. The limits specified are 45-90% phosphoric acid, 1-10% nitric acid, 2-35% water, 0.004-0.04% Cu, 0.15-4% NH_4, and 1-8% organic saturated aliphatic acid with 1½-4½ C atoms.
19. N.A. Makarov., Russian Pat. 145,105 (1961). This is essentially an ammonium nitrate solution with a relatively small addition of phosphoric acid. The limits quoted are 85-110 g/l ammonium nitrate and 11 g/l phosphoric acid used for 1½-2½ minutes at 95-110°C.
20. Virginia-Caroline Chemical Corp., U.S. Pat. 3,119,726 (1962). This covers a phosphoric/nitric brightening bath to which is added a brightening compound



where R is an alkyl radical with 7-9 carbon atoms and x is from 5-9.
21. Société Continentale Parker., Belgian Pat. 643,925 (1964). This is also a phosphorichitric acid mixture containing additives but with a special method of preparation. To 1 litre of phosphoric acid are added 12g of urea and 0.013g of sodium **dodecylbenzene-sulphonate,** it is heated to 90°C and then 25 ml of nitric acid are added.

22. Pyrene Co., Brit. Pat. 1,024,620 (1964). The brightening bath contains 50-95% phosphoric acid, 1-40 and preferably 2-5% nitric acid with 0.1-2% urea and a non-cationic surfactant. It is used at 75-105°C.
23. Stauffer Chemical Co., U.S. Pat. 3,410,803 (1965). The composition claimed is 60-83% phosphoric acid, I-5% nitric acid, 15-28% water and from 5-50 ppm of a silver salt.
24. Nippon Chemical Co., Japanese Pat. 74018697 (1970). Addition of 0.1-10% (wt) of an alkyl urea to phosphoric-nitric acid or phosphoric-sulphuric-nitric acid polishing solutions. The purpose of the urea addition is to prevent generation of nitrogen oxides.
25. I.S.Mohmoud, IBM, U.S.Pat. 4,956,022 (1990). This produces microetched surface which increases the nucleation sites for even anodic coatings. 784 ml phosphoric acid, 98 nil nitric acid, 40 g sodium nitrate and 118 ml water for 1-2 minutes at 80-90°C.

Phosphoric-nitric-acetic acid processes

Acetic acid may be added to the phosphoric-nitric bath. Thus two typical compositions contain:

phosphoric acid (d. 1.70)	70% (wt)	80% (vol)
nitric acid (d. 1.42)	2	5
glacial acetic acid	15	15
water	13	–

A similar solution described by Meyer and Brown" contains phosphoric acid (d. 1.5) 70% (vol), nitric acid (d. 1.42) 3%, acetic acid 12%, water 15%. This solution is employed at 100-120°C for 2-6 minutes.

The amount of metal removed by these solutions to obtain the optimum polish varies with the composition (particularly the nitric acid concentration) and temperature. As already indicated, in general, solutions based on phosphoric-nitric acid mixtures remove approximately 5-25 μm (0.2-1 mil) for the best results. Alloy composition is also important. As would be expected, the rate of reaction on alloys is generally faster than on aluminium.

The life of solutions containing acetic acid has generally proved to be short. Working with a bath similar to that given, the finish fell off after the solution had taken up 20-30 g/l of aluminium. Meyer and Brown state that the solution can be maintained by nitric acid and water additions to replace losses by volatilisation. New solution is added to offset drag-out losses, which are heavy due to the high viscosity of the bath. This may not necessarily be a disadvantage, as the aluminium content may be stabilised by drag-out at a level below the critical concentration, thus facilitating continuous operation without total renewal of the solution. The concentrations of the acids given are not critical.

Phosphoric-sulphuric-nitric acid processes

Several processes of this type have been in use and were developed principally in France. Typical compositions are given in Table 3-10.

TABLE 3-10

Composition of sulphuric-phosphoric-nitric acid solutions[30,,]

Type	*Phosphoric acid (d. 1.71) ml*	*Sulphuric acid (d. 1.84) inl*	*Nitric acid (d. 1.50) ml*	*Temp °C*
a	300	600	70-100	115-120
a	400	500	60-100	100-120
a	500	400	50-100	95-115
a	600	300	50-80	95-115
b	700	250	30-80	85-110
b	800	I00	30-80	85-110
b	900	50	30-80	85-I05

Strengths of acids quoted are different from those marketed in this country. Thus commercial supplies of nitric acid are generally of d. 1.42 (100 ml of d. 1.50 nitric acid + 40 ml water is equivalent to 140 ml d. 1.42 nitric acid). Phosphoric acid is commonly sold in grades of d. 1.75 and d. 1.7l (100 ml d. 1.71 phosphoric acid ≅ 95 ml d. 1.75 phosphoric acid + 5 ml water). Solutions of type (a), i.e., of a high sulphuric acid and nitric acid content, are operated at comparatively high temperatures and have a fast dissolution rate accompanied by vigorous gas evolution. They are stated to be suitable for aluminium of above 99.5% purity, and are used for smoothing coarse textures. Type (b) solutions are slower acting, due to their high phosphoric acid concentration, are more expensive, and are employed as a finishing treatment after mechanical polishing. As well as commercial grades of aluminium, they may be used on alloys of the Al-Mg-Zn and Al-Cu-Mg type, containing not more than 8% zinc or 5% copper. As in the case of electropolishing processes based on this type of solution, not more than 1% silicon should be present. **A** typical solution is made up as follows for operation at 95-115°C for 6 minutes:

phosphoric acid (d. 1.71)	70% (vol)
sulphuric acid (d. 1.84)	5%
nitric acid (d. 1.50)	5%
nickel sulphate (cryst.)	2 g/l

This solution removes approximately 1 μm (0.04 mil) per minute

The following is a list of the processes that have appeared based on this ternary composition:

26. Aluminum Company of America., U.S. Pat. 2,650,157 (1947); Brit. Pat. 659,747. This is the widely used R5 composition which has also been referred to in the phosphoric/nitric acid section (No. 9) since sulphuric acid was optional.
27. J.E. Jumer., U.S. Pat. 2,705,191 (1949). This covers the use of the sodium salts of sulphuric and nitric acids. The limits specified are phosphoric acid 100 ml, sodium sulphate 0.25-10 g and sodium nitrate 0.5-30g, used at 150-275°F.
28. General Motors Corp., Brit. Pat. 712,691 (1951). This was an early attempt to cover the addition of a range of heavy metals. The compositions specified were phosphoric acid 31-57%, sulphuric acid 11-38%, nitric acid 12-20%, water 11-37% to which could be added salts of Cr, Al, Ni, Zn, Fe, Co, Mn.
29. J. Herenguel., French Pat. 984,863 (1951). Typical compositions covered by this patent have been referred to in Table 3-10 above, and their use has been described by Herenguel and Segond.[75] Copper and nickel additions are also covered.
30. Kynalbrite Solution." This was used in the U.K. for some time and later withdrawn. It contained phosphoric acid 78% (vol), nitric acid 11%, sulphuric acid 11% and ferrous sulphate 0.8%. It was operated at 95-100°C for 15-60 seconds, removing 15-30 μm (0.6-1.2 mil) of metal per minute. Above 115°C it gave a bright satin-etched finish.
31. Minbrite Holdings Ltd., Brit. Pat. 907,787 (1960). This contained phosphoric acid 46-49%, sulphuric acid 30-33% and nitric acid 20-22% to which could be added boric acid, hydrochloric acid, titanium or vanadium salts.
32. V.A.Dmitriev *et al.*, Russian Pat. 194,512 (1965). This is very similar to the R5 process in specifying sulphuric/phosphoric/nitric acid mixtures with about 5 g/l copper nitrate. Dmitriev and Belyaeva[78] have published a study of this type of solution using phosphoric acid 780 ml, sulphuric acid 150 ml, nitric acid 70 ml and copper nitrate 10g at 96-98°C.
33. C.C.Cohn and S.L.Cohn., Brit. Pat. 1,145,881 (1966); U.S. Pat. 3,425,881 (1965). The preferred composition range cited is phosphoric acid 42.5-48%, sulphuric acid 21-25%, nitric acid 3.0-3.6%, water 15.6-19%, aluminium 1.45-3.1%, copper 0.0116-0.0126%.
34. Albright and Wilson., Brit. Pat. 1,088,287 (1967). Phosphoric acid and phosphoric-sulphuric acid solutions in which nitric acid is replaced by 0.5-20% (wt) of cupric nitrate. The benefit of the cupric nitrate in comparison with nitric acid is significant reduction of the nitrogen oxide fumes produced.
35. Albright and Wilson., Brit. Pat. 1,183,319 (1967). This improvement applies to both phosphoric/nitric acid brighteners and the ternary mixtures and covers the use of phosphoric acids upgraded by treatment with hexavalent chromium compounds.

36. Nippon Chem. Ind. Co., Japanese Pat. 4161 (1968). This covers the addition of a carbamate to either a phosphoric/nitric or a phosphoric/nitric/sulphuric acid brightening solution.
37. C.C.Cohn and S.L.Cohn., Brit. Pat. 1,258,171 (1971) and U.S. Pat. 3,575,747 (1971). This covers the addition of 0.01-1.5% (wt) phosphoric acid + sulphuric acid so that the combined acids comprise 60-95% (wt), and also 0.25-10% (wt) nitric acid and 5-40% (wt) water.
38. S.A.Vernal., Brit. Pat. 675,444 (1950). This claims the addition of a weak acid which forms a complex with the phosphoric acid, in particular molybdic, iodic, vanadic, boric or tungstic acid. Hydrochloric acid can also be added and the fluidity may be increased with concentrated acetic acid. An example is phosphoric acid 27%, sulphuric acid 65%, nitric acid 5%, boric acid 2%, hydrochloric acid 1%.
39. S.A.Vernal., Swiss Pat. 273,961 (1951);Brit. Pat. 687,774 (1953). Acetic acid also forms an addition to this bath as well as a salt of either Ni, Co, Cu, Zn, Cr or Al. An example is phosphoric acid 50%, sulphuric acid 25%, nitric acid 6.5%, acetic acid 6%, water 1.5%, nickel nitrate 3%.
40. I.S.M.L., Italian Pat. 474,228 (1952). Acetic acid forms an addition to the brightening bath, but 0.5-50 g/l of a metal acetate may also be used, the metal being Al, Fe, Cr, Cu, Ni or Ag.
41. T.R.Rooney, Albright and Wilson Ltd., Brit. Pat. 1,565,349 (1980); U.S. Pat. 4,116,699 (1978); U.S.Pat. 4,251,384 (1981). Phosphoric-sulphuric-nitric acid solution containing dissolved copper and additionally an etch inhibitor which is an aromatic ring compound such as benztriazole, benzofuroxan or benzthiazole. The purpose of the aromatic additive is *to* reduce transfer etch problems.
42. Hoechst A.G., West German Pat. DT 813870 (1978). Addition of 0.01-10% (wt) of ammonium polyphosphate to nitric acid containing brightening solution to reduce problems of nitrogen oxide fumes.
43. Nippon M. and T. Co., Japanese Pat. JAJ 80125277 (1979). Phosphoric-sulphuric-nitric acid bath containing triazine derivative (such as benzoguanamine) and copper ions.

Other phosphoric acid processes

Alternative agents for adding *to* phosphoric acid in the place of nitric acid have been proposed. These are not many in number and neither have they ever had much industrial use.

44. Aluminum Company of America., U.S. Pat. 2,613,141 (1949; publd. 1952). The brightener consists essentially of 60-80% phosphoric acid, 1-10% hydrogen peroxide and 15-35% water referred to the total weight of the components.

45. Vereinigte Aluminium Werke., Austrian Pat. 168,882 (1951). This is very similar to the Alcoa process in adding 30 ml of hydrogen peroxide to 1 litre of phosphoric acid, to be used at 90-100°C.
46. J.E. Jumer., U.S. Pat. 3,041,227 (1958). The solution contains not less than 75% phosphoric acid to which an addition is made of 0.001-1% of a fluorinated lower aliphatic carboxylic acid or a fluorinated benzoic acid.
47. Deinert and Co., French Pat. 1,210,571 (1959). This suggests the use of chlorates, bromates or iodates as alternative oxidizing agents to nitric acid in a phosphoric acid/sulphuric acid chemical polishing bath.
48. C.C. Cohn., French Pat. 1,370,525 (1963). To a bath containing phosphoric acid 40-98%, balance water is added 0.0005-1% of an insoluble oily substance in dispersion, the mixture being used at over 66°C.

Sulphuric-nitric acid process

49. British Aluminium Co. Ltd., Brit. Pat. 1, 582,134 (1980). A phosphoric acid free brightener based on 50-80% (vol) sulphuric acid and 20-50% (vol) nitric acid with 0-300 g/l boric acid, 10-16 g/l molybdic acid, 1-20 g/l copper sulphate and 5-60 g/l ammonium metavanadate.

Modern baths in current use

Most important of the phosphoric-nitric-sulphuric acid type solutions are the modifications developed by Vernet[79,80,81] which came into extensive use under the names Alupol IV and V. These are stated to contain:

	Alupol IV	*Alupol V*
phosphoric acid (d. 1.7)	53% (wt)	77.5% (wt)
sulphuric acid (d. 1.84)	41.6	15.5
fuming nitric acid (d. 1.52)	4.5	6.0
boric acid	0.4	0.5
copper nitrate	0.5	0.5

The Alupol V bath also contains 0.05% (wt) carboxy-methyl cellulose as a wetting agent. The solutions are operated at approximately 100°C for 1-4 minutes and remove an average of 3.8 μm (0.15 mil) per minute. The reflectivities obtained by Alupol IV treatment, before and after anodizing, are given in Table 3-17. Lattey and Neunzig[81] have studied the effect of metal composition on reflectivity in detail.

Phosbrite 159,[82] a solution basically similar to Alupol V, developed in Britain. established itself as the most widely-used solution in this country. This patented[8'] solution requires special plant techniques for its preparation. Its main merit is that it will give a maximum degree of smoothing as well as of specular reflectivity on a very wide range of materials, from super-purity aluminium and its magnesium

alloys, through commercial quality aluminium, to Duralumin and other heavy-metal containing alloys which do not contain a high proportion of silicon. It is thus particularly attractive to polishing contractors where materials of different (and often unknown) composition are to be brightened.

Talysurf diagrams of an aluminium surface before and after chemical polishing by this process are shown in Fig. 3-19.[84] The successful use of chemical brightening solutions of the phosphoric/nitric acid type, either with or without sulphuric acid, depends on maintaining the nitric acid concentration within the range where the maximum brightening action occurs, and since nitric acid becomes depleted during use this calls for frequent additions.

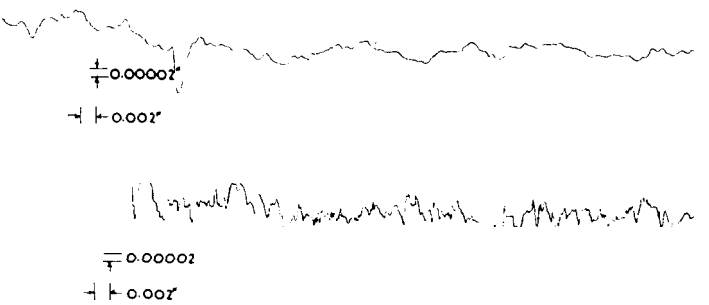


Fig. 3-19. Talysurf diagram of aluminium before and after polishing in Phosbrite 159 bath. Magnification: vertical 5000 times, horizontal 100 times[84]

Fig. 3-20 indicates some typical results that have been obtained with Phosbrite 159 solution when brightening a 99.8% base, 1% magnesium alloy (BT2) which shows that the specular reflectivity range is between 50 and 80% for that particular solution.[85] The graph also includes results for an alloy containing 4.5% Zn, 1% Mg and 0.25% Cu and this illustrates well the versatility of phosphoric acid brighteners. The measurement of specular reflectivity was made with the modified gloss head of BS 6161: Part 12: 1987 Method E, which is an instrument designed to be very sensitive to departures from a mirror finish

Fig. 3-21 records the loss of weight from BT2 sheet material when immersed in Phosbrite 159 with varying nitric acid contents. It will be seen that the maximum brightening effect takes place when the rate of attack is at its lowest, and presumably when a solid oxide coating has formed most effectively over the surface.[85]

The bath is maintained by the addition of nitric acid and its life is long as it will tolerate up to 100 g/l aluminium (corresponding to the treatment of 3-5 m^2/litre (150-250 sq.ft./gallon) before exhaustion. However the recommended operating range is shown in Fig. 3-22. As, due to the high viscosity of the phosphoric acid, the drag-out is fairly high (estimated at 1.6 ml/dm^2 (15 ml/sq.ft.) of flat surface), even partial discarding of the solution is often unnecessary under normal conditions.

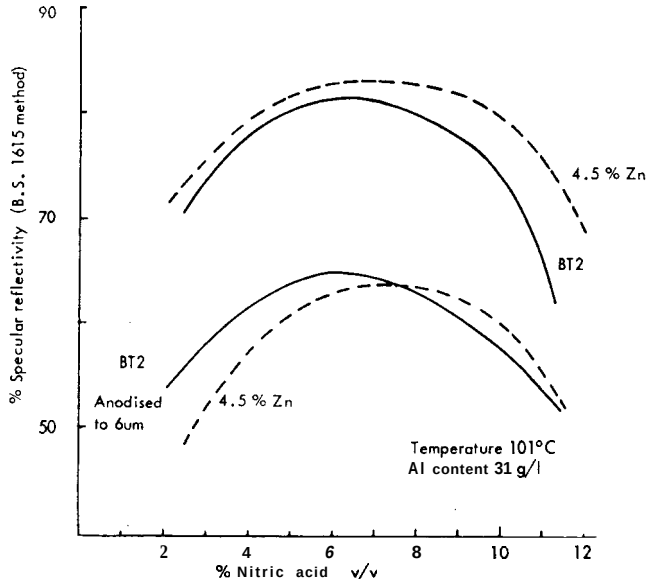


Fig. 3-20. Specular reflectivity of BT2 and 4.5% Zn alloy sheet brightened in Phosbrite 159

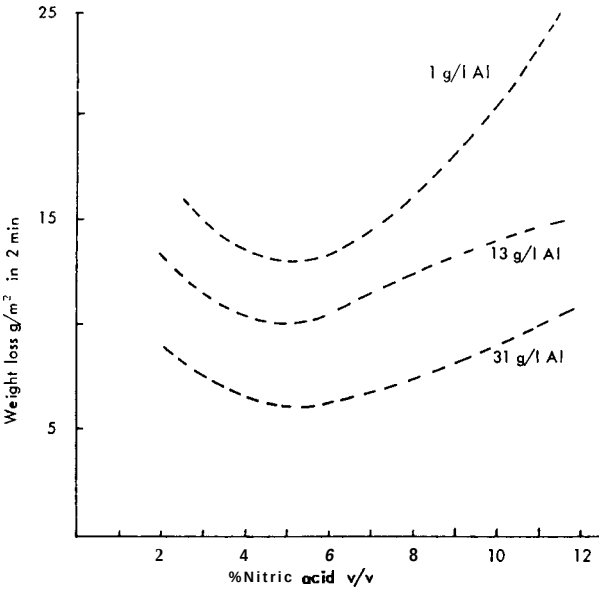


Fig. 3-21. Weight loss of BT2 sheet in Phosbrite 159 at various nitric acid concentrations

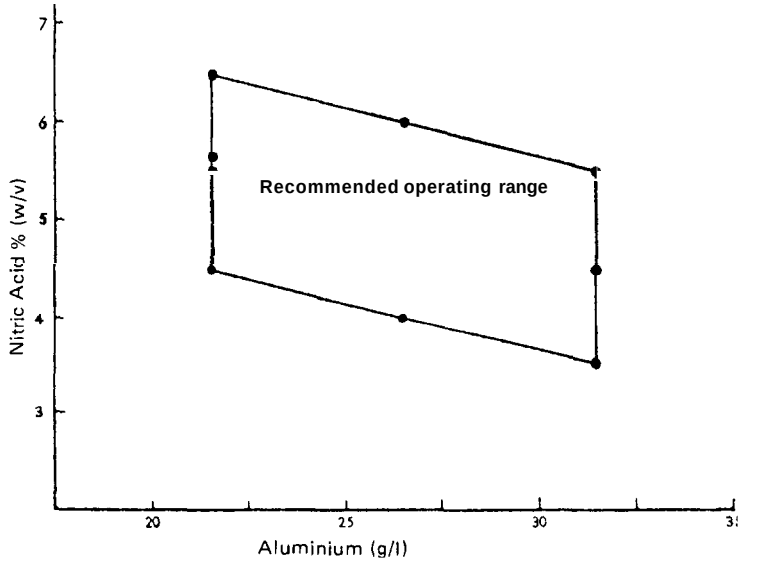


Fig. 3-22. Recommended nitric acid range for various aluminium contents of Phosbrite 159

[Courtesy Albright & Wilson Ltd.]

The surface of aluminium is not etched readily by the cooling solution when removed from the bath so transfer times are not too critical. However with the high cost of phosphoric acid there has been a tendency to increase the proportion of sulphuric acid, and this makes transfer etching more likely. In addition the higher strength Al-Zn-Mg alloys are sensitive to transfer problems, particularly with automatic plants where short transfer times are often not possible. Arrowsmith, Clifford and Crowther[86] studied the transfer etch problem in detail and confirmed that it became more prevalent as the sulphuric acid level was increased. However they showed that, rather than being an etching process, the dulling is caused by precipitation of aluminium sulphate on the surface during transfer. Addition of corrosion inhibitors such as benzotriazole reduce this effect[83] and Arrowsmith shows that the nitrated benzotriazole present in the brightening solution is adsorbed on the deposited copper, inhibiting the cathodic evolution of hydrogen. This in turn slows the rate of dissolution of aluminium and delays precipitation of aluminium sulphate.

Chemical polishing with the Phosbrite 159bath has been shown to improve the light fastness of colour anodized aluminium, probably because less light is absorbed as compared with the untreated surface. In case of any extended delay between chemical polishing and anodizing, the parts may be stored in 2% sodium chromate solution to avoid corrosion.

Similar in composition to the Swiss Alupol processes are the Alubril solutions developed by the Istituto Sperimentale di Metalli Leggieri (Milan). Two compositions of this class given by Hug[87] are detailed in Table 3-11. The second bath is less strongly acid and requires a longer treatment time but correspondingly less gas is evolved.

TABLE 3-11

Alubril chemical polishing solutions

	I	*II*
Phosphoric acid	48% (wt)	86% (wt)
Nitric acid	31	–
Sulphuric acid	21	–
Sodium sulphate	–	4
Sodium nitrate	–	9
Copper acetate (optional)	1	
Cadmium nitrate	–	1
Temperature °C	110	100-130
Time	15-60 sec	up to 10 mm

Solution control

Chemical control of phosphoric acid brighteners is relatively simple and an experienced operator can tell immediately whether additions are needed by studying the type of effervescence, the rate at which it declines during the first few seconds of immersion, and by looking for the characteristic nitrous oxide fumes. **A** very rapid test can also be carried out in a beaker by adding sufficient nitric acid to a small amount to raise the level by 1, 2 or 3% and seeing whether the brightening action improves.

It is normally sufficient to determine nitric acid concentration by chemical analysis and an electronic instrument has been developed in the U.S.A. for continuous monitoring of the nitric acid concentration in larger chemical polishing plant." The concentrations of phosphoric acid and other constituents are less frequently determined.

The following analytical methods have been described:

Nitric acid

One needs to be clear about the conventions employed for describing nitric acid concentration and what they mean. The common practice in the finishing

industry in Britain is for 1% nitric acid to mean 1 ml of pure concentrated acid of relative density 1.42 in 100 ml of brightening solution. Since nitric acid in this form contains 70% by weight of the compound HNO_3, then 1% v/v also indicates a content of 0.994 g of $HN0_3$ in 100 ml, or approximately 1% w/v. Therefore, for nitric acid 1% v/v = 1% w/v.

When percentage by weight is referred to, as is common in the U.S.A., 1% means 1 g of the compound HNO_3 in 100 g of brightening solution, and since the density of this may be about 1.75 the volume of solution involved is only 57.1 ml. Therefore 1% w/w = 1.75% v/v approximately, the exact relation depending on the density of the brightener used. Nitric acid will generally be measured by volume and added to a known volume so that v/v is generally the most useful value to know.

First method. volumetric[7']

Make up 25 ml of the cool chemical polishing solution to 250 ml with distilled water in a volumetric flask and pipette 10 ml into a 250 ml flask. Add 15 ml water from a measuring cylinder, 15 ml standard ferrous sulphate solution from a pipette and 20 ml conc. sulphuric acid from a measuring cylinder. Prepare a blank in the same way without the chemical polishing solution. Heat both sample and blank to boiling for 3 minutes to expel NO, fumes. Cool and add 75 ml water to each flask and mlx well. Add two drops of Ferroin indicator solution and titrate against potassium dichromate solution to the bright blue-green end point. Then:

$$\text{Nitric acid (\% wt)} = \frac{(\text{ml blank titration} - \text{ml sample titration}) \times 0.00315 \times 100}{\text{specific gravity of solution}}$$

$$\text{Nitric acid (\% vol)} = (\text{ml blank titration} - \text{ml sample titration}) \times 0.00315 \times 100$$

The second designation is mostly used in Britain.

Reagents:

(1) The **standard dichromate solution** is prepared by dissolving 7.356 g K, Cr, **O,** in water and diluting to 1 litre.

(2) Make the **ferrous sulphate solution** by adding 20 drops 50% H_2SO_4 (348 ml conc. acid plus 600 ml water) to 100 ml water. Add 55 g $FeSO_4.7H_20$ and 20g NaCl while stirring. Warm to dissolve. Allow to cool. Dilute to 1 litre with 50% H_2SO_4 solution.

(3) **Ferroin indicator.** Available at 0.01 M solution or add 0.595 g o-phenanthroline monohydrate to 90 ml warm water, stir until dissolved and add 0.28 g $FeSO_4.7H_20$. Stir and dilute to 100 ml.

Second method: Albright and Wilson Phosbrite 159 method.[88]

Reagents (All should be of A.R. quality)

(1) Ferrous sulphate solution. Cautiously add 50 nil conc. sulphuric acid to about 700 ml distilled water. Cool, add approximately 250 g ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2 0$) and stir until dissolved. Make up to 1 litre, mix well and transfer to a clean dry bottle with a well-fitting stopper. Standardise monthly.

(2) Phosphoric acid (sp. gr. 1.75).

(3) Standard phosphoric-nitric acid solution. Using a burette or a safety pipette, add 25 ml 60% nitric acid to a 500 ml volumetric flask, and make up to the mark with phosphoric acid (1.75 sp. gr.). Mix well, keep stirred and store in a cool place. Make up freshly every three months.

Standardisation of ferrous sulphate solution

Accurately measure 5.0 ml standard phosphoric-nitric acid solution into a dry 250 ml beaker: a conical flask must not be used for this titration. A burette with a wide aperture is the most convenient way of measuring the viscous solution. Add 100 ml phosphoric acid. Stir and heat to 40-45°C. Titrate with ferrous sulphate solution until the first permanent golden brown colour is formed. Towards the end of the titration there will be numerous gas bubbles dispersed throughout the solution and reddish-brown fumes are evolved. At the end-point no fumes are evolved.

Let A ml be the volume of ferrous sulphate used

Procedure

Measure 5.0 ml Phosbrite solution into a clean dry 250 ml beaker, and proceed as described in the previous section, titrating against ferrous sulphate.

Let B ml be the volume of ferrous sulphate used.

Calculation

% by volume of 60% nitric acid in the Phosbrite is $\frac{B}{A} \times 5$

Third method: with Monsanto nitric acid nieter

The Monsanto Chemical Co. Monsanto nitric acid meter'' is both a recording and a control instrument which incorporates a potentiometer circuit and can be set either for intermittent addition of nitric acid, a red light showing when this is required, or for continuous addition.

Copper

Copper concentration in phosphoric acid based solutions may be determined electrolytically. 400 g of solution are diluted with 700 ml water in a beaker, stirred and heated to 50-60°C. Electrolyse, using a weighted platinum gauze cathode which extends 6 mm (0.25 inch) above the solution level, at 50–60°C and 3.0-3.5 volts. After 2 hours add 25 ml water and continue to electrolyse for a further 10 minutes. When no more copper is deposited (visible on the freshly-immersed top of the gauze), slowly raise the electrode, rinse in water, rinse in acetone, dry in air for 15 minutes and reweigh.

$$\%\ (\text{wt})\ \text{Cu} = \frac{100 \times (\text{wt of gauze} + \text{copper}) - \text{wt of gauze}}{\text{weight of sample}}$$

Aluminium phosphate, free phosphoric acid and water[73] (phosphoric acid-nitric acid bath only) (Monsanto method)

The following method of calculating the aluminium phosphate and free phosphoric acid concentrations from the specific gravity and viscosity of the solution has been developed for simple phosphoric-nitric acid solutions and is not directly applicable to solutions containing other major constituents. Cool 300-400 ml of the solution, which should have a nitric acid concentration of 2.8-3.2% (wt), and determine the viscosity and relative density (see below). Then read off the aluminium phosphate and free phosphoric acid concentrations from the graphs in Figs. 3-23, 3-24 and 3-25. Water content is obtained by difference.

Relative density

The relative density (specific gravity) of a chemical polishing solution is measured at a definite temperature (e.g. 35°C) on a filtered solution by means of a hydrometer. Mohler[89] has studied specific gravity as a single control factor for bright dip baths and this is a simple and practical method, but it must be closely related to the specific brightening solution being used.

Viscosity

The following method has been developed at Monsanto Chemical Co.[73]

Place 30 ml of the solution in a 100 ml beaker. Invert the viscometer (Ostwald-Fenske) over the solution. Place the tip under the liquid level and suck the liquid into the tube by means of the suction bulb. Remove the tube and invert so that the sample runs towards the large bulb of the viscometer. Release suction, place viscometer in a 30°C water bath. After 5 minutes force the liquid back up the small bore tube to fill the lower small bulb and partially fill the upper small bulb.

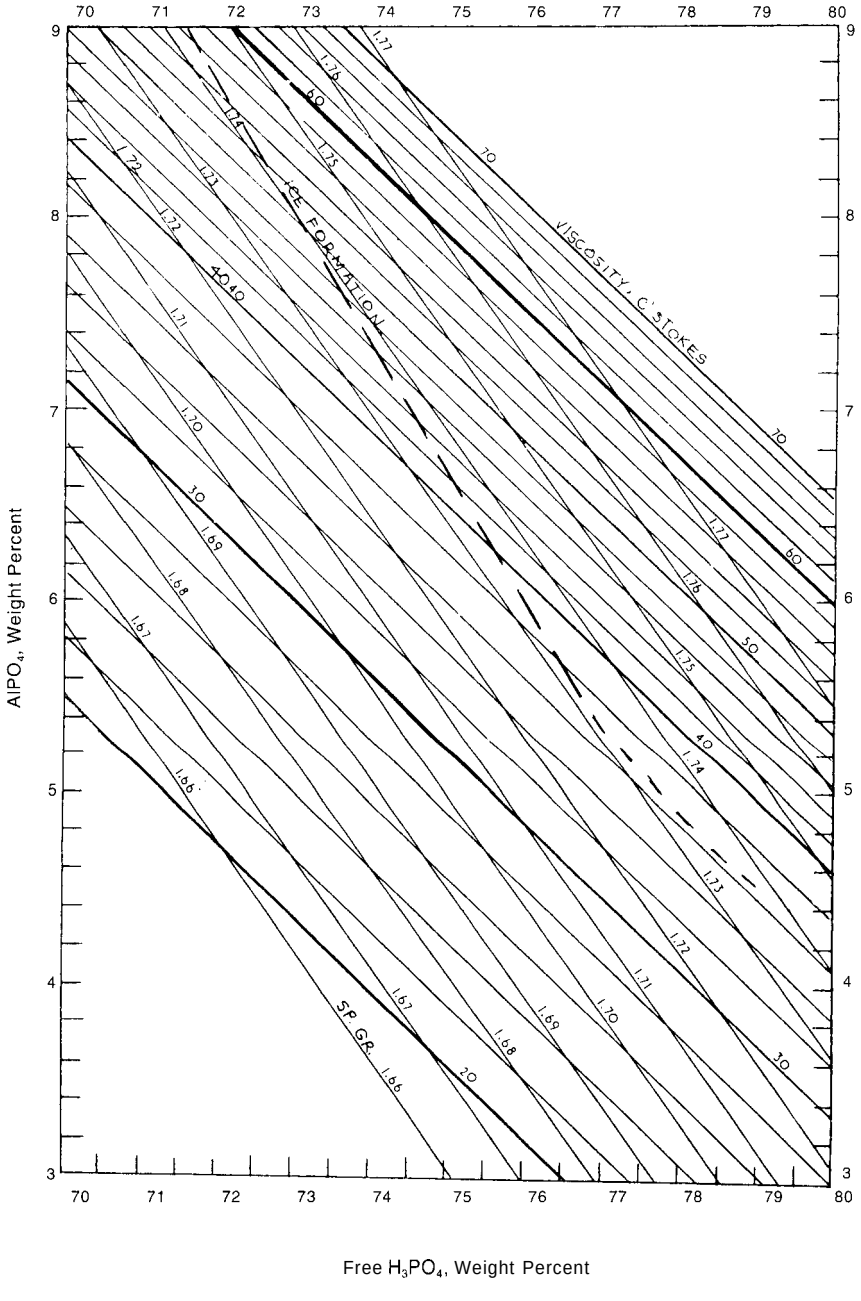


Fig. 3-23. $AlPO_4$ and free H_3PO_4 concentrations (% wt) from viscosity and specific gravity of phosphoric-nitric acid solutions in the composition range HNO_3 2.8-3.2%(wt.), AlPO, 3-9%, H_3PO_4 70-80%[73]

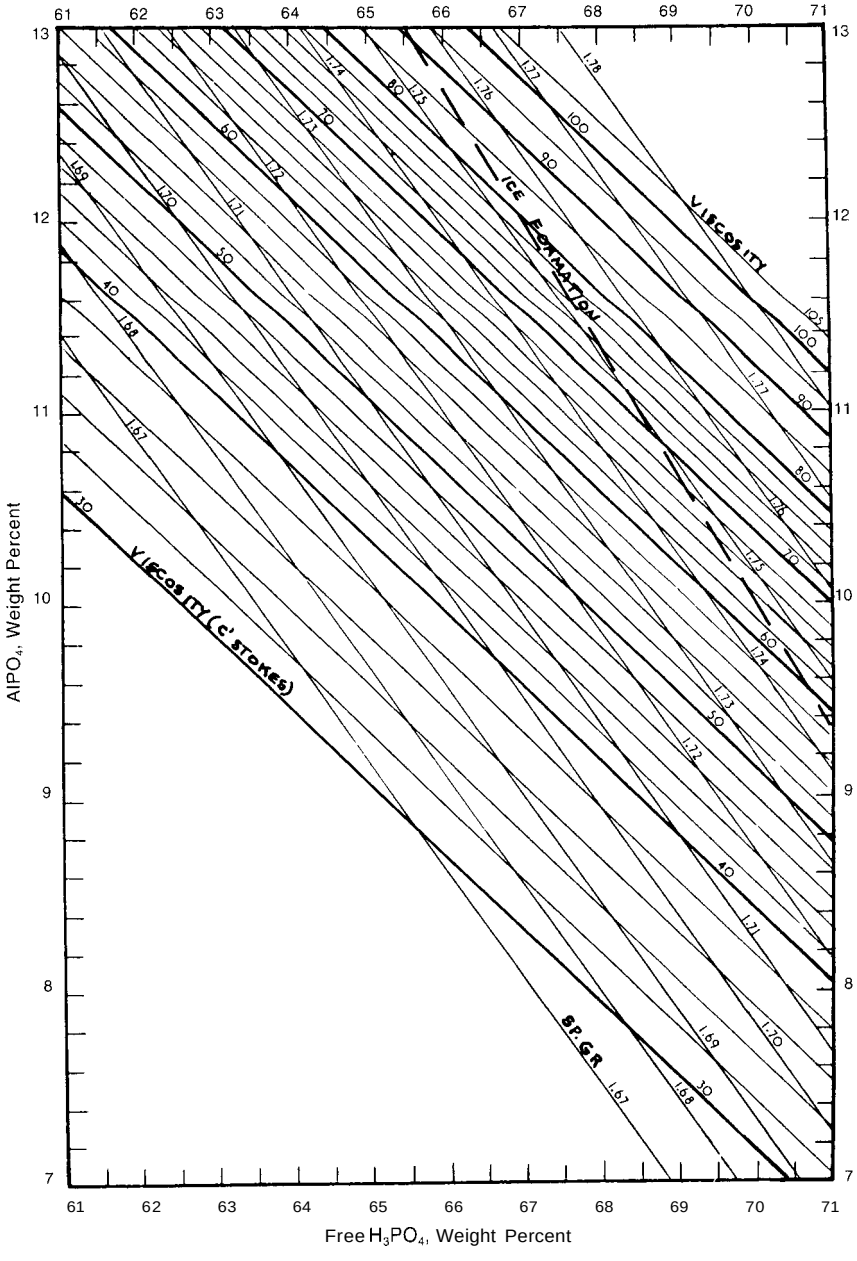


Fig. 3-24. $AlPO_4$ and free H_3PO_4 concentrations (% wt) from viscosity and specific gravity of phosphoric-nitric acid solutions in the composition range HNO_3 2.8-3.2%(wt.), $AlPO_4$ 7-13%, H_3PO_4 61-71%[73]

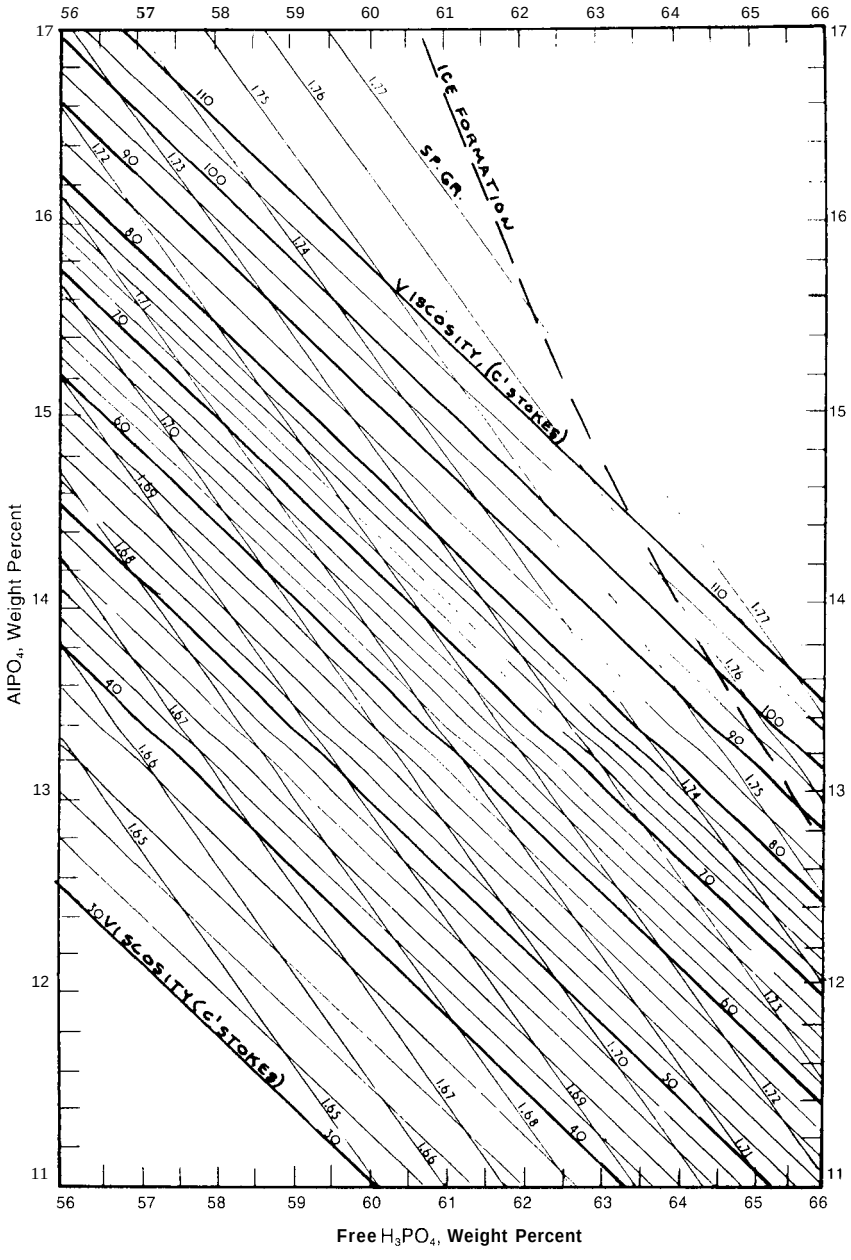


Fig. 3-25. AlPO, and free H_3PO_4 concentrations (% wt) from viscosity and specific gravity of phosphoric-nitric acid solutions in the composition range HNO_3 2.8-3.2%(wt.), AlPO, 11-17%, H_3PO_4 55-66%[73]

Remove the suction bulb and take the time on a stopwatch between the meniscus of the liquid reaching the upper and lower marks on the tube. Take the average of several readings. Multiply the flow time by the tube factor to obtain the viscosity in centistokes. The tube factor is obtained by dividing the viscosity of phosphoric acid by the time of flow in seconds on a calibration run using pure phosphoric acid of known viscosity:

	(% wt)	*relative density*	*viscosity (cs)*
Phosphoric acid	75	1.57	10.0
	80	1.62	13.0
	85	1.68	18.9
	90	1.74	27.0

Aluminium content of phosphoric-sulphuric-nitric acid baths (Albright and Wilson method")

Principle of the method

An aliquot of diluted Phosbrite solution is taken and buffered, and EDTA added in excess to produce the aluminium-EDTA complex. The excess of uncomplexed EDTA is taken up by titrating with copper sulphate solution. Sodium fluoride is then added in sufficient quantity to decompose the aluminium-EDTA complex, and the released EDTA is further titrated with standard copper sulphate. This last titration is a measure of the aluminium concentration.

Reagents (All should be of A.R. quality)

(1) Copper sulphate solution. 0.1 molar. Dissolve 24.97 g copper sulphate pentahydrate in distilled water; add one or two spots of concentrated sulphuric acid, transfer to a I-litre volumetric flask and dilute to the mark with distilled water. Mix well.

(2) EDTA solution. 0.1 molar. Dissolve 37.2 g EDTA disodium salt dihydrate in distilled water. Transfer to a 1-litre volumetric flask and dilute to the mark with distilled water. Mix well.

(3) PAN indicator solution. 0.1% w/v. Dissolve 0.1 g 1-(2-pyridyl-azo)-2-naphthol (PAN) in 100 ml industrial methylated spirits.

(4) Buffer solution. Dissolve 500 g ammonium acetate in distilled water; add 20 ml glacial acetic acid and dilute to 1 litre with distilled water.

(5) Sodium fluoride.

Procedure

Measure 5.0 ml Phosbrite from a burette into a 100-ml standard flask, allowing time for complete drainage. Dilute almost to the mark with distilled water and mix thoroughly. Cool and top up to the mark and again mix.

Pipette 20 ml of the prepared solution into a 600-ml beaker and dilute to 350-400 ml. Add 200 ml buffer solution and 25 ml 0.1M EDTA. Warm and add 1.0 ml PAN indicator. Bring to the boil, cool to 60°C and titrate with standardised 0.1M copper sulphate solution. The end point is shown by a sharp change from green to deep blue.

Add 1-2 g sodium fluoride to decompose the aluminium-EDTA complex and again bring to the boil. Cool to 60°C and titrate the liberated EDTA with 0.1M copper sulphate to the blue end-point. Call this titration 'z' ml. Then 'z' × 5.4 = g/l aluminium.

Other Processes

Nitric acid — fluoride-type solutions

A number of solutions have been developed which contain nitric acid in rather more dilute solution with the addition of fluorides and sometimes other compounds.

While high-purity aluminium will dissolve readily in M hydrofluoric acid, if ammonium fluoride is added to the solution a white salt film, believed to be AlF_3,[90] is formed until passivation is almost complete at a concentration corresponding to M ammonium bifluoride (57 g/l NH_4NF_2). Addition of nitric acid liberates hydrofluoric acid from the solution and will tend to suppress the passivation film. It is possible to brighten aluminium in HF-NH_4F-$NiCl_2$ solution.[91]

E.W. process

Best known of the nitric acid – fluoride processes is the E.W. (Erftwerk) process which was widely used in Germany. This process was characterised by a high dissolution rate 25-50 μm (1-2 mil) per minute and was applicable only to high-purity aluminium and the high-purity aluminium-magnesium or aluminium-magnesium-silicon alloys which have been developed particularly for electrolytic and chemical polishing.

A typical solution composition is:[92]

nitric acid	13% (wt)
ammonium bifluoride	16
lead nitrate	0.02

and the solution was normally operated at 55-75°C for 15-20 seconds. The best results are obtained on high-purity aluminium and certain of its alloys with

magnesium on which the reflectivity obtained by this process is extremely high (approximately 90%) and drops only slightly on anodizing. The E.W. solution is generally exhausted after treating 0.25-0.35 m^2/litre (13-18 sq ft per gallon) but can be regenerated by addition of 12-14 g/l hydrofluoric acid, i.e., approximately 39-46 gm hydrofluoric acid per m^2 of metal treated (or approximately 3.6-4.2 gm per sq ft).[93]

A modified solution composition was later introduced which contained approximately 1% dextrin. This reduces the previous high rate of attack by approximately 50% — a substantial improvement in practice. Peek and Brace[94] found the addition of dextrin also increased the bright range, though the process was not generally suitable for conventional material of 99.85% purity or lower. The M.E.W. modified Erftwerk bath has been used in Germany with success on the solution heat-treated Erftal-type aluminium-magnesium alloys which are based on 99.9% aluminium and contain a maximum of 0.04% silicon and 0.035% iron.

An example of a similar modification containing gum arabic, used for chemical polishing 99.8-99.95% aluminium and its alloys, contains:[95]

nitric acid	135 ml
hydrofluoric acid	33 ml
ammonium fluoride (lead-free)	50 g
lead nitrate	0.3 g
gum arabic	30 g

This solution is used at 65-85°C for 40-60 seconds and is regenerated with a solution containing 15 ml hydrofluoric acid and 0.08 g lead nitrate per litre of brightening bath after every 1%-2 sq ft (14-19 dm^2) of aluminium treated.

Simmons[96] claimed a similar process using nitric acid 0.05-5.0 ml, hydrofluoric acid 0.5-10 ml, with a lead compound such as lead carbonate 0.05-5 g/l, and a primary aromatic amine (aniline, o-toluidine or 2:6-xylidine).

Control of the E. W. process

In the Erftwerk chemical polishing solution, free acid can be determined by titration with N caustic soda using bromothymol blue as indicator,[97] while ammonia and nitrate are determined by distillation from a strongly alkaline solution into excess standard acid, the nitrate being reduced by Devarda's alloy. Fluoride is then obtained by difference.

In practice, the ammonia concentration must be fairly closely maintained for the best results particularly when the aluminium contains more than 0.002% iron.[97] For this reason fluoride, which is lost progressively during use, is sometimes made good by additions of hydrofluoric acid solution rather than ammonium bifluoride.

Operating the E. W. process

The sequence for the E.W. process was usually as follows:

Pre-polish (120-150 grade emery) if required
Trichloroethylene (or alkali) degrease
Etch in dilute sodium hydroxide solution for 15-30 secs if required. (Alternative to pre-polishing)
Rinse
Chemical polish
Rinse
Passivating dip (0.06% chromic acid)
Rinse
Anodize in sulphuric acid
Rinse
Seal in boiling water

The passivating dip after the E.W. process was particularly useful where the work stood for some time before being anodized. Besides chromic acid, a solution of 20 g/l sodium chromate could also be used for up to 100 minutes.[98]

The effect of metal composition on response to Erftwerk treatment has been investigated by Cooke and Spooner[99] in a detailed series of experiments in which they also covered the behaviour of R5 type brightening baths with and without copper additions, and the effects of subsequent anodizing. The specular reflectance values given in Table 3-12 are measurements made after Erftwerk brightening only using a Photovolt Glossmeter, Model 660M, calibrated against a chromium plate standard, and represent only a few of the results obtained. They confirm that silicon and manganese up to 0.20% and titanium up to 0.03% have very little effect, while copper has little effect up to 0.05% but becomes seriously detrimental after that, and iron is progressively and seriously damaging over 0.008%.

TABLE 3-12

Effect of Cu, Fe, Si, Mn and Ti on the response to Erftwerk treatment of Alcan X-1086 Base Aluminium[99]

Impurity content%	*specular reflectance values %*				
	Cu	*Fe*	*Si*	*Mn*	*Ti*
0.001	–	–	84	83	82
0.003	87	84	–	–	–
0.008	–	80	*85*	–	–
0.03	84	–	–	–	80
0.05	85	–	83	81	–
0.10	10	***55***	–	82	–
0.20	–	*26*	80	80	–

Kaiser bright dipping procedures

Somewhat similar but more dilute solutions were introduced by Kaiser Aluminum of America as bright dipping procedures prior to anodizing. They were designed for the treatment of a wide variety of alloys and the solutions are covered by a numerous group of patents taken out by Kaiser and General Motors. The bath contained essentially nitric acid and ammonium bifluoride, a heavy metal such as copper, silver, platinum or gold, chromic acid and an organic material which might be sugar or glycerol.[100,101,102]

Typical solution compositions are listed in Table 3-13, and these were used for *0.5-5.0* minutes at *90-96°C* after the new bath had first remained for not less than 30 minutes at the operating temperature.

TABLE 3-13

Kaiser and General Motors Solutions

	Kaiser solution[100]	*General Motors solution*[101]
Nitric acid	2.25% (wt)	3.75% (wt)
Ammonium bifluoride	0.6	0.65
Chromic acid	0.6	0.65
Glycerol	0.6	–
Ethylene glycol	–	0.6
Copper nitrate	0.05	0.0025

The active ingredients were nitric acid and hydrofluoric acid from the acid fluoride, and as in the case of the Erftwerk solution these must be maintained at the correct ratio or etching will result. Chromic acid improves the levelling action, sugar or glycerol keep the chromium in the trivalent state, while copper assists in the formation of the polishing film and promotes uniformity of action. Bath operation depends on keeping an accurate record of the area processed and making regular maintenance additions of nitric acid, ammonium bifluoride and sugar.

These solutions did not provide the high specular surfaces which could be obtained with Erftwerk or Phosbrite. A brightening action takes place on the first 8-10 sq ft per gallon processed (16-20 dm^2/l) after which the bath exerts a good cleaning action preparatory for anodizing on a further 200-300 sq ft.

One of the Kaiser patents (U.S. 2,640,806)proposed connecting the work to a more noble metal, such as gold or platinum, immersed in the solution to improve brightening. (Other similar suggestions have included the use of graphite electrodes in phosphoric-nitric acid baths[51] and in pure nitric acid.'')

Alkaline solutions

A number of alkaline chemical polishing baths has been proposed but these are now little used in industry as the finish is no better than that obtained by the acid solutions and the rate of attack is apt to be violent. Among these are the Alupol I bath based on caustic soda-sodium nitrate and containing smaller amounts of sodium nitrite and sodium phosphate.

In a rather specialised process for polishing television screens in Russia, wet blasting was followed by an alkaline chemical polishing process and sulphuric acid anodizing.""

Alkaline chemical polishing solutions were generally employed in stainless steel tanks, the minimum tank capacity recommended being 50 gallons (220 litres) to avoid rapid alteration in composition during operations. Baskets are of stainless steel.

The following is a summary of the alkaline chemical polishing solutions that have been proposed:

1. General Electric Co., U.S. Pat. 2,671,717 (1950). The aluminium is immersed in a hot aqueous solution of sodium or potassium hydroxide 1-6 oz/gal (6-40 g/l) and sodium or potassium nitrate 2-6 oz/gal (12-40 g/l) used at 60-80°C.
2. British Thomson Houston, Brit. Pat. 718,024 (1951). This is identical to the above patent, the preferred concentrations being given as sodium hydroxide 1.75-3 oz/gal (11-20 g/l) with sodium nitrate or nitrite 3-3.75 oz/gal (20-24 g/l).
3. Diversey Corp., U.S. Pat. 2,673,143 (1951). The polishing bath contains caustic soda, sodium gluconate and an oxidizing agent.
4. Alluminio Lombardo Premontese. Ital. Pat. 464,725 (1951). The composition of this proposed bath is caustic soda 20 parts, sodium nitrate 20 parts, sodium silicate 3 parts, water 5 parts used at 120°C.
5. S.A.Vernal, Swiss Pat. 272,273 (1951). This was the Alupol I bath containing the following mixture to be used at 80-140°C:

sodium hydroxide	300-600 gm
trisodium phosphate	100.300
sodium nitrate	200-300
water	100-300
heavy metal	1-5

   The metal could be Ni, Cu, Co, Zn, Sb, Pb or **As** added as sulphate or nitrate.
6. Takahashi J., Japanese Pat. JAJ 80113883 (1979). Bath consisting of 10 parts sodium hydroxide, 2-4 parts sodium nitrate or nitrite, 4-8 parts sodium phosphate, 0-0.008 parts copper nitrate, 0-0.08 parts sodium fluoride, 40-60 parts water, 10-20 parts sodium carbonate.

6. NOTES ON PLANT OPERATION

Before electropolishing or chemical polishing, components are usually given an alkaline clean (see Chapter 4). Immediately after alkaline cleaning, they should be rinsed and then immediately transferred into the polishing bath since dust particles and the like may settle on the surface. If not immediately placed in the polishing solution, they may need to be re-rinsed, or even re-cleaned, to ensure uniformity of polishing.

Venn and Bartowski[104] have found means of avoiding the "rainbow" coloration sometimes found after chemical brightening. Components are rinsed in chromate and then dipped in sodiun bi-sulphite solution which reduces Cr(VI) to Cr(III). Items so treated can be coloured, if desired, using a metal salt solution and alternating current, and then dyed using an azo dye.

Jigging

Where jigs are employed, e.g., in an anodizing sequence, these may be of aluminium alloy, preferably of similar material to that treated, although it must be realised that these dissolve in the solution and, apart from the cost of replacement, the aluminium dissolved from them shortens the life of the solution. Table 3-14 gives the rate of metal removal from various aluminium rack materials in the Brytal and Erftwerk chemical polishing baths. Values for the newly-prepared normal Erftwerk solution and the dextrin inhibited modification (M.E.W.) are lower by about 33% and 50% respectively.

While stop-offs are available, the trend is towards all titanium jigs (Fig. 3-26), as although they are more expensive their life is very long. Further details of jigs for chemical polishing-anodizing sequences are given on page 573.

Mechanical agitation is to be recommended to avoid streaking by gas bubbles. Depending upon the volume of work treated, the bath may need to be cooled even at the high temperatures employed, due to the considerable heat evolution of the reaction. Thermostatic control is advisable.

TABLE 3-14

Metal removal from aluminium alloy racks in the Brytal and Erftwerk baths

Process	*Time (min)*	*CD. (amp/sq ft)*	***Temp.*** *(°C)*	*Metal removal (g/sq ft)*			
				99%Al	*AI-7%Mg*	*Ai-Mg-Si*	*AI-12%Si*
Brytal	10	50	78-80	30	10	25	20
Erftwerk	0.25	–	58-60	55	45	85	30

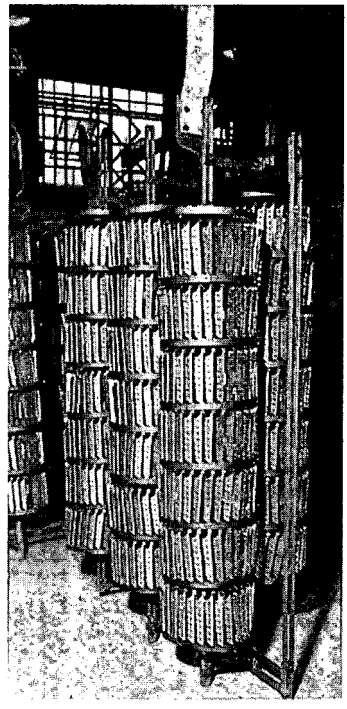


Fig. 3-26. Components jigged for bright anodizing on titanium jigs
[Courtesy Norman Radcliffe Ltd.]

Fume extraction

Efficient fume extraction should be provided. Meyer and Brown[57] recommend a total air flow of 60-75 m^3 per second per m^2 of surface (200-250 cu ft/ sq ft of surface). Another recommendation[77] gives a rate of air flow of 0.6 m (2 ft) per second across the top of the solution.

A simple design for fume extraction plant and scrubbing tower for a tank of 1150 litres (250 gal) capacity is shown in Fig. 3-27.

In practice, the hot rinsing tank and chemical polishing bath may be put under the same hood. The fan capacity is calculated from the dimensions of the tank, and the ducting, which should be of stainless steel or plastic material, should be kept as short as possible, i.e. 3.5-4.5 m (say 12-15 ft) is normally sufficient. The scrubbing tower should work with a circulation of about 570 litres (125 gal) of 2% caustic soda solution per minute. The outer casing may be constructed of acid resistant brick or steel, in which case care is required to keep the solution alkaline at all times. The unit in Fig. 3-27 is 120 cm (4 ft) in diameter and is packed to a depth of 225 cm (7 ft 6 in) with 5 cm by 5 cm (2 in by 2 in) stone rings supported on a grid carrying courses of stacked rings. The caustic soda solution is circulated by the pump

and is distributed over the top of the tower by a perforated distribution plate, a spray eliminator being inserted in the gas outlet line. 2.5 cm (1 in) diameter stand pipes 30 cm (12 in) high may be inserted into the top of the enclosed tower to deal with excess liquor accumulating in case of blockage in the distribution plant. If a longer unit is required, i.e. a tower diameter of above 135 cm (4 ft 6 in), the depth of the caustic soda solution above the heater plate should be at least 1/6 of the tower diameter. Efficiencies of 97% absorption are stated to be obtained with plant such as this.

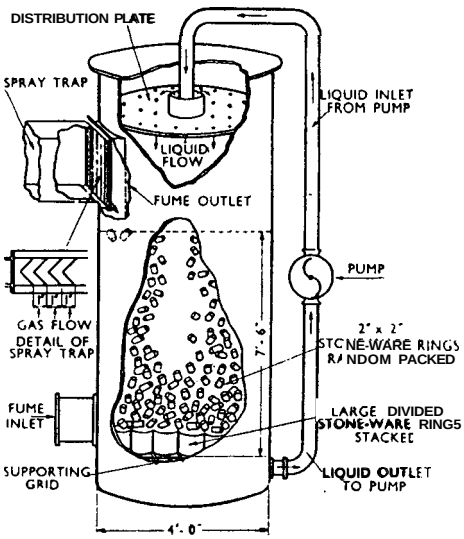


Fig. *3-27.* Simple design of fume extraction plant and scrubbing tower

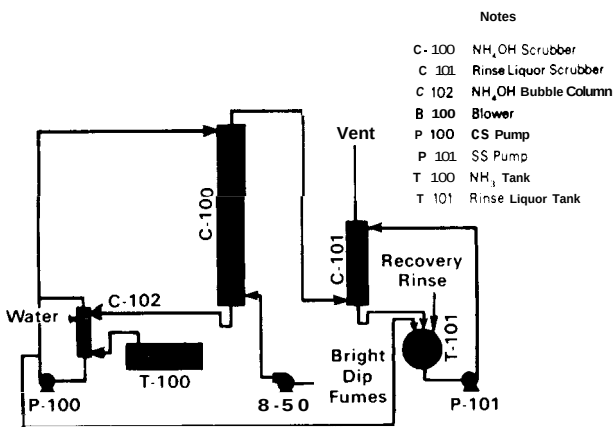


Fig. *3-28.* Process flow diagram

Another system has been developed which uses an ammonium hydroxide-phosphoric acid two column scrubbing system,[106] and this is shown diagrammatically in Fig. 3-28. This unit is designed to remove 90% of the NO_x fumes at a typical gas flow rate of 15,000 cfm. It is claimed to be more efficient than conventional systems.

Practical methods of fume suppression have been suggested by White[107] who advocates ways of reducing the amount of nitrogen oxides generated as well as use of scrubbing systems. Use of minimum nitric acid level, temperature and processing time are all suggested together with rapid transfer from the brightener to the rinse. Use of a fume suppressant (diammonium phosphate) is advisable, and the elimination of organic contamination (e.g. from oil or polishing compound) in the brightener is important.

Attempts have also been made to deal with the fume problem by chemical means. Thus fuming in phosphoric-nitric acid solutions is claimed to be inhibited by additions of urea and similar compounds.'''''''In phosphoric-sulphuric-nitric acid processes addition of cupric nitrate rather than free nitric acid gives a significant reduction of nitrogen oxide fumes,[83] as does the addition of ammonium polyphosphates.[108]

Regeneration and impurity control

By the nature of the chemical polishing process, the life of the solution is 'finite', i.e., when the metal concentration reaches a certain limiting value, the solution ceases to operate satisfactorily. Chemical polishing solutions vary widely in the amount of metal they can tolerate, normally between 30 and 300 gm per litre.

Neither chemical precipitation nor electrodeposition can be used for extracting dissolved metal from chemical polishing solutions. In many baths, of course, the metal concentration is kept at a harmless level by normal drag-out. While this ensures that the bath can be worked continuously, it is a wasteful procedure. Frequently drag-out is insufficient to keep the aluminium concentration down and the solution has to be replaced. In one American company using a 2,000 gallon tank, for example, the aluminium concentration was kept at 40 g/l by replacing 500 gallons solution per week although 2,500 gallons concentrated acid were added to replace drag-out. A method of estimating chemical consumption and costs from the rate of dissolution has been described by Nelson.[74]

Some progress has been made in the use of ion-exchange for this purpose. Ledford and Jumer''[1] describe plant designed using a sulphonated polystyrene divinyl benzene 8% cross-linked resin which has been claimed to work successfully in the U.S.A. It is rarely possible, however, to treat the concentrated chemical polishing solution by ion-exchange as, while reasonable loadings of the resin may be obtained in solutions of 40-60% phosphoric acid (a weak acid), the upper limit for strong acids is generally below 1% for nitric and hydrochloric acid and 1-2%

for sulphuric acid. In order to render the process economic, it is necessary to dilute the chemical polishing bath by from 6:1-9:1, with an evaporation stage following ion-exchange. As a result, regeneration plant that has been built so far is both large and expensive and is generally suitable only for large installations using chemical polishing baths of 2,000 gallons or more.

While aluminium is the most important 'impurity' in chemical polishing solution, others carried over from the previous operating stages, or derived from alloying constituents in the material which is polished, may be harmful. Approximate maximum limits in the phosphoric acid-type solutions are: iron 5 gm per litre; lead 2 gm per litre; hydrochloric acid 1 ml/l; hydrofluoric acid 3 ml/l.

Organic impurities derived from polishing compositions, for example, do not generally affect the finish when present in concentrations lower than 1 g/l, but may increase gassing or foaming. Activated carbon treatment (3 lb per 100 gallons) followed by filtration is useful in cases of serious contamination.

Drag-out and drain time

The volume of drag-out from the phosphoric acid-type of polishing bath is primarily dependent on the drain time, as seen from Table 3-15.[72] This rate is very slow, not only because of the high viscosity of the solution but also because gassing continues for some time after the part is removed from the solution and causes a movement in the opposite direction to drainage."

TABLE 3-15

Volume of drag-out on a flat panel from a phosphoric-nitric acid chemical polishing bath[72]

Drain time (sec)	*Average drag-out*	
	(ml/ft²)	*(ml/dm²)*
1	16.2	1.7
2	9.0	0.97
5	*1.2*	*0.11*
10	5.4	0.58
20	4.8	0.52

In the phosphoric-nitric acid solution the limiting drain-time which will not detract significantly from the results achieved by the polishing process is somewhere near 10 seconds, which is satisfactory for the recovery of solution from flat surfaces; on more complex shapes drainage may of course be appreciably slower.

Even under ideal conditions however, experience shows that a practical lower limit for drag-out, which cannot be decreased by extending the drain time, is

equivalent to the removal of a film of solution between 38 and 50 μm (1.5 and 2.0 mil) thick. Drag-out therefore represents a high phosphoric acid loss and several methods of recovery of this acid have been suggested.

Rushton[112] has discussed the question of recovering the phosphoric acid with a vacuum evaporation plant, either after the removal of aluminium by ion exchange procedures when the acid can be re-used, or without its removal when the acid can be sold at 75-85% concentration for fertiliser manufacture. Nelson[111] has outlined a counter-flow rinse procedure which concentrates the rinse up to 30% acid and he concludes that for most plants the direct sale of acid at this strength is the most attractive proposition because of its low capital requirement, negligible operating costs and high return on investment. Newton describes several systems ranging from complex units removing aluminium by ion-exchange followed by evaporation to achieve a concentrated acid yield, to a much simpler system involving storage and evaporation only.

As indicated previously, direct ion-exchange of the brightening bath is rarely possible, but recovery of the phosphoric acid from the rinses can be economically attractive. Eco-Tec, with their special reciprocating flow ion exchange systems, which involve fine resins, short resin beds and short cycle times, recommend phosphoric acid recovery systems.[111]

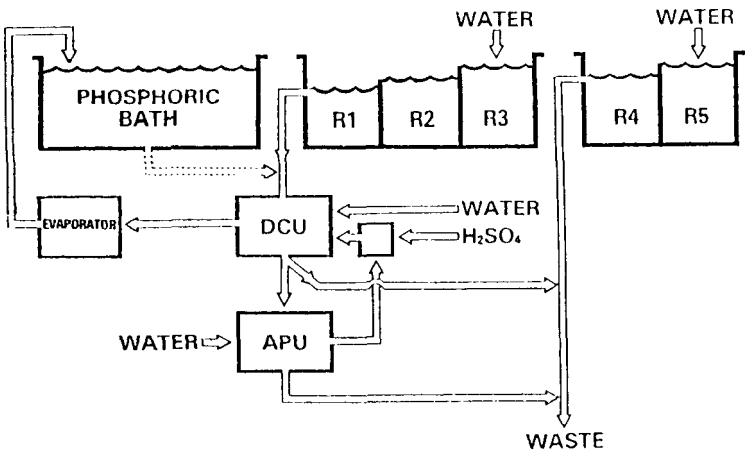


Fig. 3-29. Phosphoric acid recovery system

A typical system is shown in Fig. 3-29. A counterflow rinse system ensures recovery of as much acid as possible and this passes through a decationiser unit (DCU) which removes the aluminium. An acid purification unit (APU) recycles the sulphuric acid used to regenerate the DCU and an evaporator concentrates the

phosphoric acid before returning to the processing baths. Such a system is claimed to give a large saving per year on a plant consuming 500 tons/year of phosphoric acid.

Anodizing after chemical polishing

As distinct from some of the electropolishing processes employing either alkaline, fluoborate or chromate-containing acid electropolishing solutions, the chemical polishing processes do not confer any protection. On the contrary, it appears rather that chemically polished aluminium may be substantially more free from oxides after rinsing, and it is advisable that the surface be protected by anodizing or some other surface treatment as soon as possible. Stronger colours are reported after anodizing and dyeing which is presumably due to the greater specular reflectivity of the chemically polished surface compared with a buffed one. If not anodized, adequate and quick rinsing and drying is required to prevent stains forming on the polishing surface.

Greater decrease in reflectivity with anodizing time after chemical polishing of high purity aluminium was demonstated by Tajima.[116] On the other hand, the best resistance to abrasion and corrosion is to some extent incompatible with the maximum brightness, the former being better after anodizing at low acid concentrations and high voltages while reflectivity is higher after anodizing at high acid concentrations and lower voltages. This is discussed in more detail in Chapter 12.

7. REFLECTIVITY, BASIS METAL AND ANODIC COATING THICKNESS

The success of the electrolytic and chemical polishing processes is greatly dependent on the composition and structure of the basis metal. In general, the best results are achieved with fine grain material of a pure metal or single phase alloy.

The effect of impurities in commercial aluminium and of alloying constituents on the reflectivity of electropolished and chemically polished surfaces varies greatly and few hard and fast rules can be given. Generally it appears, however, that the processes involving the formation of anodic coatings of substantial thickness are the most sensitive to impurities. This is often due less to the action of the polishing bath than to the effect of the impurities and alloying constituents on the transparency of the anodic oxide film.

It is different in the case of heterogeneous or multiphase alloys, e.g., alloys which have been solution heat-treated and precipitation hardened. In such cases, the degree of finish will depend on the characteristics of the polishing bath itself. The achievement of a uniform smoothness depends on uniform attack, i.e., on the

degree to which such differences in potential are minimised by the overall resistance across the anolyte layer, and the character of the oxide film present in the polishing reaction. Generally, therefore, factors which lead to increase of thickness of the oxide film improve the finish; these include increase in current density, decrease in temperature, and in the case of chemical polishing, the concentration of oxidizing agents, i.e., undissociated nitric acid, hydrogen peroxide, etc.

Effect of metallurgical structure

As well as the composition, the metallurgical structure of the metal is of importance. A number of workers have found fine line markings with the appearance of subgrains on the surface of electropolished[117,118,119,120] and chemically polished aluminium. Their type and spacing is not normally a function of the internal structure of the metal[121,122,123] but varies with the electrolyte and polishing conditions. On the other hand, materials of fine grain size often give greatly superior finishes in comparison with metals of coarser crystal structure. The latter produce an effect usually observable as orange-peel, and is doubtless due to the fact that the suppression of etching is only partial. Again, the nearer conditions are to passivation, the better the finish. On the other hand, grain-size itself is only one factor in determining brightness after chemical polishing. Thus, increasing the titanium content from nil to 0.2% reduces grain-size but detracts from the brightness of aluminium-magnesium or aluminium-magnesium-copper alloys after chemical polishing and anodizing.[124]

According to this theory, it might be expected that heat-treatment and cold working would have a marked influence on the finish obtained after electrolytic polishing. Any treatments which produce fine grain size or distort and break up the crystal lattice short of producing fissures should be beneficial. It is indeed found in practice that cold working does improve the surface in this way.[125] Work carried out by Herenguel and Segond[75] showed that aluminium-magnesium alloys containing 3 or 5% magnesium and produced from 99.995% aluminium are particularly suitable for electropolishing. In order to obtain a fine grain size they are cooled as rapidly as possible from the melt, and this helps also in the dispersion of Al_2Mg_3. In deep drawing, these authors found that deformation should be between 25% and 200%-300% each stage. Below 25% the grain tends to coarsen, while above the range orientation may take place. Reheating at 325-425°C should be as rapid as possible, i.e., it should be carried out in a salt bath or continuous conveyorised furnace.

The brightness of aluminium-magnesium alloys based on 99.9% pure aluminium depends to a considerable extent on the structure of the cast material. Ginsberg and Neunzig[126] report that it is favoured by a homogeneous globular structure which remains fine grained even after homogenising heat treatment for 2-10 hours. In certain cases, even relatively coarse grained material will polish well if the metal has been extensively cold-worked to break up the crystal lattice in the

surface layer, though this will obviously apply only if the amount of metal dissolved in the polishing process is relatively small. It has been found possible in this way to obtain good results by barrel polishing followed by chemical polishing to remove up to 10 μm (0.4 mil) of metal.

Maier and Schwall[127] indicate the importance of high temperature homogenisation with 99.85% Al based magnesium alloys. Homogenisation at 620°C affects the iron and silicon bearing impurities, converting many of the constituents to $FeAl_3$ rather than the Al-Fe-Si compounds. The former have been shown by Guminski, Sheasby and Lamb,[128] in a study of the effect of a range of common intermetallics on chemical brightening, to be very much less damaging to surface quality in both chemical brightening and anodizing, as they react at a similar rate to the aluminium matrix. In contrast constituents such as Mg, Si react very much faster than the matrix, leading to pitting; this is the cause of the dulling effect often seen on bright trim alloys when Mg, Si is incorrectly precipitated.

Effect of alloy composition

As stated, the chemical composition of the metal is of great importance though various polishing processes react differently in this respect. As a general rule it may be said that the best results are always obtained with high purity aluminium or one of the high-purity-base alloys described below. Some processes, notably the Brytal and Alzak fluoborate and the Erftwerk chemical processes, cannot normally be used on material of a lower grade of purity.

It has been found that the iron content of high-purity aluminium has a significant effect on the specular reflectivity of aluminium brightened by the Erftwerk process, particularly when the metal has been annealed at lower temperatures. There is a considerable drop in reflectivity if more than 0.032% iron is present, and in Germany this observation was made use of in the production of Erftal[46,129] and Remiral primary aluminium ingot of about 99.9% purity which contained less than 0.035% iron and 0.04% silicon and which brightened almost as well in the Erftwerk bath as super-purity material.

At the same time, in 99.9% Al-0.5% Mg alloy, even 0.025-0.035% silicon or iron produce a significant deterioration in the brightness, e.g., due to the presence of Mg_2Si,[126] after chemical polishing in the Erftwerk bath and anodizing, unless the alloy is homogenized, e.g., at 590-600°C for 1 hour.[130] A further reduction in purity of the aluminium to 99.85% causes a significant drop in the reflectivity after Erftwerk chemical polishing.

Copper levels greater than 0.06% cause a serious drop in reflectivity after Erftwerk treatment but silicon and manganese up to 0.3% have no effect, neither has titanium up to 0.03%, while zinc may be present at 0.3% or more provided that it is in solid solution.[46]

The phosphoric-nitric acid based solutions on the other hand will achieve good results on commercial quality aluminium and many wrought alloys, usually,

however, with a fairly pronounced loss in reflectivity after anodizing. American experience in producing bright anodized aluminium for motor trim has also been mainly with alloys of this type, examples of which are shown in Table 3-16. On the other hand, experience with bright anodizing has shown that results almost equivalent to those produced on super-purity metal are obtained on 99.7-99.85% materials which have come into use for this purpose.

TABLE 3-16

Bright anodizing alloys
(Values are in wt.%)

Country	*Designation*	*Magnesium*	*Other Constituents (range or maxima)*
British	BTR 1	0.3-0.8	Fe 0.10, Si 0.10. Cu 0.15, Mn 0.2, Ti *0.05*
(B.S.	BTR *2*	0.7-1.2	Fe 0.10, Si 0.10, Cu 0.15, Mn 0.3, Ti 0.05
4300/2/4)	BTR 6	0.4-0.8	Fe 0.15. Si *0.2-0.5*, Cu 0.20, Mn 0.05, Ti 0.05
German	A199.98R	–	Fe 0.006, Si 0.010, Cu 0.003, Zn 0.01, Ti 0.003
(DIN	Al 99.9	0.01	Fe 0.05, Si 0.06, Cu 0.01, Mn 0.01, Zn 0.04,
1712,			Ti 0.006
Part 3 &	A199.8	0.02	Fe 0.15, Si 0.15, Cu 0.03, Mn 0.02, Zn 0.06.
Part 1)			Ti 0.02
	A199.9 Mg 0.5	0.35-0.6	Fe 0.04, Si 0.06, Mn 0.03, Zn 0.04, Ti 0.01
	A199.9 Mg1	0.8-1.1	Fe 0.04, Si 0.06, Mn *0.03*, Zn 0.04, Ti 0.01
	A199.85 Mg0.5	0.30-0.6	Fe 0.08, Si 0.08, Mn 0.03, Zn 0.05, Ti 0.02
	Al 99.9 MgSi	0.35-0.7	Fe 0.04, Si 0.35-0.7, Cu 0.05-0.2, Mn 0.03.
			Zn 0.04, Ti 0.01
	Al 99.85 MgSi	0.35-0.7	Fe 0.08, Si 0.35-0.7, Cu 0.05-0.2, Mn 0.03,
			Zn 0.05, Ti 0.02
	Al 99.8 ZnMg	0.7-1.2	Fe 0.10, Si 0.10, Cu 0.20, Mn 0.05, Zn 3.8-4.6,
			Ti 0.02
French	A9 (1090A)	–	Fe + Si < 0.10
	A8 (1080A)	–	Fe + Si < 0.20
	A7(1070 A)	—	Fe + Si < 0.30
	A85GT (SiSQA)	1.3-1.7	Fe + Si < 0.15, Cu 0.10, Mn 0.03, Zn 0.10
American	5357	0.8-1.2	Fe 0.17, Si 0.12, Cu 0.2, Mn 0.15-0.45
(Aluminium	5457	0.8-1.2	Fe 0.10, Si 0.08, Cu 0.2, Mn 0.15-0.45
Association)	5557	0.4-0.8	Fe 0.12, Si 0.10, Cu 0.15, Mn 0.1-0.4
	6463	0.45-0.9	Fe 0.15, Si 0.2-0.6, Cu 0.2, Mn 0.05
	7016	0.8-1.4	Zn 4.0-5.0, Fe 0.12, Si 0.10, Cu 0.45-1.0,
			Mn 0.03
	7029	1.3-2.0	Zn 4.2-5.2, Fe 0.12, Si 0.10, Cu 0.5-0.9,
			Mn 0.30

TABLE 3-17

Reflectivity of chemically polished aluminium before and after anodizing to various coating thicknesses,

			Alupol IV process				*E. W. process (12 secs 54-56°C)*	
Basis metal	*Anodic coating thickness*		*Metal removed*	*Reflectivity Total*	*Specular (against Ag mirror)*	*Metal removed*	*Reflectivity Total*	*Specular*
	(mil)	*(μm)*	*(g/m²)*	*(%)*	*(%)*	*(g/m²)*	(%)	*(%)*
Al 99.5%	–	–		90.0	83.6		63.1	12.0
	0.08	2	26	79.0	61.0	64	55.8	9.0
	0.2	5		75.2	53.0		49.0	6.0
	0.4	10		66.7	41.0		38.7	4.5
	0.6	15		59.0	31.0		35.9	4.0
Al 99.8%	–	–		90.0	84.3		82.0	36.0
	0.08	2	29	82.8	73.0	71	77.2	34.0
	0.2	5		81.4	67.0		74.7	30.0
	0.4	10		79.5	58.0		73.3	26.5
	0.6	15		77.1	53.0		71.8	22.5
Al 99.99%	–	–		90.7	85.4		90.8	88.0
+ 2.0%Mg	0.08	2	18	85.4	80.8	61	86.4	82.5
	0.2	5		85.0	79.0		86.4	81.1
	0.4	10		84.7	75.4		86.2	78.8
	0.6	15		84.5	74.0		86.2	76.8
Al 99.99%	–	–		91.3	87.4		91.3	87.0
+ 2.0%Mg	0.08	2	31	85.9	79.1	67	86.4	79.5
	0.2	5		85.4	71.8		85.9	77.5
	0.4	10		84.0	68.6		85.7	76.0
	0.6	15		82.5	66.5		85.0	71.5

Table 3-16 gives some typical compositions of grades of aluminium and Al-Mg alloys which were developed for bright anodizing.

Table 3-17 shows the effect of the composition of the basis metal on reflectivity after chemical polishing and before and after anodizing.[131,132]

As a comparison, Table 3-18 gives corresponding values obtained by the Brytal process.

TABLE 3-18

Reflectivity of aluminium and its alloys electrobrightened by the Brytal process

Basis metal	*Reflectivity*	
	Total %	*Specular % (against silver mirror)*
Al (99.99%)	*86-87*	83-84
+ 0.5% Mg	*86-87*	83-84
+ *2.0%* Mg	85.5-86.5	82-83

As is seen, the highest reflectivity after anodizing for a coating thickness satisfactory for ensuring good protection against corrosion and wear, that is, approximately 10 μm (0.4 mil), is obtained on the high-purity metal and the high-purity aluminiurn-magnesium alloy with the nitric acid-ammonium bifluoride chemical polishing solution.

In practice a compromise has often been necessary between brightness and protective value of the coating. On many alloys a 10 μm (0.4 mil) coating is too thick to achieve the high finish required, e.g., for motor trim. For this reason B.S.1615:1987 gives a lower grade, AA5 (5 μm; 0.2 mil), which may be used for this purpose. On the other hand, the durability of thinner coatings may be poor. Thus, as a result of a survey undertaken in the U.S.A. by the Ford Motor Co., it was found necessary to increase anodic coating thickness on this Company's motor trim from 0.12 to 0.3 mil (3 μm to 7.5 μm). This has been made possible by the development of the 5457 and 5557 alloys, which can take the higher thickness of anodic coating without significant loss in image clarity.

In more recent times, experience gained with the various bright anodizing alloys has eased the problem considerably and a 10 μm coating produced on suitable material using a moderately high acid concentration and temperature and lower anodizing voltage will now ensure that good protection over a number of years can be obtained without loss in brightness, provided the coating is cleaned at regular intervals.

The effect of alloy composition on the reflectivity is very marked and the effect is rather different in the case of the phosphoric-nitric acid based Alupol solution and the nitric acid-ammonium bifluoride E.W. solution. In the former, the commercial purity aluminium can be chemically polished to a high reflectivity but this drops rapidly after anodizing. High-purity aluminium and its alloys, on the other hand, can be anodized after Alupol treatment with little loss of reflectivity. In the E.W. process (see Table 3-17) only high-purity aluminium and its alloys can be polished. In general, the 0.5% magnesium alloy has a slightly higher reflectivity

than the 2% magnesium alloy, but the latter possesses superior mechanical properties. In practice, a number of compositions based on high-purity aluminium and containing up to 5% magnesium are employed on the Continent.

In the U.K., these alloys came into use rather later, but most aluminium companies made high-purity based aluminium-magnesium alloys in sheet form, with heat-treatable high-purity aluminium-magnesium-silicon alloys used for extrusions. The reason for the magnesium or magnesium-silicon additions is to increase strength, typical AI-1%Mg bright trim alloys having mechanical properties equivalent to 3003 (Al-1¼%Mn).

The interest in materials of much greater strength for car bumper applications led *to* the development of high-purity **based aluminium-zinc-magnesium-copper** alloys, particularly in North America.[133]

With high-purity aluminium, the grain size is of great importance as there is a tendency to grain growth. Grain size is a function of the deformation before annealing and of the annealing conditions themselves. It is important, therefore, to specify fine grain material and, if possible, a range of permissible grain sizes from the metal supplier. Table 3-19 shows the mechanical properties of some German high-purity alloys.

Annealing in manufacturing stages should be avoided where possible, but where it is essential, the temperature should be kept down to 250°C-350°C.

In general, trends both in the U.S.A. and in Britain have been towards the use of 99.7-99.85% aluminium which, chemically polished in phosphoric acid based solution, has proved to give an excellent and economical finish.

De-smutting after electropolishing or chemical polishing

Electropolishing and chemical polishing leave a fine particulate material on the surface of the metal – referred to as "smut". The composition of smut varies with the alloy and the polishing solutions. It usually consists of the oxides of the alloying metals, mainly aluminium oxide. Chromated acid solutions remove smut (see Chapter 4) but are environmentally undesirable. Schultz and Askin have developed a chromate-free solution based on 15-95 vol% nitric acid, 1-80 vol% acetic acid, 1-40 vol% total water and at least 35 g/l fluoride – preferably 135 g/l ammonium bifluoride. To remove more tenacious types of smut, the addition of 5-20 vol% phosphoric acid is recommended. De-smutting is carried out for 0.5 – 2 minutes at room temperature.

Reflectivity after anodizing

Apart from the reduction in specular reflectivity which results from the inclusion of foreign metals in the anodic oxide coating, anodizing of aluminium alloys containing heavy metals may also itself cause a roughening of the surface.[135] This is shown in Table 3-20.

TABLE 3-19

Mechanical properties of German high purity aluminium and Al-Mg alloys

Material	*Condition*	*Form*	*Ultimate tensile strength tons/sq.in*[1]	*Elastic limit tons/sq in*[1]	*Elongation (%)*	*Brinell hardness kg/sq mm*
High purity Al 99.99%	Annealed	All materials in sheet	2.5-3.8	1.0-1.5	60-40	13-18
	½H		4.4-5.6	1.9-4.4	15-8	18-25
	H		6.9-6.8	6.2-8.1	8-4	26-35
+ 0.5% Mg	Annealed	Rod, tube and wire	4.4-6.2	1.2-2.5	40-20	22-28
	½H		6.9-9.4	6.2-6.8	15-6	35-45
	H		10.0-12.0	9.5-11.2	6-2	40-50
+1% Mg	Annealed	Annealed and ½H	6.2-8.1	1.9-3.1	35-20	30-35
	½H	materials in	6.8-10.6	6.2-9.3	15-8	40-50
	H	extruded sections	11.2-15.6	10.0-13.1	6-2	50-60
+ 2% Mg	Annealed	Annealed and ½H	10.5-12.5	3.1-6.2	35-20	40-50
	½H	materials in	13.1-15.6	11.2-14.3	15-6	55-75
	H	extruded sections	15.6-21.8	15.0-20.0	5-2	70-85

[1] 1 ton/in^2 = 15.4443 MN/rn^2.

TABLE 3-20

Reflectivity of anodized aluminium of different purities[135]

Film thickness		99.99% purity Specular reflectivity			Total	99.8% purity Specular reflectivity			Total	99.5% purity Specular reflectivity			Total
mil	*μm*	B	A	O	T	B	A	O	T	B	A	O	T
0.08	2	90	87	88	90	88	68	83	89	75	50	70	86
0.2	5	90	87	88	90	88	*63*	85	88	*75*	*36*	64	84
0.4	10	90	86	88	89	88	58	85	87	75	26	61	81
0.6	15	90	85	88	88	88	53	85	86	75	21	57	77
0.8	20	90	84	80	88	88	57	85	84	75	15	53	73

All the samples were anodized in 7% (vol) sulphuric acid at 20-22°C and 10 amp/sq ft (1 A/dm^2). The specular reflectivity before and after anodizing is given in columns B and A respectively, while column O gives the specular reflectivity after stripping the anodic coating in chromic-phosphoric acid solution and thus shows the decrease in reflectivity due to the roughening effect of anodizing itself. It is seen that on super-purity metal and on 99.8% Al the roughening effect of anodizing plays no significant part, while on 99.5% material this effect contributes quite appreciably to the loss in reflectivity (difference between B and O) although the effect of impurities within the film itself (difference between A and O) is still the more important.

There is some evidence that particles of impurities between 0.3 and 0.5 μm in diameter have the most effect on specular reflectivity. Smaller particles seem to be too small compared with the wavelength of light to have any visible effect while larger ones will be few in number.

Anodizing conditions themselves may also exert a profound influence on the specular reflectivity. The influence of current density and temperature of the anodizing bath as well as of the acid concentration is shown in Table 3-21.

It can be seen that the highest reflectivity values are obtained at elevated temperatures, lower current densities and high acid concentration, which unfortunately are the conditions under which the coating is soft and least resistant to abrasion. As a result, where abrasion resistant coatings of good reflectivity are required, a compromise must be effected. The reasons for deterioration in brightness during anodizing have been studied by Cooke,[136] who showed that they were associated with the anodizing voltage used. He suggested that inert constituents, such as Al-Fe-Si compounds, Si, and Mn Al$_6$ have a higher conductivity than the matrix around them and therefore cause a local concentration of current; this results in the formation of what he called a 'conical asperity' beneath them. The growth of such an asperity is illustrated in Fig. 3-30.

TABLE 3-21

Effect of temperature, concentration and current density on specular reflectivity of anodized 99.7%Al-1%Mg alloy[135]

H, SO, concentration (v/v)	5%		20%	
Current density (amp/sq ft)	10	15	10	15
(A/dm^2)	1	1.5	1	1.5
Temperature (°C)	*Specular reflectivity* (%)			
10	21	14	37	25
15	31	19	44	34
20	43	27	50	43
25	51	40	53	50
30	56	52	56	55

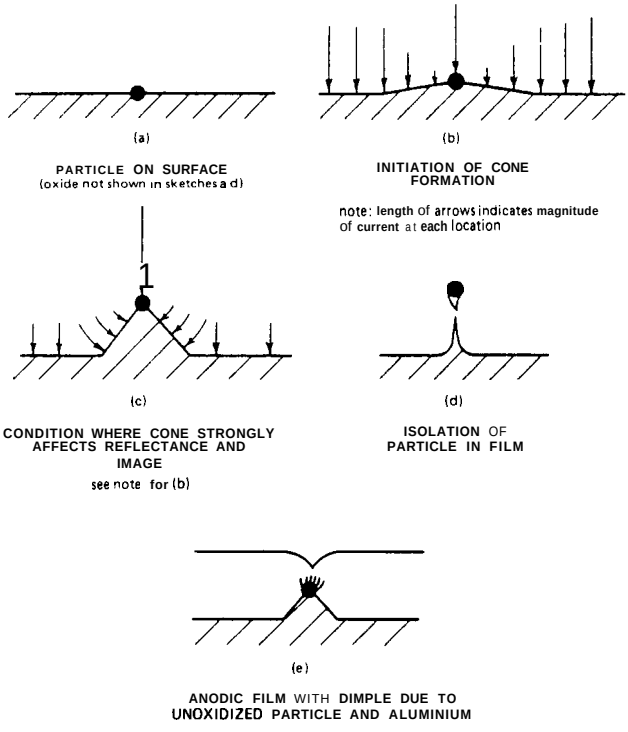


Fig. 3-30. Various stages of isolation of non-anodizing, semiconducting particles in an anodic film

It can grow to many times the size of the original particle and the extent to which it produces roughening at the aluminium/aluminium oxide interface is strongly dependent on the anodizing voltage used, roughening increasing considerably as voltage rises. Thus lower anodizing voltages, used as a result of higher acid concentrations and temperatures and lower current densities, are in large part responsible for the improved brightness obtained.

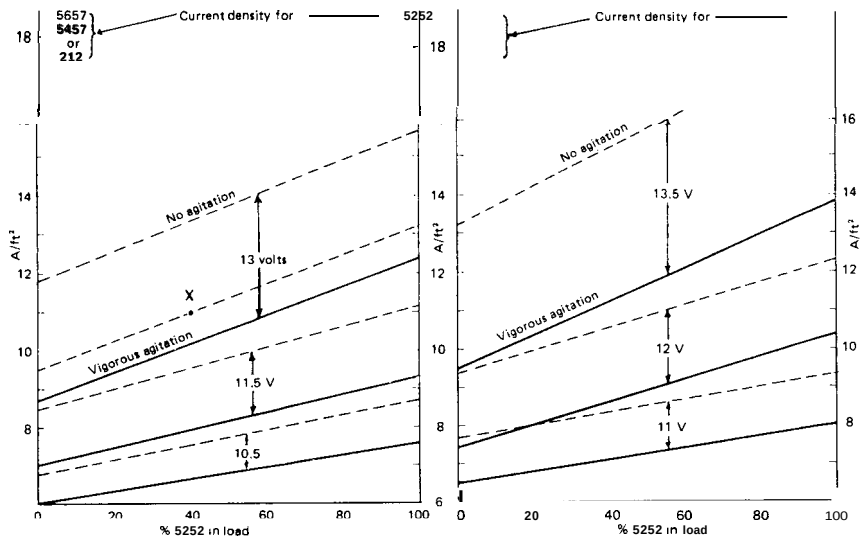


Fig. 3-31. Current density distribution in mixed loads of car trim alloys

Jackson and Thomas[137] have investigated similar effects, and stress the practical importance of anodizing conditions on specularity, particularly with mixtures of alloys present in a load. They looked at the effect of alloys containing different magnesium levels and recommended a maximum anodizing current density of 1.1 A/dm^2 (10 A/ft^2). Since such a current density is achieved at a significantly lower voltage with an Al-2%Mg alloy than with an A1-0.5%Mg alloy (about 2 V less), segregation of such materials during anodizing is recommended. The effect of increasing the proportion of the higher magnesium alloy (5252) in a load is shown in Fig. 3-31. If such a mixture of materials cannot be avoided, it is best to anodize the whole load at a relatively low current density of, say, 0.75 A/dm^2 (8 A/ft^2).

In order to obtain the optimum results from the bright anodizing sequence it may be necessary to remove the oxide formed in some electropolishing processes. For this purpose a short immersion in very dilute caustic soda or phosphoric-chromic acid solution has been used. Sulphamic acid has been stated to give the best results."'

Durability of the bright anodized finish

The durability of the electropolished or chemically polished finish has frequently proved superior to that of mechanically polished surfaces. Thus Batashov[139] observed that the loss of reflectivity of electropolished aluminium after 7 days exposure to 3% sodium chloride solution was only *3%* compared with 15% on mechanically polished specimens. This by itself does not permit the inference that the corrosion resistance is improved by electropolishing, for similar results obtained by Jacquet[140] on brass immersed in both acid and alkaline solutions showed that lower loss in reflectivity on electropolished material may well be accompanied by a higher loss in weight. What it does show is that the metal is removed more uniformly from the electropolished surface. On the other hand, there is no doubt that on aluminium at least, the corrosion resistance of electropolished, or chemically polished, metal is generally superior to that of mechanically polished material, partly due no doubt to the nature of the oxide film, but also possibly because of a reduction in the potential difference between grain boundaries and the grains.""

More surprisingly, perhaps, the effect of electropolishing on the corrosion resistance of aluminium is also noticeable after anodizing (see Table *3-22).* In this instance, in which the reflectors were electropolished in phosphoric acid-butyl alcohol or perchloric acid-glycerol solution,"' the improvement over the mechanically polished surfaces may be seen. In general the results shown in Table *3-22* confirm service experience, in which electropolished and anodized aluminium reflectors have been shown to have markedly better durability than reflectors made of other materials.

TABLE 3-22

Change in reflectivity after:
A. 56 days humidity test at 40°C, 94-98% relative humidity;
B. 30 days intermittent salt spray (5 min. in 2 hours), 3% NaCl, 35°C[10]

Reflector	*As finished*	*Loss of rejlectivity after test A*	*Loss of reflectivity after test B*
1. Cu, plated with 0.6 mil (15 pm) tin-nickel	46.4	–	2.2
2. Cu, plated with 0.6 mil (15 pm) nickel	62.4	1.7	7.0
3. Cu, plated with 0.6 mil (15 pm) nickel + 0.04 mil (1 μm) chromium	63.5	–	3.0
4. Reflectal, mechanically polished	79.6	12.5	14.5
5. Reflectal, electropolished in H_3PO_4-butyl alcohol, 30 V, 10 min.	92.0	6.2	7.6
6. As 5, then anodized in 20% H_2SO_4, 12 V, 5 min	90.5	3.9	4.9
7. Vacuum deposited aluminium	90.5	4.5	19.3

8. APPLICATIONS

The chemical and electrochemical brightening processes are of considerable importance to the metal finishing industry, and, in addition to their original use on holloware, jewellery, fountain pens, razor parts, etc., they are widely used for finishing trim components, particularly for domestic appliances and automotive applications (Figs. 3-32 and 3-33). There are increasing numbers of applications in high value added electronic components especially for computers and data storage devices.

In the automotive field, in particular, bright anodized aluminium has been subjected to many competitive pressures. Thus in the 1960s it was itself replacing the established material, which was then chromium plated steel, on the basis of higher corrosion resistance, lower production cost and better process control. Components such as grilles, headlamp bezels and window trim were usually bright anodized aluminium, and in a few cases, notably the Triumph Vitesse and many Volvo models, even the bumpers were anodized aluminium. The Vitesse bumper was essentially a decorative component, being made from a high-purity based Al-Mg-Si extrusion alloy, but the Volvo bumpers were more functional, using high strength, but high-purity based, Al-Zn-Mg alloy extrusions.

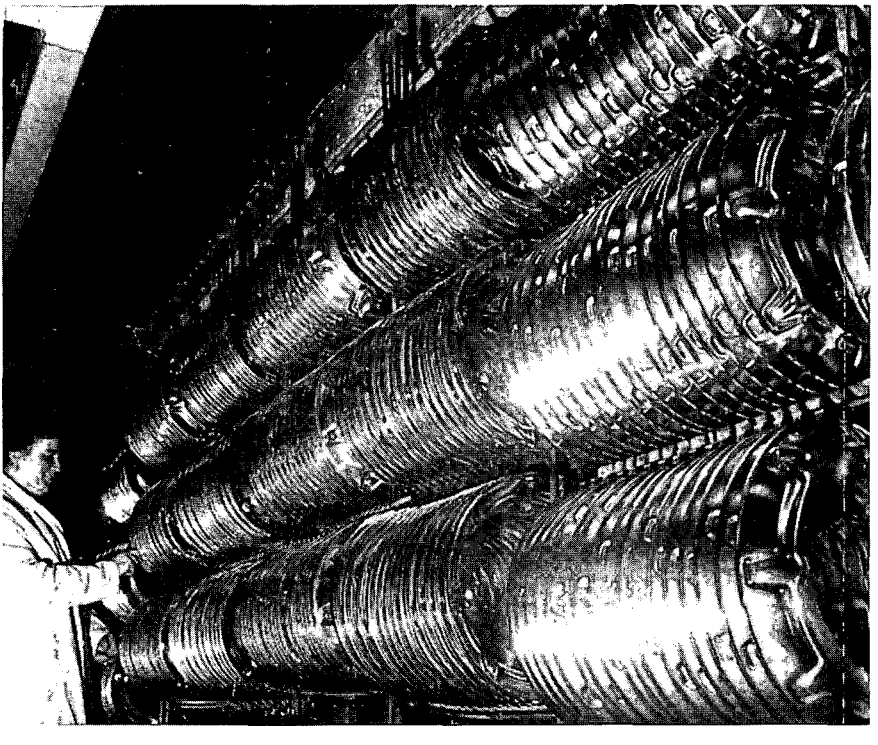


Fig 3-32 Polished wheel embellishers at Pressweld Aluminium Ltd.

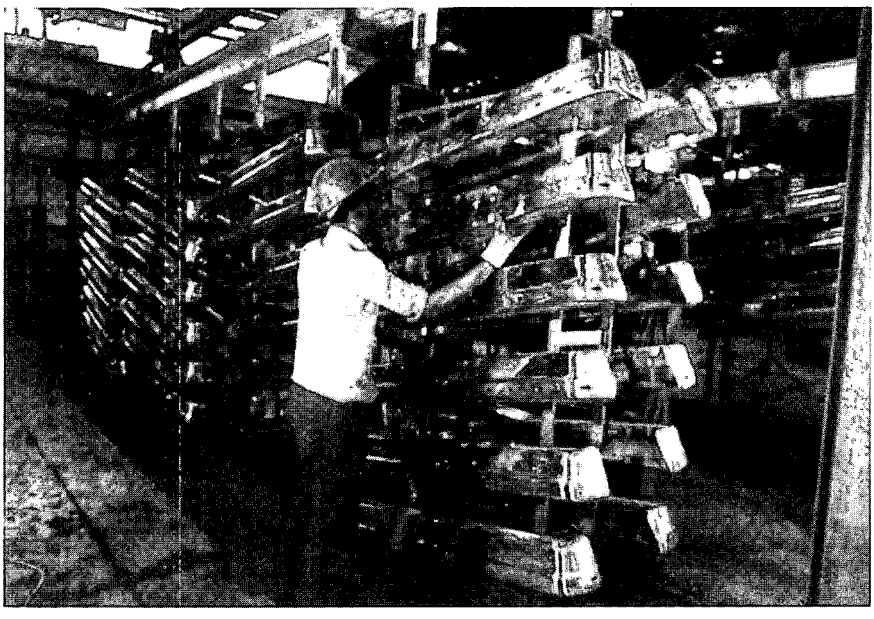


Fig. 3-33. Bumpers to be anodized in the plant of Reynolds Metals Co.

However, with the growth of the plated plastics industry and the move towards less reflective trim in the 1970s, both the bright anodizing and the chromium plating industry suffered considerably. This situation started to change in the mid 1970s with the growing significance of fuel costs, and the need to reduce these by weight saving. In all these situations the excellent corrosion resistance of the bright anodized aluminium is important and Bigford and Thomas[142] have indicated that the main factors contributing to this are the use of high purity aluminium and the intrinsic requirements of the anodizing process which demand that the metal be homogeneous, clean, defect-free, and handled with great care at every stage of production and use. The anodizing process must be carried out under carefully controlled conditions to produce the desired appearance and this generally ensures work of uniformly dependable quality. Careful observation over ten years has shown that aluminium trim has always maintained an excellent finish with the minimum of cleaning or maintenance; there has been no experience of staining or discolouration or loss of brightness, and where the film has been subject to damage the loss of appearance is completely localised and not followed by any deterioration additional to the initial immediate damage. This is in marked contrast to painted or plated finishes over mild steel where the base is not inherently resistant to corrosion and penetration of the coating is the worst event. The contrast is best appreciated in wheel trim, where such damage is a contingency, and here anodized aluminium has scored notably.

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CHAPTER 4

Chemical Cleaning and Etching

The importance of the cleaning and surface preparation stages of a finishing operation is difficult to overestimate, as they are fundamental to the success of later finishing operations. These processes involve operations such as degreasing, deoxidizing, acid and alkaline etching and desmutting, and these are covered in this Chapter.

1. CLEANING

As the first stage of the process, cleaning or degreasing is particularly important, as if this is not carried out correctly all subsequent processes may be compromised. This may affect factors such as uniformity of appearance, or less immediately obvious factors such as performance in service. For these reasons it is important *to* know that cleaning has been carried out correctly, but it is probably one of the most difficult factors to check in a production plant, and problems may only come *to* light when the final product is tested or used. As a result it is important always to use good cleaning practices and *to* maintain and renew cleaning solutions at frequent intervals.

Cleanness

In metal finishing, a differentiation is often made between physically and chemically 'clean' surfaces. Physical cleanness in the sense of apparent freedom from solid dirt, grease, or other contamination is, in general, insufficient to ensure either the successful application of a finishing operation or maximum corrosion resistance.

Chemical cleanness, or the absence of any contamination, is often confused with a 'water-break-free' surface, i.e., the ability of the metal to be 'wetted' by water. While freedom from water-break on rinsing often constitutes a rough guide as to the presence or absence of insoluble oils and greases, etc., it depends on the surface tension of the contaminants and the thickness of the water film, and may be obscured by evaporation, or the presence of wetting agents on the metal surface.

When designing a cleaning cycle for a finishing operation, or when testing the efficiency of different cleaners or cleaning conditions, it is often desirable, therefore, to test the cleanness of a metal surface in some more definite way.

The cleanness of surfaces can be analysed in great detail using Electron Scanning Chemical Analysis (ESCA). This type of analysis is capable of identifying the contaminant and in many cases a semi-quantitative analysis of the contaminant may be possible, but it is only available in large laboratories.

A simpler and less sophisticated test based on surface energy, which can be related to surface contamination, entails using a series of pens containing compounds that react to various levels of surface energy. Standardising the reaction of the pens to a defined 'satisfactory' chemically clean surface and various types of contaminated surfaces allows them to be used as a method for measuring the effectiveness of cleaners. This is available as acommercially packaged test kit' and is suitable for shop floor use. Alternatively the following surface tension testing technique can be used.

Surface Tension Test

Take a perfectly dry sample then progressively add a drop of each solution (see Table 4-1) onto the surface until the one drop loses its spherical shape and completely wets or spreads over the surface. Report the result as the number of the solution immediately preceding the one that spreads over the surface of the metal.

Baumgartner et al[2] make the point that in general these tests are subjective or comparative and not very sensitive. They advocate the use of an electrochemical technique that is applicable to wet surfaces, based on both two and three electrode polarisation. It is claimed this method is easy to use, reliable enough to give reproducible results and is rapid and cost effective.

Other surface conditions

The cleanness of a metal surface is only one aspect of the influence of the condition of the basis metal in the application of surface treatments. The most important properties required of a cleaning cycle for the pretreatment of aluminium-alloy surfaces are given below, but it is important to realize that different materials and surface conditions may require different cleaning treatments.

Porosity

Aluminium castings showing surface porosity present special problems to the finisher. In some cases, superficial pores may be closed by 'flowed' metal during

polishing; in other cases castings may have to be rejected. Contamination remaining in the pores adversely affects the corrosion resistance of the metal and the adhesion of a coating. Hot-water rinsing after the various process stages may be beneficial. This opens up the pores and facilitates better removal of the trapped chemicals. Conversely, processing porous castings in hot cleaners, etches or other processes opens up pores, which then fill with the chemicals. Rinsing in cold water can trap these chemicals in the pores; they are then released in the next hot process stage. The net result can be contamination of process solutions with elements that are detrimental to their operation.

TABLE 4-1

Composition and surface tension (dynes/cm) of the solution used in cleaning quality test

Solution No.	*% by volume*		*Apparent surface tension*	*Density*	*Actual surface tension*
	Ethanol	*DI water*			
0	80.0	20.0	21.2	0.850	24.5
1	51.0	49.0	31.2	0.922	28.2
2	33.0	67.0	36.0	0.955	32.7
3	21.5	78.5	41.9	0.970	38.4
4	14.3	85.1	*41.3*	0.978	43.7
5	9.3	90.7	53.4	0.985	49.1
6	4.5	95.5	**61.3**	0.991	57.6
7	1.0	99.0	70.1	0.995	66.6
	potassium carbonate				
8	220		80.0	1.171	75.8
9	520		91.2	1.377	86.3
10	800		96.1	1.535	101.2

Alloy composition

The effect of alloy composition on the individual finishing processes will be discussed in due course. With a few exceptions, little difference is encountered, however, in the cleaning of various alloys.

In alkaline cleaning, alloys containing copper, manganese or silicon are left with a black surface smut, due to insoluble compounds of these metals. This smut can normally be removed from the alloy surface by a nitric acid dip or, in the case of silicon, by a mixed nitric acid-hydrofluoric acid solution.

Surface smoothness or roughness

A great variety of mechanical surface treatments may take place before cleaning, and the nature of these and the final appearance required will affect the cleaning

treatment used. For example a coarse mechanical finish may require a highly active cleaner to remove any loose debris and imbedded abrasive particles, whereas a polished finish will usually require a cleaner that gives no surface attack at all.

Functions of a cleaning cycle

The factors determining a successful cleaning cycle are complex and processes may have to satisfy many different requirements. For example removal of one or more of the following may be required:

1. Protective oils and greases, which may come from the aluminium fabrication processes or have been applied for protection or lubrication subsequently.
2. Polishing compounds, e.g., stearin and paraffin waxes, containing abrasive and absorbent material, e.g., fine silica, diatomaceous earth products, lime, colloidal clay, etc.
3. Surface oxides or corrosion products.
4. Handling grease, fingermarks, etc. These are mainly fatty acids and nitrogenous compounds.
5. Dust, metal chips, solid dirt, foreign matter, etc.
6. Welding or brazing fluxes, corrosive salts and welding or annealing scales after welding.
7. Moisture, particularly before the application of organic coatings to prevent corrosion taking place between the coating and the metal.
8. Faulty organic coatings, e.g., paints, lacquers, etc., or organic coatings applied for corrosion protection during storage.
9. Faulty electrodeposits for refinishing.
10. Oxide films or faulty anodic or chemical coatings.

Cleaning methods

The process used for cleaning aluminium is dependent upon the work and the nature of the contaminants and therefore there is no universal practice suitable for all situations. The aim, to obtain a chemically clean surface with the greatest economy, must in each case be suited to the job. Suggested cleaning cycles will be given subsequently in this chapter and in later chapters where they are an integral part of a finishing process. The important factors relating to industrial cleaning operations are indicated below.

Vapour degreasing

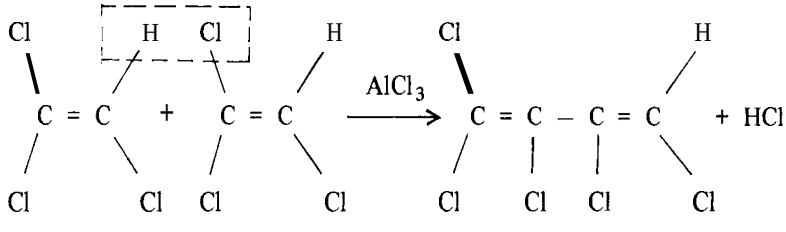
This cleaning process removes oils and greases as well as solid dirt particles from metal surfaces and is widely used in between processing stages and as a precleaner before finishing operations. Vapour degreasing, however, will not

produce a chemically clean surface and is usually, to this end, supplemented by alkaline cleaners.

Non-inflammable chlorinated hydrocarbon solvents are employed, the most common of which was trichloroethylene. Methylene chloride, which possesses a lower boiling point and is more difficult to control, was used for a time on the Continent, while tetrachloroethylene, also called perchloroethylene, is now being increasingly used in many countries. Other solvents of the group find a more limited application. Fluorocarbon solvents are also employed for vapour degreasing and in spite of their higher cost they may often have advantages which can justify their use.[3]

Trichloroethylene boils at 87°C and has a density of 1.5. It is non-inflammable and has a low specific heat (approximately 0.25), requiring correspondingly little heat to raise its temperature. Its vapour is approximately 42 times as heavy as air, which makes it easily controllable in the degreaser. This must, however, be fitted with condensing equipment, as the vapour is toxic at concentrations of 2,000 ppm and fatal at 4,000 ppm. In the presence of burning cigarettes, etc., it decomposes into the extremely poisonous phosgene gas. Perchloroethylene has similar properties and boils at 121°C and has a density of 1.6, but its higher stability and lower hazards have made it more popular than trichloroethylene in many countries. Both solvents have a low surface tension, and their consequent easy penetration into pores, seams and crevices, etc., mean that they are useful in the cleaning of complex and porous work.

For use with aluminium and its alloys, trichloroethylene must be 'stabilised' to prevent the corrosive effects of decomposition into hydrochloric acid. This reaction is photochemical in nature and is brought about by ultra-violet light, aided by the catalytic action of acids present in solvents, forming oils, etc. The stabilising agent is added to neutralize the acid as it is formed and to set up a safe margin of alkalinity. An aliphatic amine, or a mixture of amines, possessing a boiling point slightly higher than the solvent, is commonly used in concentrations of 0.1%. Solvents are obtainable stabilised according to specifications.[4] There is evidence that halides, in particular, are the catalytic agents in the decomposition reaction[5] which has been written:[6]



Perchloroethylene does not present the dangers associated with the use of trichloroethylene on aluminium, and is, therefore, increasingly used. It is also preferred for cleaning light gauge materials and is sometimes used for vapour drying of such things as jewellery and nameplates.

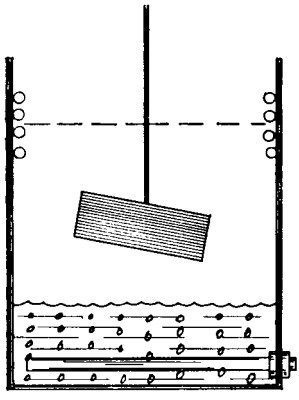
Degreasers may be of the one-, two-, or three-compartment types, or may include solvent sprays. The most effective are those combining solvent liquor, vapour and spray, and these will deal effectively with all types of contamination except soap-emulsions or heavy soap-base drawing compounds which are only partially removed (Fig. 4-1).[7]

A common type of degreaser has three sections, two for immersion of the work in solvent liquor, the third for a final vapour clean. The work is immersed in the first tank for about one minute, removing dirt, turnings, heavy grease and oil. In the case of polished articles, the hot liquor dissolves the grease bond and liberates the abrasive from the surface, the agitation in the boiling solvent dispersing the composition. In the second compartment the work is rinsed for approximately 15 seconds prior to the vapour cleaning. The solvent in this section is sometimes cold in order to cool the work to improve condensation in the vapour stage. After rinsing, the work is held in the third section for 15-30 seconds where the condensing solvent vapour washes off oil and grease. To keep the work cool enough for solvent condensation, metal with a high rate of heat transfer is frequently immersed several times rather than treated by a single immersion in the vapour.

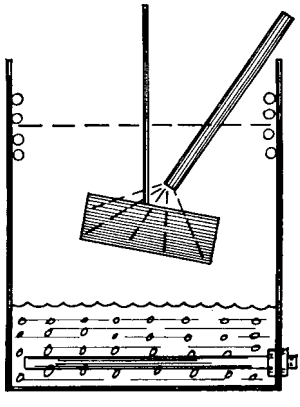
Degreasers may be fitted with conveyors, and such units usually include a spray section, useful for treating work contaminated with soap-base compounds. Other units may operate with a continuous recovery process. By one method, contaminated solvent is gravity fed from the sump of the degreaser into an external still, operating at a higher temperature than the degreaser itself, returning the distillate direct to the tank.

In the simpler type of unit, the degreaser must be stopped and the solvent distilled from one section to another, according to the type of machine. The tank is then scrubbed out with sodium carbonate solution and dried thoroughly before refilling. The frequency with which the tank is cleaned depends on the rate of contamination, and the period between should not generally exceed two weeks. The degreaser should, however, be cleaned out when the boiling of the solvent has risen to 93-95°C (200-204°F). Automatic degreasing units have come into use in some installations.

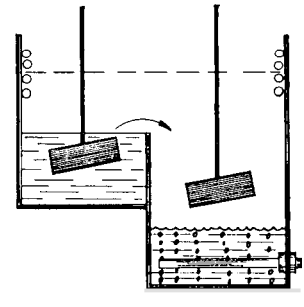
Fluorocarbon solvents are also used for vapour phase cleaning. The pure chemical trichlorotrifluoroethane, sold by Dupont as Freon TF, boils at 47.6°C to give a heavy vapour and is effective in removing oil, grease and other contaminants. It is extremely stable, does not react with water, oils, paints, varnish, plastics or elastomers and can therefore be used in many situations where chlorinated hydrocarbons are inadmissible. In addition it has a very low toxicity, no irritating odour, and a high density vapour so that the ventilation requirements are less than with conventional vapour degreasing plant.[3] By combining the fluorocarbon with other solvents such as acetone, methylene chloride, ethyl alcohol or isopropyl alcohol a range of effective azeotropes or emulsions of low boiling point can be prepared for tackling any of the more exacting cleaning jobs.



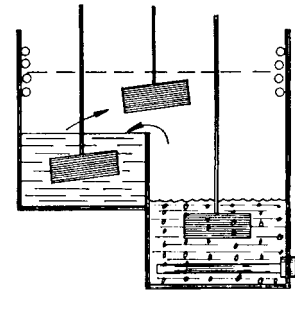
(a) Vapour: The work is suspended in the vapours of boiling solvent. The vapours condense on the cool nictal surface. The condensed solvent dissolves the greasy contaminants and drips back into the degreaser.



(b) Vapour-Spray-Vapour: The work is suspended in the vapours of boiling solvent. **A** spray of warm liquid solvent is directed over the work, and after this, the work receives a vapour rinse before removal.



(c) Warm Liquid-Vapour: The work is immersed in warm liquid solvent, then suspended in a bath of solvent vapours.



(d) Boiling Liquid-Warm Liquid-Vapour: The work is immersed in boiling solvent to utilize the mechanical action of the boiling phase. It is then rinsed with the cooled liquid solvent, and finally in the vapours of the boiling solvent.

Fig. 4-1. Basic degreasing cycles'

Legislation affecting the use of chlorinated solvents

The Montreal Protocol,' an agreement restricting the production of chemicals affecting the global environment, was a result of the 1987 UN Environmental Conference convened to investigate strong evidence that chlorofluorocarbons were depleting the ozone layer in the atmosphere. The provisions of this pact went into effect on 1 July 1989. The original aim was for a 50% reduction in the use of chlorofluorocarbons by the year 2000. A subsequent UN Environmental Conference in London in 1990 agreed that there would be a 100% reduction by the same deadline. Then, at a similar gathering in Copenhagen in 1992 the phase out was brought forward to 1995. Other solvents such as 1,1,1 trichloroethane were also restricted and this particular solvent was phased out on 1 January 1996. The Environmental Protection Act is the primary legislation' affecting companies which use chlorinated solvents. Probably about 50% of vapour degreasing operations[10] have always used trichloroethylene rather than 1,1,1 trichloroethane, CFC 113 or other solvents. Although trichloroethylene is considered to represent a potentially greater health risk than the ozone depleting solvents being phased out, many degreasers will switch to this particular solvent. Providing the vapour degreaser is correctly designed, installed, maintained and operated, the use of trichloroethylene is a safe option. The USA Environmental Protection Agency's Significant New Alternatives Policy (SNAP) has approved'[11,12] trichloroethylene, perchloroethylene and methylene chloride as replacements for 1,1,1 trichloroethane.

New low temperature and 'environmentally friendly' solvents have also been developed as alternatives for vapour degreasing. Duponts Vertrelâ (azeotropes based on HFC 43-10) and 3M HFE's (hydrofluoroethers) are examples of these.

The use of water-based cleaners is common for general degreasing of aluminium sheet and extrusions but solvents are usually prefered where heavy oils or dried on polishing compounds have to be removed. Kresse[13] compared the effectiveness of several water-based cleaners with vapour degreasing, and suggested that some industrial cleaning tasks could only be achieved in a technically satisfactory way by using chlorinated hydrocarbons. Bird[14] presented some data that indicated alkaline cleaners could achieve cleaning efficiencies comparable to organic solvents, and concluded that enhancements such as agitation, spray washing and ultrasonic techniques can help to improve cleaning efficiencies.

Ultrasonic cleaning

Ultrasonic cleaning is increasingly used for difficult cleaning jobs where simple immersion or spraying is unsatisfactory. However it requires expensive equipment and is normally only feasible for relatively small parts. With aluminium it has been used in conjunction with vapour degreasing for small intricate parts,' with a 3-stage cycle involving firstly precleaning to remove adherent soil, secondly immersion in the degreasing solvent which is ultrasonically agitated, and finally solvent spraying with the uncontaminated distillate.

Missel[15] has studied ultrasonic cleaning in a variety of solutions, both acid and alkaline, and recommends nitric acid of varying concentrations for this purpose. The ultrasonic cleaning step is preceded by vapour degreasing and followed by a solvent rinse for optimum results.

The value of ultrasonic cleaning lies in the mechanical scrubbing action that occurs as the fluid is ruptured and then reformed and this takes place at a rate equal to the frequency of the energy input. Ultrasonic generators can either be sealed in sheaths made of material such as stainless steel, to allow immersion in an aqueous or emulsion cleaner, or may be mounted on the outside of the tank and require less protection.

Shenoi *et al*[16] produced a comprehensive review of ultrasonic cleaning. They suggest that the technology and application of ultrasonic cleaning are progressing at a faster rate than the theoretical aspects. However, they conclude that the frequencies employed are in the range 17 to 50 kc and that there is no advantage of using frequencies above 100 kc. They consider that the use of ultrasonics in cleaning is well established and that it has started to make inroads in pickling, phosphating, anodizing and electroplating. A more recent paper by Fuchs[17] describes the practicalities of ultrasonic cleaning and lists the factors that need to be considered when integrating ultrasonic cleaning into a multi-stage production process.

Emulsion cleaning

The function of emulsion cleaners is similar to that of vapour degreasers, which they often replace. They have the advantage of dealing rather more effectively with solid dirt and water-soluble materials such as soaps and sulphonated oils. They are quick working and may be used at room temperature. They require a minimum of equipment and space, but, like vapour degreasers, they do not provide a chemically clean surface and, if this is required, emulsion cleaning should precede treatment in an alkaline cleaner.

Emulsion cleaners have no action on aluminium and are extremely flexible in the choice of solvent, control of alkalinity and metal to be cleaned.

There are three methods which may be employed:

(1) In the first, the cleaning liquid is in two or more phases which are generally immiscible, one of which is an aqueous solution, the other an organic solvent which should have a flashpoint above 38°C (100°F). The latter may be mineral oil, paraffin, naphtha or benzene, etc.

The two phases are separate, i.e., one floats on the other and, by dipping the work in the cleaning medium, the work is in contact alternately with the aqueous and non-aqueous phase.

The surface tension is reduced and wetting facilitated by the use of detergents containing groups possessing an affinity for the two phases. An example of this is triethanolamine and oleic acid. As well as forming

the soap triethanolamine oleate, a proportion of the triethanolamine goes into solution in the water, while part of the oleic acid dissolves in the organic solvent.

An example of this type of cleaner may contain by volume:

paraffin	8.0%
triethanolamine	0.25%
oleic acid	0.5%
pine oil	2.25%
water	89.0%

It has been suggested that those parts of the soil which are soluble in water will be removed, together with parts soluble in the organic solvent.[18]

(2) In the second process, the cleaning is done in two stages. The work is first sprayed with or dipped in the non-aqueous solvent which, in the latter case, should preferably be agitated. Care must be taken to keep the work dry before immersion. As in the di-phase cleaner, a soap is added to aid emulsifying properties on rinsing, and the solution may consist of approximately 5-10% of a suitable soap dissolved in the organic solvent. Examples may include triethanolamine in mineral oil, or sodium naphthenate in cresol. A white, milky film is formed on the surface, and the work is transferred to a water rinse, where the solvent and contamination are washed off.

The cleaning process itself takes place in the rinse; hence there is little contamination of the cleaner. A hot-water rinse is most effective or, in other cases, an alkaline cleaning bath may be inserted before the rinse."

(3) The third process uses a similar solution to the di-phase cleaner in washing machines of the pressure-spray or rotary-tumbler type. Here the temperature is raised to 60-90°C (140-190°F).

Solvent emulsions loosen the bond between the contamination and the metal surface, and the solid dirt particles are left coated with a soap or wetting agent. The deflocculated particles are easily rinsed off and the cleaned surface is physically but not chemically clean. For the application of enamels and for storage purposes, emulsion cleaning may often be sufficient. In other cases, a further alkaline cleaning operation is necessary.

Corona discharge cleaning

The tendency for a high voltage corona discharge generated at a metal surface to both clean and activate the surface is well known and alternating voltages of 5,000-20,000 are required for this purpose. In a development of this idea[20] Rheinische Blattmetall have claimed that by using very much higher voltages of

400,000-600,000 at frequencies greater than 25 kHz it is possible to improve substantially the adhesion of lacquers and inks and also to promote excellent adhesion of polyolefines of high molecular weight which do not normally adhere very well to aluminium. The method is particularly applicable to coiled aluminium strip where the metal is made one electrode and passes 0.5-3 mm beneath the counter electrode in the form of a rotating barrel coated with insulating material: a high frequency alternating voltage of 600,000 V at 75 kHz is applied using a model T 300/3 generator made by Deutsche Vetaphone, and the strip can be prepared for coating at speeds of up to 60 metres per minute (200 ft per minute). Where adhesion is not easy to produce the corona discharge treatment can supplement conventional degreasing.

In a patent related to corona discharge cleaning Swiss Aluminium Ltd. have described and patented details of a complex counter-electrode system consisting of an array of wires embedded in insulating material, designed to ensure that the corona discharge is stabilised and uniformly distributed over the surface to be degreased.[21]

Washing machines

Two main types of washing machine are in use for cleaning aluminium and other metals: viz., the rotary-drum type, and the pressure-spray type. Neither is very flexible in use and they cannot be relied upon to clean a variety of different articles.

Rotary-drum machines

These consist of a rotating drum fitted with spiral partitions which advance the part through the machine by rotation. The drum may include scoops to throw solution over the work on the inside of the drum or it may be so constructed that the drum itself dips into the solution. Various combinations are, however, possible to suit different work and cleaning cycles. The last stage in the cycle is a drying unit.

Pressure-spray machines

These are mainly used in intermediate operations between processing and are less frequently used as a pretreatment for finishes. A stream of solution is forced against the work from various carefully chosen angles with a pressure of 90-100 lb/sq in (approx. 6-7 kg/cm^2; 6-7 bar). The work is moved through the spray on a conveyor, and the force of the spray and its detergent properties remove oil, grease and inorganic dirt. The cleaning material must be non-foaming. These machines are valuable for dealing with recessed work, as the stream will enter recesses with considerable force.

Alkaline cleaning

Of all cleaning processes, this is the most important. As distinct from most other metals, aluminium is amphoteric and is readily attacked by alkaline solutions. Alkaline cleaners for use with aluminium and its alloys must work, therefore, at comparatively low alkalinity, and are 'inhibited' in order to form a protective film over the surface, which will prevent attack of the metal during cleaning. The modern alkaline cleaner needs to be strictly controlled, and the ideal cleaner should satisfy the following conditions:

(1) The salts should be completely and easily soluble and the cleaner should be stable and possess good rinsing properties.
(2) Its alkalinity should be suited to the metal, i.e., for aluminium preferably between pH 9 and pH 11. It should also be buffered to help maintain constant activity of the cleaner.
(3) It should possess good wetting power.
(4) It should have a high emulsifying power to break up and disperse such oils and greases as can form soluble soaps.
(5) It should be able to deflocculate dirt particles and disperse them throughout the solution by colloidal action.
(6) The cleaner should be inhibited to minimise attack on the basis metal.
(7) It must be non-irritant to the skin, and should preferably be non-toxic.
(8) The cleaner should act as a water softener and so prevent precipitation of hard-water salts on the metal surface.
(9) Last, but not least, the cleaner must be economical.

Inhibitors

The function of inhibitors in alkaline cleaning is to provide a protective film which is formed by reaction of the inhibitor with the aluminium or the oxide surface, or, in the case of silicates, a mono-molecular layer of hydrated silica may be formed superficially. Compounds commonly employed for the purpose may include silicates, chromates, phosphates, fluorides, silicofluorides or organic materials. Care must be taken, however, not to inhibit the cleaner too strongly by forming too tenacious a film, the aim being a minimum of visible etching, at the same time allowing a mild chemical attack which speeds up the cleaning cycle. When the protective film is slight, gassing occurs at the solution interface, but, after a period, this diminishes and stops. This is the induction period during which some microscopic etching takes place.

Excessive induction periods may occur as a result of corrosion spots, formed by chemical action, moist air or faulty storage, and such areas may etch during the whole period of the alkaline treatment. Such corroded areas should be cleaned prior to alkaline treatment in an acid dip.

Depending on the type of surface required it is possible to formulate and use either etching or non-etching alkaline cleaners. The etching action of sodium

hydroxide on aluminium can be only partly reduced by the use of silicate inhibitors and it is not possible therefore to formulate such a non-etching cleaner based on sodium hydroxide. The etching action of sodium carbonate or sodium phosphate can however be practically stopped by the addition of inhibitors. The non-etching alkaline cleaners for aluminium contain a balanced mixture of sodium carbonate, sodium phosphate and sodium silicate, together with wetting agents, surface active agents and emulsifiers. For minimum etching action on the aluminium it is recommended that the silicate should be present as sodium metasilicate and in an amount equal to at least 25% of the combined sodium metasilicate and sodium carbonate content. The pH is also important and this is usually buffered to the range of 11.1-11.7.[22] Sodium orthosilicate does not provide the necessary inhibiting action.[23,24]

Silicated cleaners have sometimes given problems with aluminium, due to the effect of silicate residues on subsequent processes. In particular, if a film of alkaline cleaner remains on the surface after rinsing and the work is then transferred to an acid bath, the soluble silicate is converted to insoluble silicic acid, which interferes with subsequent processes such as brightening, anodizing or conversion coating.[22] For this reason partially inhibited alkaline cleaners, based only on sodium carbonate and sodium phosphate, are often preferred.

Wetting, emulsification, deflocculation, saponification

It is important that the cleaning solution should wet the surface uniformly and immediately in order to produce a uniformly finished surface. Alkalis by themselves are poor wetting agents, and water, with a surface tension of 73 dynes/cm, does not readily wet oils, which have relatively low surface tensions. By the addition of wetting agents, the surface tension of the solution is reduced to a similar value to that of the contaminant. The wetting of the contaminant and, equally important, of the metal surface is, therefore, of primary importance in alkaline cleaning. In the presence of wetting agents, surface oils are removed quickly and an increased penetration of the cleaner is obtained, enabling it to clean out pores. They also have an emulsifying action, preventing the redeposition of oil and keeping it suspended for long periods of time. Surface activity aids rinsing, also the prevention of hard dried-on layers or films which may develop between cleaning and rinsing.

The use of soaps as wetting agents should be avoided as they form insoluble metal soaps. Numerous wetting agents have been described, including also detergents, emulsifying and rinsing agents.[25,26]

Among the major functions of the cleaner is its power to emulsify liquid, and deflocculate solid, contaminants and prevent redeposition on the surface. These properties are controlled by the interfacial tension between the solution and the soil and are thus directly dependent on the wetting power of the solution.

Where water-soluble alkaline cleaners easily remove dirt, the alkali must neutralize acid and maintain the emulsion. Fatty oils and waxes may be saponified, the soap formed acting as a wetting and emulsifying agent. The bath may thus

actually improve with age until saturation is reached. This mechanism has been exploited in cleaners not containing wetting agents, the practice being to add a bucketful of old cleaner when a new bath is made up. It is also exploited in some patented cleaning processes.[27] Completely soluble alkalis have little direct mechanical action in dirt removal, the actual cleaning resulting from the mechanism described.

To obtain the maximum effect of convection currents, the heat should not be applied at the bottom of the tank, but at the side in order to produce a rolling action upwards and backwards throughout the tank. This will also remove surface oils and scum towards the rear of the tank and avoid redeposition. The effect of temperature on the efficiency of an alkaline cleaner is very marked, and the efficiency has been stated[28] to be increased by as much as 100% for each 20°F rise in temperature above 120°F (100% for each 11°C rise above 49°C); agitation of the solution is also useful and enables lower concentrations of the cleaner to be used.

Agitation may either be by air or steam jets and helps to keep grease in an emulsified condition; it will also help to prevent redeposition of loose oil on the metal surface. In laying airlines for air agitation, they should be fitted lengthwise along each side, resting six inches above the bottom of the tank. The lines should be perforated at an upwards and inwards angle so that emergent air streams from the two sides would, if projected, meet along the centre line of the surface.''

In some agitation designs the holes are drilled on the underside of the pipe at an angle of 45" to the vertical. It is claimed that this helps to prevent the problem of the holes silting up with particulate matter in the degrease solution or with hard water salts.

For use with hard water, calcium and magnesium sequestering agents are sometimes added to the cleaner in order to prevent precipitation of hard-water salts on the work. The sequestering materials also hold back floc formation and have a peptising effect on dirt.

Cleaning materials

Mixtures of trisodium phosphate or sodium pyrophosphate with sodium metasilicate are widely used for cleaning aluminium. The component proportions are very variable and are adapted to suit particular purposes, but cleaner concentrations are normally between 10 and 60 g/l (2-10 oz/gal).

Other typical formulae include:

1.[30]	sodium carbonate	5-15 g/l	(0.8-2.4 oz/gal)
	trisodium phosphate	5 g/l	(0.8 oz/gal)
	temperature	80-95°C	(176-203°F)
2.[31]	sodium carbonate	25 g/l	(4 oz/gal)
	trisodium phosphate	25 g/l	(4 oz/gal)
	surface active agent	0.1 g/l	(0.02 oz/gal)
	temperature	75°C	(158°F)

3.[31]	borax	25 g/l	(4 oz/gal)
	sodium metasilicate	15 g/l	(2.4 oz/gal)
	sodium carbonate	5 g/l	(0.8 oz/gal)
	trisodium phosphate	5 g/l	(0.8 oz/gal)
	surface active agents	1 g/l	(0.2 oz/gal)
	temperature	60°C	(140°F)

Wetting agents and chelating agents of the EDTA type are also often incorporated. Thus, a solution used in the U.S.S.R. for cleaning aluminium precision components before anodizing contains:[32]

monosodium phosphate plus polyethylene glycol ester	3-4 g/l
disodium phosphate	10-15 g/l

and is used at 80-95°C (175-200°F) and pH 5.5-7.5.

A two-minute immersion at 200°F (95°C) in a solution containing 2 oz/gal (12.5 g/l) each of anhydrous sodium carbonate and trisodium phosphate is recommended as a preparatory treatment prior to a zinc-immersion plating process," while a 1-2 oz/gal (6-12 g/l) solution of equal parts by weight of sodium metasilicate and sodium carbonate is also useful for cleaning aluminium surfaces with a minimum of etching. Solutions based on borates with the addition of 0.1 to 10 g/l vanadium ions have also been proposed.[34]

Inhibited alkaline cleaners based on caustic soda have also been used. Thus Henkel[35] in Germany have patented the use of water soluble aromatic nitro-compounds for this purpose, claiming that aluminium can be cleaned in 10% caustic soda with 4% m-nitrobenzoic acid without any attack. In a later formulation[36] they have added to caustic soda the reaction products of propylene oxide with aliphatic amino or aliphatic polyalcohols. Another proposed cleaner uses caustic soda with an alkaline gluconate, ethylene glycol and ethanolamine.[37]

As in other areas of metal finishing, the increasing cost of energy is influencing cleaning operations, and, in particular, the cost of maintaining the cleaning solution at relatively high temperatures (70-80°C) becomes significant. Even so Bird[14] carried out a cost analysis of alkaline cleaners and concludes that they are cost-effective when compared with solvent or vapour degreasing. He suggests that some savings may be made, while at the same time the liabilities associated with storing, handling and transporting waste solvents are eliminated. Jansen and Tervoort[38,39] have considered this problem and have developed formulations for low-temperature alkaline cleaning. They indicate that reducing temperature of a 3000 litre bath from 70°C to only 50°C results in an energy cost reduction of about £2500 ($3750) per year for electrical heating and more than £1000 ($1500) for steam heating. The move to lower temperature aqueous alkaline cleaners is made possible by the use of optimised and increased surfactant contents in combination with highly active dispersants. Both anionic and non-ionic surfactants are required and these are added to appropriate mixtures of the normal phosphates, carbonates and silicates. Under these conditions, temperatures as low as 30°C can be used for

normal contaminants, with higher temperatures (50°C) only required when high melting point greases or pastes, or aged and hardened residues are present.

The time of immersion in cleaners depends on the composition, the degree of contamination, the operating temperature and whether or not the cleaner is agitated. It also varies largely with the age of the cleaner. The operating time will usually vary between two and five minutes. The time interval between operations must be kept to a minimum and the solution must never be allowed to dry on the work; slow-moving hoists should be avoided. If the work is heavily contaminated, an auxiliary alkaline precleaner may be employed which may be made up from old solution from the main tank. No rinse is required between the two operations.

To reduce drag-out and contamination of the rinse, a row of hot-water spray jets may be installed along the top edge of both sides of the tank. The sprays are controlled by a valve, and are turned on to spray each load as it is removed from the cleaner, with clean hot water. Tanks are normally of steel and should be fitted with an over-flow.

Control of alkaline cleaner

The pH of the cleaner and its specific gravity should be measured at least once a week, and additions made accordingly. Alternatively, the alkalinity may be determined by titration against standard acid. After some time, the speed of the cleaner will decrease due to the increased oil load. When cleaning time is excessive or the cleaner is visibly contaminated, the solution is discarded and the tank cleaned out thoroughly. After the rinse following the cleaner, the work should be inspected for waterbreaks and, if present, should be returned to the cleaner and a check made on cleaner strength. Waterbreak may be due also, however, to oil or grease present in the rinse.

Chemical control of the cleaner is not frequently undertaken except when testing different cleaners for comparative purposes. Standard methods for determining the concentration of alkalis, fatty acids, resins, soaps, silica, phosphates, sulphates, chlorides, carbonates and organic matter, etc., are available,[40] as well as indirect performance tests, e.g., for colloidal and water-softening properties, conductivity, solvent action, instability, and wetting and emulsifying power.[41]

Table 4-2 overleaf shows some of the common faults of cleaners and their control.

Electrolytic alkaline cleaning

Electrolytic alkaline cleaning is not often used in the pretreatment of aluminium and its alloys because of the high rate of attack on the metal of this form of treatment and the effectiveness of hot alkaline soak cleaners. A few processes exist, however, which use the ordinary alkaline cleaners with the passage of a low-voltage current.

TABLE 4-2

Control of alkaline cleaners[42]

Problem	*Cause*	*Remedy*
Excessive corrosion in cleaner.	pH too high or loss of inhibitor.	Adjust pH; make up inhibitor.
Corrosion spots.	Alkali left on surface.	Dip in $NaHSO_4$ or HNO_3 and rinse
Does not clean properly.	Weak or worn-out cleaner.	Make up or renew, adjust pH and wetting agent.
Does not clean properly.	Excess foreign matter on work.	Prior degrease in vapour or solvent emulsion cleaner.
Smut formation on work.	On copper-containing alloys if pH is too high.	Reduce pH, avoid free caustic cleaners, use sufficient inhibitor.
Excessive floc formation	Breakdown of Cu, Mg and Si sequestering agents: excess carbonates used in original formula; addition of acid to cleaning solution.	Select cleaner with ample reserve of sequestering agents, e.g., polyphosphates. Use cleaner with no CO_3^{2-} content. Avoid acid addition by supervision
Insoluble film formation interfering with anodizing, wetting, etc.	Too highly inhibited; excessive transfer time between cleaner and rinse.	Select proper amount of inhibitor which is soluble. Reduce transfer time and select cleaner with wetting agent which promotes good rinsing. Use non-silicated cleaner

The advantage of electrolytic cleaners lies in their increased activity and the scrubbing action of the gas produced at the electrodes. Voltages of 6-12, and current densities of 40-100 amp/sq ft (4-10 A/dm^2) are employed, the solution being operated either at elevated or room temperature. The tanks should be of steel or lined steel, and should not be used as electrodes, as electrolysis may cause failure of the welds in the tank. Electrodes are either of steel or, preferably, nickel-plated steel, as nickel does not deposit in alkaline solutions of the type normally employed. The electrode edge area is frequently increased by hanging separate electrodes or perforating them. The electrolysis may be either cathodic or anodic, or alternating current may be used, but cathodic cleaning is the most common. It is sometimes found preferable to use a reversing switch to change the direction of the current during cleaning.

Cleaning materials include those used in soak cleaning, and proprietary solutions are available. The Krome-Alume electroplating process used a d.c. electrolytic treatment in dilute sodium cyanide[43] while two other cleaning solutions were recommended by the U.S. Ordnance Department,[44] containing:

(1)	sodium orthosilicate	85%
	sodium carbonate (anhydrous)	10%
	sodium resinate	5%
(2)	sodium carbonate (anhydrous)	46%
	trisodium phosphate	32%
	sodium hydroxide	16%
	rosin	6%

Rinsing

The rinsing operations in a cleaning cycle are as important as the cleaning operation itself and the work of the most effective cleaners may be undone by contaminated rinses. Both cold and hot water rinses are used, the latter having the advantage of keeping the pores open to permit removal of cleaning compound and entrapped emulsified oil. They are particularly valuable after alkaline and acid treatments and will also speed up drying. If only one rinse tank is available, however, a cold clean running rinse is more effective than a contaminated warm one and, where cleaners are easily soluble and rinsable, cold water is satisfactory provided that an efficient drying operation is added. Where two or more cold rinse tanks are used consecutively, the counter-flow principle makes the most efficient use of the water. In this the tanks are connected by a system of weirs, water entering the last rinse of the series and travelling in the opposite direction to that in which the work proceeds.

The importance of good rinsing practices in the case of silicated cleaners has already been indicated,[22] but Clarke,[45] in a detailed study of rinsing operations, has shown that alkaline materials such as sodium hydroxide are difficult to remove

from metal surfaces. Agitation of the rinse water accelerated dilution of the sodium hydroxide film, but to a lesser extent than was observed for other residues.

Rinse tanks are normally of steel, often rubber or polypropylene lined (essential after acid cleaning), and a continuous influx of water at one end and an overflow trough at the other should be arranged. The aim should be to change 5-10% of the water each minute, but counterflow rinsing will reduce the volume of water required. Hot water rinses are usually operated between 60 and 70°C (140 and 160°F)though in special cases temperatures up to boiling may be used. Agitation is desirable and this may be by steam or air. Periodically, the pH of rinse water should be tested. It is important that no delay be allowed between the cleaner and the rinse, as a cleaner which has dried on to the metal surface may be very difficult to remove in the rinse. Frequently cold and hot water rinses are used consecutively after which the work is dried, either by hot air or by heating to about 150°C (300°F) in an oven.

2. ACID CLEANING AND ETCHING

Various treatments using acid solutions are available for different purposes which include:

1. Cleaning with little or no etching prior to the application of a suitable chemical conversion coating prior to the application of organic coatings or electroplated coatings.
2. As a desmut bath or neutraliring rinse after alkaline etching.
3. Removal of oxide, mill scale, corrosion products, heat treatment scale or welding fluxes.
4. Matt etching or bright etching for decorative effects.
5. Deep selective etching for patterns in relief.
6. Very deep etching for chemical milling or contouring.
7. Etching to increase the surface area of electrolytic capacitor anodes.
8. Undercut etching to give a mechanical key for PTFE application.
9. Electrolytic etching for lithographic printing purposes.

Acid cleaners

The non-etching solutions usually contain nitric acid or chromic acid, the former attacking aluminium only very slowly, while chromic acid both passivates aluminium and tends to confer a passivating action on any other solution to which it is added.

Nitric acid is principally employed as a desmutting bath after alkaline etching, but is also an important prior treatment for magnesium-containing alloys, since it removes magnesium oxide scale which can often interfere with caustic etching or other surface treatments. It attacks aluminium and aluminium oxide only very

slowly, but will produce an attractive satin finish in about 24 hours. It is useful however in helping to strip thick hard anodic coatings, such as are produced in integral colour anodizing electrolytes, because caustic soda removes these very non-uniformly unless the coating is first softened by a prolonged soak in nitric acid. Nitric acid is also good for removing corrosion products.

When fuming nitric acid is mixed with chromic acid crystals it provides a powerful cleaning medium which is essentially slow acting but will completely remove corrosion products or thick layers of carbon or grease.

Another effective cleaner generally used for removing oxides, including anodically formed coatings, is a mixture of chromic and phosphoric acids. **A** typical composition is 7% by volume phosphoric acid and 4% by weight of chromic acid used at 98-100°C, which will rapidly dissolve any oxide, with no effect at all on aluminium or most alloys, provided that no heavy metals are present in the solution and any galvanic action is absent. **A** further solution sometimes used for this purpose contains sulphuric acid 10% and hydrofluoric acid (as sodium fluoride) 4% but care must be taken to avoid prolonging the treatment if metal attack is to be avoided. Kape[46] has described a range of stripping methods for anodic coatings, and points out the importance of removing organic materials such as paint, lacquer and grease before attempting the stripping operations.

The cleaning media most frequently employed for preparation of aluminium surfaces for painting or plating are the so-called chrome pickles containing chromic and sulphuric acids in various proportions, although phosphoric acid may also be present. Three recommended mixtures are:[47 48 49]

(1)	chromic acid	5%
	sulphuric acid	15% (vol)
(2)	chromic acid	175 g/l
	sulphuric acid	35 g/l
(3)	50% chromic acid solution	1 pt (vol)
	conc. sulphuric acid	10 pt (vol)

Such mixtures attack aluminium only very slowly, e.g., formulation number 3 dissolves less than 1 mg/dm^2/hr (10 mg/ft^2/hr)[50] at temperatures below 40°C (100°F). It is important that parts are dry before cleaning. 1 litre of solution can be used to clean 400-800 dm^2 of aluminium (200-400 ft^2/gal). The article is immersed for up to 20 min. at a temperature of 40-65°C (110-150°F), a clean, slightly etched surface being obtained.

The chrome pickling operation is frequently used to remove heat-treatment films and to prepare aluminium alloys for zinc-immersion plating, chromic acid anodizing, painting, and chemical treatments. It helps to eliminate surface irregularities caused by oxide inclusions or embedded buffing particles and does not, in general, remove as much metal as caustic soda, while it leaves the surface

clean and semi-bright. The acid may be used in tanks of stainless steel (18-8 stabilised), stainless steel-clad material, or lead-lined or other acid-resistant materials. The solution may also be used at room temperature if the immersion time is increased.

Acid etch cleaners

Instead of a chrome pickle, a light etch in a nitric-hydrofluoric acid solution may be given. This process has been investigated by Bullough and Gardam,[51] who used it to obtain adherent nickel electrodeposits using the zinc immersion method. The solution recommended contains by volume:

hydrofluoric acid (40%)	10%
nitric acid (d. 1.42)	10%
water	80%

and may be used at room temperature (20°C) in plastic containers. The work, which has been degreased prior to etching, is immersed for two to five minutes.

A two-stage process in which aluminium alloy is first immersed in nitric-chromic acid solution and then in a nitric acid-ammonium bifluoride bath has been used in the aircraft industry.[52]

The addition of an alkyldimethylamine oxide surfactant to mixed acid cleaners containing peroxo acid and/or peroxide, used at 50 to 80°C, has been claimed[53] to improve their cleaning efficiency. The effectiveness of any fluoride containing cleaner is very dependent upon the control of the level of fluoride in the solution. Pyrene describes a method for controlling the level of fluoride combined with an automatic replenishment system.[54,55]

Environmental concerns are putting pressure on the use of cleaners containing chromium or fluoride ions and this has resulted in a number of formulations that are acid based but chromium and fluoride free. Aqueous acid cleaners usually based on phosphoric and sulphuric acids and containing various additives have been described. Phosphoric acid up to 50 g/l with the addition of up to 170 ppm ferric ion (Fe^{3+}) and up to 3 g/l of an oxidising agent in combination with an aluminium ion 'masking agent' has been proposed by Tanaka et al.[56] Suitable 'masking agents' are said to be sulphuric acid, boric acid, condensed phosphoric acids, organophosphoric acids and phosphorous acid.

A sulphuric acid based cleaner containing ferric ion, a surfactant and the oxidation products of diphenylamine or diphenylbenzidine ions has been described[57] by Henkel.

Shimakura claims[58] that the addition of bromine ions, oxidised metal ions, a surfactant and, if required, an oxidising agent to an inorganic acid solution produces a long life acidic aqueous cleaner that can be operated below 60°C.

A similar low temperature cleaning solution, containing inorganic acids, oxidised metal ions, a surfactant and polyhydric alcohols has been proposed by Ikeda.[59]

None of the acid solutions, except those containing hydrofluoric acid, will deal effectively with high-silicon alloys. While silicon and silica derived from Mg_2Si, etc., in the low-silicon alloys can be dealt with by many of the solutions given above, alloys containing 10% or more silicon leave a grey surface and require special treatment. For this purpose, Bullough and Gardam recommended that high-silicon alloys be treated first in conventional HNO_3/HF for 10 minutes, after which they are rinsed and immersed for four minutes in a solution containing:

nitric acid	98%
hydrofluoric acid	2%

before the application of a zinc coating. **A** similar solution has also been suggested containing nitric acid with 3-15% hydrofluoric acid, 0.5-2.5% hexavalent Cr ions, less than 25% water and optionally up to 10% sulphuric acid.[60] Manganese-containing alloys do not require this last dip but should also be given 10 minutes in the normal etch.

The time of treatment, as well as depending on the alloy composition, should vary with the required state of the surface. If no roughening is required, a 30 second immersion may be sufficient. To obtain a microscopic etch exposing the crystal planes and giving the best base for subsequent deposits, slightly longer times may be required. The latter method gave adhesion of nickel deposits approximately equal to the ultimate tensile strength on commercial aluminium, as well as on alloys containing magnesium, silicon, manganese and copper. The complete cycle was: degreasing etch: rinse; (acid dip); rinse; sodium zincate immersion; rinse: copper or brass deposition; rinse; nickel deposition. The maximum adhesion was obtained irrespective of the roughness or smoothness of the surface, showing that no benefit is obtained by producing a rough 'key' for zinc-immersion plating.

As will be seen later, solutions containing nitric and hydrofluoric acid are also employed in desmutting aluminium-alloy surfaces after alkaline treatment.

For the purpose of cleaning aluminium before conversion coating and painting on continuous strip lines, acid cleaners are increasingly used. They are based on mixtures of acids such as sulphuric acid with HF and are sometimes used as low-temperature cleaners. Amchem claim priority for a sulphuric acid/HF cleaner and have studied a range of cleaner compositions.[61] The benefits of adding polyalkylene glycol based surfactants have also been claimed.[62]

Phosphoric acid based solutions are also used for preparing surfaces for organic finishing, and these, in addition to cleaning, produce a thin film of aluminium phosphate which aids corrosion resistance and is a good paint base. **A** low temperature cleaner of this type[63] contains 6-15 g/l H_2SO_4, 3-22 g/l H_3PO_4 and 0.1-7.5 g/l of a suitable surfactant.

One such process[64,65] employs a mixture of phosphoric acid and alcohols,

the latter acting as grease solvents as well as wetting agents, emulsifying agents, etc., to aid cleaning. A typical standard formula contains by volume:

orthophosphoric acid (85%)	10%
butyl alcohol	40%
isopropyl alcohol	30%
water	20%

Several proprietary cleaners similar to that given above are available, and mixtures recommended include phosphoric acid as well as monobutyl ether of ethylene glycol and a soluble salt of an alkylated naphthalene sulphonic acid as a wetting agent;[66] an alkali metal fluoride and metaphosphoric acid or ammonium dihydrogen phosphate;[27] and mixtures of a soluble bisulphate and sulphate to which ammonium monohydrogen phosphate and an organic sulphonate have been added.[67] A solution suitable for copper-containing alloys contains phosphoric acid with up to 0.1% benzotriazole and surface active agents,[68] whilst a general cleaner based on a mixture of phosphoric acid and nitric acid, with a non-ionic surfactant, has been described.[69] Effective adhesion of organic coatings has also been claimed with a cleaning solution containing glycol ether, triglycol dichloride and 1-30% nitrosulphuric acid.[70] Boeing[71] have patented a process based on phosphoric acid anodizing that is designed to clean the surface of the aluminium and replace the natural aluminium oxide film with an oxide of controlled thickness and topography. The resultant surface is claimed to be suitable as a substrate for adhesive bonding.

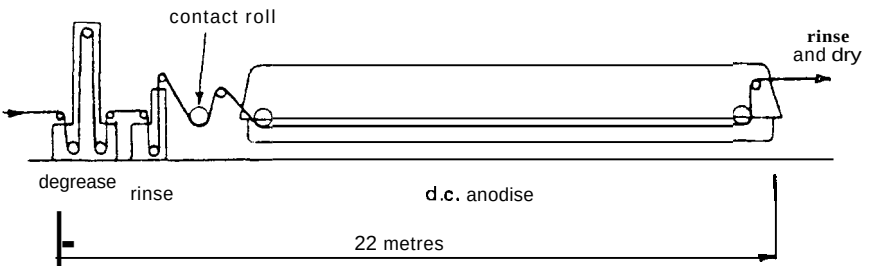
Electrolytic cleaning in acid solutions

Sulphuric acid is used in many cleaning formulations and hot sulphuric acid is a relatively good degreasing solution by itself but its action can be considerably improved by using it electrolytically.

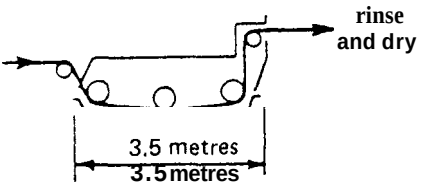
This technique has been used particularly in the aluminium industry, in the preparation of materials used for packaging purposes. It was first used by Nordisk in Norway,[72] who developed a continuous cleaning line, with alkaline degreasing followed by d.c. anodizing under conventional conditions in a sulphuric acid electrolyte, to give anodic film thicknesses of 0.1-0.3 microns. This provided a good pretreatment for subsequent application of lacquers for canning purposes, but was a relatively slow multi-stage operation.

Alcan later demonstrated that degreasing and surface preparation of strip could be carried out at very high strip speeds (up to 450 m/min) by using a hot sulphuric acid electrolyte (above 40°C) under either a.c. or d.c. conditions.[73,74] The hot acid and the vigorous evolution of gas produced by the electrolytic action, combine to give a thorough degreasing treatment. Under these conditions an electrolytic pretreatment time of only 2-3 seconds is required, compared to 20-35 seconds for more conventional processes. Consequently the hot electrolytic pretreatment equipment is very compact[75] and this is illustrated diagrammatically in Fig. 4-2.

Electrolytic treatment in sulphuric acid, whilst thoroughly degreasing the strip surface, also produces an anodic oxide film, and this coating is typically about 0.05 microns in thickness. The high degree of oxide attack and roughening produced by the elevated electrolyte temperature (40-100°C) is an important factor in the success of this pretreatment for lacquering, and strip degreasing lines working on this principle are now in use in several countries.



(a) d.c. anodising section



(b) Hot electrolytic pretreatment replacement

Fig. 4-2. Floor space required by d.c. anodizing versus hot electrolytic pretreatment[75]

More recently Alcan[76] have described a new high-speed electrolytic cleaning line which has been installed in their plant in Nachterstedt in Germany. This is a line with a maximum width of 2.2 m, a maximum gauge of 2.5 mm and a maximum linespeed of 150 m/min. The line is designed to give rapid cleaning of a range of alloys, including those with a high magnesium content, and a phosphoric acid electrolyte is used. This is capable of etch rates of up to 6-10 $g/m^2/min$ and is said to provide a very clean surface. The line is also capable of producing a thin anodic coating as a pretreatment for application of organic materials, and again the electrolyte is phosphoric acid.

Cleaning is achieved by treatment under conditions where dissolution of the anodic film formed is faster than the rate of film growth and only a thin barrier film is produced.[77] The high speed anodizing stage is operated at temperatures just below the point where the rate of dissolution overtakes the film growth rate, so a relatively open porous structure results. Typical conditions for these treatments are shown in Table 4-3.

The cell is a horizontal type but is quite different to conventional designs. **A** conventional cell of the type used in the lines described earlier in this section is shown in Fig. 4-3. The strip is passed through 'pillar box' shaped electrodes made of graphite, which are connected to either side of a single-phase ac power supply. Because of the higher resistance of the phosphoric acid electrolyte, this design is less suitable than for sulphuric acid cleaning. The new cell design (Fig. 4-4) aims to minimise inductive and resistive losses. In this design the electrodes are not immersed in the electrolytic bath, but electrolyte is pumped, counter to the strip direction, into the gap between the electrodes and the strip, and it then falls into a collecting tray. Squeegee rolls are used to contain the electrolyte and maintain strip position. The cells are operated in the liquid contact mode, and the full line arrangement comprises three pairs of single phase cells that can each be operated in either a cleaning or anodizing mode, and this gives a great deal of flexibility. This line is also monitored by means of impedance measurements, so the cleaning and anodizing processes can be controlled.

Electrolytic cleaning in phosphoric acid has also been described by Boeing,[78] and Felisari[79] covers cleaning by what he describes as 'hyperanodizing'. This takes place when the electrical field intensity during anodizing is higher than the breakdown density of the film. Under such conditions extremely intense energy exchanges are said to occur in the surface regions, and this immediately removes surface impurities and leaves a very clean surface for further processing, particularly in continuous processes. In practice low concentration (2-5%) acidic electrolytes are used at moderately high temperatures (80-90°C).

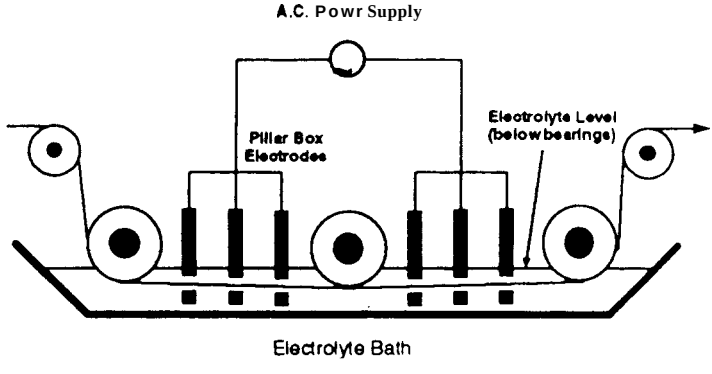


Fig. 4-3. Horizontal dip immersion cell arrangement[76]

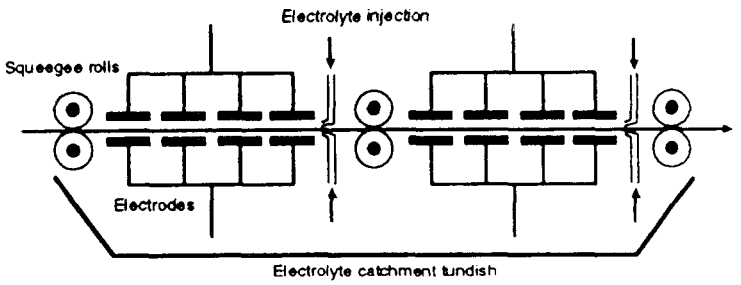


Fig. 4-4. Schematic diagram of cell pair showing counter flow nozzle arrangement[77]

TABLE 4-3

Typical values for cleaning and anodizing[76]

	Cleaning	*Anodizing*
Temperature ("C)	80-90	50-70
Acid Concentration (g/l)	150-300	150-300
Aluminium Concentration (g/l)	0-10	0-10
Voltage (volts)	20-30	50
Current Density (kA m^{-2})	1-5	1-4
Charge Density (kCoulombs m^{-2})	0.5-12(60)	0.25-15
Time **(s)**	2-10(60)	0.25-6
Film Thickness (nm)	2-5	5-200

Matt etching in acids

A 5% ammonium bifluoride solution can be used at 50°C (120°F) to give a matt surface on mechanically polished aluminium and aluminium alloys. After polishing, the parts are degreased in trichloroethylene, cleaned in alkali and dipped in nitric acid before treatment in the ammonium bifluoride solution which is contained in a rubber- or plastic-lined tank. After the initial hydrogen evolution, an aluminium fluoride film forms on the surface and almost stops the reaction. With super-purity material, 0.02% copper sulphate is added to the solution.[80] Subsequently the surface is dipped in 50% (vol) nitric acid to remove the fluoride film and is then anodized to a thickness of 5 μm (0.2 mil). At higher film thicknesses the coating reverts to the normal appearance as the etched layer is removed.

Interesting effects can be produced with mixed acid solutions. It is known for instance that the Erftwerk chemical polishing bath described on p. 127 will produce matt etched effects on aluminium of commercial purity or will etch high purity aluminium when it is used outside the polishing range. Paolini and Sacchi[81] have made a detailed investigation of the system ammonium bifluoride/hydrofluoric acid/nitric acid over a wide range of concentrations and conditions, and they have defined a region of the ternary diagram where the most attractive and uniform satin finishes can be obtained. They recommend a composition:

ammonium fluoride NH_4F	105 g/l
hydrofluoric acid HF	56 g/l
nitric acid HNO_3	15 g/l
lead nitrate $Pb(NO_3)_2$	0.03 g/l

With this composition the metallographic etching is suppressed and the action is similar to that which takes place during the first few seconds of Erftwerk treatment, but the etching mode is sustained and true polishing conditions are not set up. The studies did not include the degeneration in use of this bath, or the maintenance required to keep it operating.

Hydrofluoric acid has also been added to other acid mixtures to produce decorative etched surfaces. Phosphoric acid 10-50 g/l with hydrofluoric acid 2-10 g/l has been suggested,[82] and another proposal uses aqua regia and a nitrate ion in an amount sufficient to produce a reddish brown colouration in the solution,[83] while a further patent uses hydrochloric acid, potassium nitrate and hydrofluoric acid.[84]

Solutions based on complexing agents, e.g., E.D.T.A. or gluconate baths, as well as alkaline and ferric chloride solutions are also sometimes used to obtain surfaces ranging from satin to matt, as are some chemical polishing baths based on phosphoric-sulphuric acid (see Chapter 3).

Acid dips associated with alkaline cleaning

If, before alkaline cleaning, the aluminium surface shows signs of corrosion or staining due to chemical attack or poor storage conditions this may affect the efficiency of the cleaner. Some aluminium alloys may have a mixed oxide film[85] containing aluminium oxide and magnesium oxide on their surface. If the surface corrosion deposits or oxide films are not removed by the cleaner, preferential attack of the aluminium surface may result. This may occur in the cleaner itself if it is of the light etching type or, if the oxides or corrosion products are not removed in the cleaner, then preferential attack will take place during the subsequent alkaline etch stage.

A short dip in 50% nitric acid at room temperature or a flash anodizing treatment in a sulphuric acid anodizing electrolyte before the cleaning stage will remove the offending films or deposits, resulting in a more uniform alkaline etch.

This treatment is not a solution to dealing with corroded aluminium, as where the surface is heavily corroded the corrosion pits will be opened up and further exaggerated by the etching process.

Acid desmutting treatments

After cleaning in hot alkaline solutions, or after a sodium hydroxide-based etch, a black smut is left on the aluminium surface. This smut tends to be heavier the lower the purity of the aluminium and the more highly alloyed it is, and it is particularly heavy on copper-based alloys. It consists of particles of oxide, intermetallics, silicon, etc., which are insoluble in the alkaline solution, and in general are quite loosely held on the surface. Smut is usually removed by a dip in an acid solution, most commonly 25-50% (vol) nitric acid, used at ambient temperature. This removes normal smut layers, including those on high copper containing alloys, quite quickly, and a dip of 3-5 minutes is usually sufficient to give a clean surface. Not all smut, however, is removed so easily, and additions to the nitric acid may be required. In particular, alloys having a high silicon level will nearly always require treatment in an acid solution containing small amounts of fluoride. For normal 6063 extrusions, desmutting solutions based on sulphuric acid (spent anodizing electrolyte), with addition of 1-2% (vol) of nitric acid, have been effectively used.

Desmutting solutions based on sulphuric acid or acid sulphates and chromic acid. with or without fluorides, have been used with a variety of alloys, and a typical composition, again used at ambient temperature, is:

chromic acid	100 g/l
sulphuric acid	60 g/l
ammonium bifluoride	3-4 g/l

However the general reluctance to use solutions containing hexavalent chromium, because of effluent treatment problems, has reduced the popularity of this type of desmut solution, and alternatives based on ferric sulphate have taken its place. A problem with this type of solution is the maintenance of the iron in the ferric form, and oxidizing agents such as hydrogen peroxide are often added to achieve this. Pennsalt[86] have described a concentrated mixture based on the following:

sodium bisulphate	70% (wt)
ferric sulphate	25%
sodium fluoride	3%
magnesium carbonate	2%

This is used at a concentration of about SO g/l (8 oz/gal). The magnesium carbonate is added to improve the flow characteristics of the solids, rather than imparting any improvement in desmutting characteristics.

Amchem[87] describe mixtures based on 5-21 g/l ferric ion, 0.1-2 g/l of thiourea and 0.5-2 g/l fluoride used at pH 0.1-1.8, and another patent[88] is based on ferric sulphate and urea nitrate. Diversey[89] cover mixtures of ammonium persulphate, acid sulphates and inorganic nitrates with a typical composition of

ammonium persulphate	20 g/l
sodium bisulphate	60 g/l
ammonium nitrate	17 g/l

The benefit of the nitrate is that it prevents corrosive attack of the aluminium, if left in contact with the solution for longer than normal times.

The Martin Marietta Corp. have a patent[90] for a de-smutting process based on nitric acid containing an alkali metal or ammonium halate salt. Sodium or potassium bromates are the preferred salts. Ammonium vanadate, molybdate or tungstate may be used as activator in a weight ratio of 1:1 to 1:2.5 activator to bromate.

Acid etching for designs

Designs, letters, graduations, etc., may be obtained on aluminium surfaces by etching in acid solutions. Etched designs of this kind may then be filled in with pigmented lacquer or enamel or they may be colour-anodized.

The first step in design etching is to clean the surface thoroughly to ensure adhesion of the stop-off and promote uniformity of attack. For this purpose the work is degreased and given a hot alkali cleaning. After cleaning, the required portions are stopped-off from a master plate or roll, and the material is fired or baked on to improve its protective value and to permit the article to be handled more easily. In applying the stop-off, the design is printed on the metal surface with etching ink. While the ink is still tacky, the surface is dust printed with finely divided asphaltum, bees-wax and resin, and the loose non adherent powder is removed from uninked areas by low-pressure air-blast or by dusting with talcum powder. The asphaltum should then be fused by heating the work to about 200°C (400°F).

Two solutions may be used for the actual etching process. The work may be dipped into an aqueous solution of hydrochloric acid. In this solution, streaks are produced unless the surface is uniformly clean. They may be avoided, however, by a preliminary dip in nitric-hydrofluoric acid solution. A somewhat smoother etch is obtainable by solutions of hydrochloric acid saturated with sodium chloride. This process may be accelerated by addition of a small quantity of nickel or cobalt chloride. A coating of metallic tin may be obtained, on the other hand, by dipping the work in an aqueous solution of stannous chloride prior to etching. If a deeply etched surface is required, the work should be periodically removed from the bath and the sides of the engraving blocked up with a suitable resist in order to prevent undercutting of the metal. The solution should preferably be agitated to prevent local attack which would result in non-uniformity of depth of etching.

A process for etching aluminium name plates has been described by Anders.[91] In this the metal is etched in a bath containing:

10% ferric chloride solution	2 pt (vol)
10% cupric chloride solution	2 pt (vol)
conc. hydrochloric acid	1 pt (vol)
denatured alcohol	2-6 pt (vol)

The aluminium is stopped-off with bituminous paint which can subsequently be removed with petrol. The commercial manufacture of some aluminium name plates is described in Chapter 10.

According to an American patent," decorative effects are obtained by annealing and cold forming the aluminium to reduce its thickness by up to 15% and heating to 600-1150°F (320-620°C) for up to 3 hours to develop large crystals. Subsequently the surface is etched to expose the crystal faces, anodized and sealed.

Acid etching for lithographic plates (Electrograining)

The so-called 'graining' process for aluminium or zinc plates to render them suitable for the lithographic offset printing process was originally carried out mechanically using glass or steel balls to gently rub a fine damp abrasive into the sheet with a circular oscillatory motion. This lengthy procedure has now been replaced by electrochemical etching techniques which can give an equivalent finely textured matt etch with no directional effects or metallurgical features in evidence.

The electrolytic etching or electrograining process is usually carried out in a dilute hydrochloric acid electrolyte (about 15 g/l) at temperatures of 20-30°C. It is an a.c. process and alternating current is passed between pairs of plates, placed parallel to each other and 10-20 cm apart. Current densities of 200-500 A/m^2 are used at voltages of about 8-15 V. Etching is typically carried out for 5-10 minutes and produces a heavily pitted, but very uniform, matt surface (Fig. 4-5). This surface is important in the printing operation as it controls the water carrying characteristics of the lithographic plate, and control of the pit distribution and the pit depths produced is important to the plate manufacturer.

Although the process has been used industrially since the 1950s, very little detailed information was available in the literature for many years. An early patent[93] refers to the known process described above, and claims benefit from using an interrupted current supply, for example 1 minute etching periods followed by intervals of about 20 seconds. Another patent[94] indicates the importance of cleaning the aluminium sheet surface, by conventional etching and desmutting, before the electrograining process. More recently, however, detailed studies of the hydrochloric acid electrograining process have been made by Thompson and Wood[95] and by Dowell.[96]

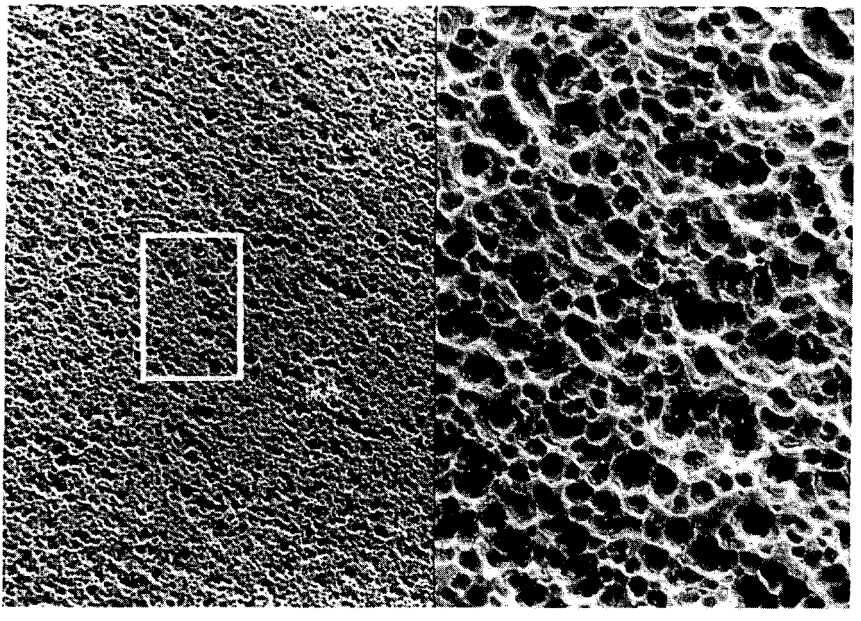


Fig. 4-5. Typical electrograined surface

The former authors showed that initial pit formation occurs by local attack of metal at pre-existing flaws in the air-formed oxide film on the surface of the aluminium. During the first stages of the process a large population density of small pits is rapidly produced, and some of these develop into much larger pitted regions. Later, when a steady state is reached, the rate of attack of the aluminium, as measured by weight loss, is approximately constant with time, indicating little resistance to pit growth by deepening and lateral growth. During this period substantial underming of the flat regions takes place between the coarse pits, leading ultimately to an overall pitted and convoluted surface. During the pitting process the formation of a surface film is apparent, particularly after long treatment times. This is visible on the final electrograined surface as a grey film, which can readily be removed by a short dip in a dilute sodium hydroxide solution, or a conventional chromic acid/phosphoric acid stripping solution. This film is mainly composed of hydrated alumina and it is probably discontinuous, as it does not appear to hinder dissolution of the aluminium. It is very thin and represents only 2-3% of the weight loss by metal dissolution under typical conditions. The hydrated alumina is apparently produced during the negative half cycle of the a.c. treatment by a dissolution/precipitation mechanism, caused by the production of a high local pH due to hydrogen evaluation, or alternatively by protonation and hydration of the initial air-formed film.

Processing of plates in the hydrochloric acid electrolyte leads to build up of aluminium in the solution and loss of acidity, and the changes in electrograined surface produced were studied by Dowell.[96] He showed that samples from a freshly prepared electrolyte exhibit fine, even pitting with roughly hemispherical pits. After processing a few panels there is a tendency for the pits to become more 'worm-like' in shape, and further processing produces more irregular pitting patterns with localised, relatively unattacked plateaux. Superimposed on these changes from one surface type to another is a general increase in the coarseness of the etched surfaces. This latter effect was probably due to the increasing voltage used *to* maintain the chosen current density, and increasing aluminium content and decreasing acidity caused other changes. The effect of aluminium content **is** recognised by Kodak,[97] who claim the benefits of removing the aluminium by means of cationic ion-exchange resins.

Dowell shows that the effect of the electrolyte temperature is small, but that electrolyte concentration is important. Low acid concentrations lead to the pit and plateau type structure, whilst higher than normal concentrations give much more irregular dissolution. Additions of sulphate to the electrolyte produce increasing coarseness of pitting and progressively greater proportions of plateau area.

Since then extensive studies of the electrograining process have been carried out by Terryn, Vereecken and Thompson.[98,99] They confirmed the formation of a high density of hemispherical pits which merge with time during the electrograining process. Through variation of the electrograining frequency and anodic or cathodic charge, the hemispherical pits propogate through the development of a high population density of cubic pits during the positive half cycle, which form the wall of the hemispherical pit. The size of the cubic pits decreases with increase in frequency, leading to relatively smooth hemispherical pits. On the negative half cycle, etch products deposit as highly porous hydrated alumina over the relatively uniformly pitted aluminium surface. The film is deposited as colloidal material containing fine, amorphous $Al(OH)_3$ particles, together with appreciable quantities (about 90%) of water. Metallic aluminium particles, up to 2 microns in size, resulting from undermining of the substrate during pit propogation, are also present in the film, and are responsible for the 'smutting' or blackening of the electrograined surface. From a.c. frequency studies it was shown that the film develops during the negative half cycles when sufficient boundary layer alkalinity occurs. Thus for a.c. waveform frequencies below about 250 Hz, hydrogen evolution causes a significant local increase of pH allowing the formation of aluminate ions. The aluminate ions are only soluble in the high pH interfacial region, and precipitate as $Al(OH)_3$ upon contact with the bulk acid electrolyte.

The development of a distinct morphology correlates with the ratio between the number of sites where key pits are initiated and the propogation rates of the sites.[100] The number of sites and their susceptibility to pit initiation, is determined by the surface condition of the aluminium substrate.[101,102] The activation of sites

depends on the electrolyte conditions,[98,103] and the propogation rate of sites is controlled by the applied alternating current and the proportion of the current concentrated at the pit site.[104,98,101]

Depending on the electrograining conditions three different morphologies can be produced,[105] the desired uniform morphology characterised by hemispherical pits, their walls decorated with a high population density of cubic pits, a similar but non-uniform morphology, and an etched morphology comprising an abundant number of uniformly distributed cubic pits. The effect of electrograining current density and acid concentration in a hydrochloric acid electrolyte in determining the desirable operating area is shown in Fig. 4-6.[106,107]

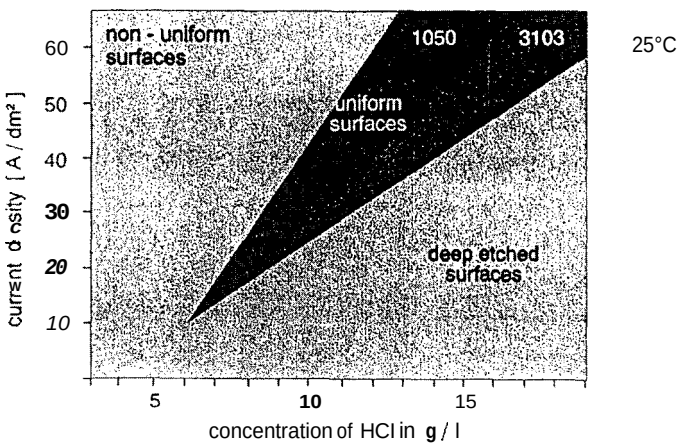


Fig. 4-6. EC Graining in HCl. Effect of Mn[106]

In the past the bulk of commercial electrograining was carried out in hydrochloric acid electrolytes, but more recently many plate makers have switched to nitric acid electrolytes. Comparisons of electrograining in hydrochloric and nitric acids have been reported by Laevers *et al.*,[103,101], Suzuki *et al.*,[108] and Koroleva et al.,[109] the latter work particularly concentrating on the role of second phase particles. The work has shown that the morphologies obtained by electrograining in the two electrolytes are fundamentally different. As indicated earlier, in hydrochloric acid the morphology is built up from hemispherical pits containing fine cubic pits which are crystalographically oriented. On the other hand the basic morphology in a nitric acid electrolyte is a small, flat-walled hemispherical pit in which the anodic dissolution of aluminium occurs isotropically. The susceptibility for pitting and hence for graining is much higher in chloride electrolytes and pits are initiated much faster and at lower

potentials, and they grow at much higher rates. These effects are shown diagrammatically in Fig. 4-7.

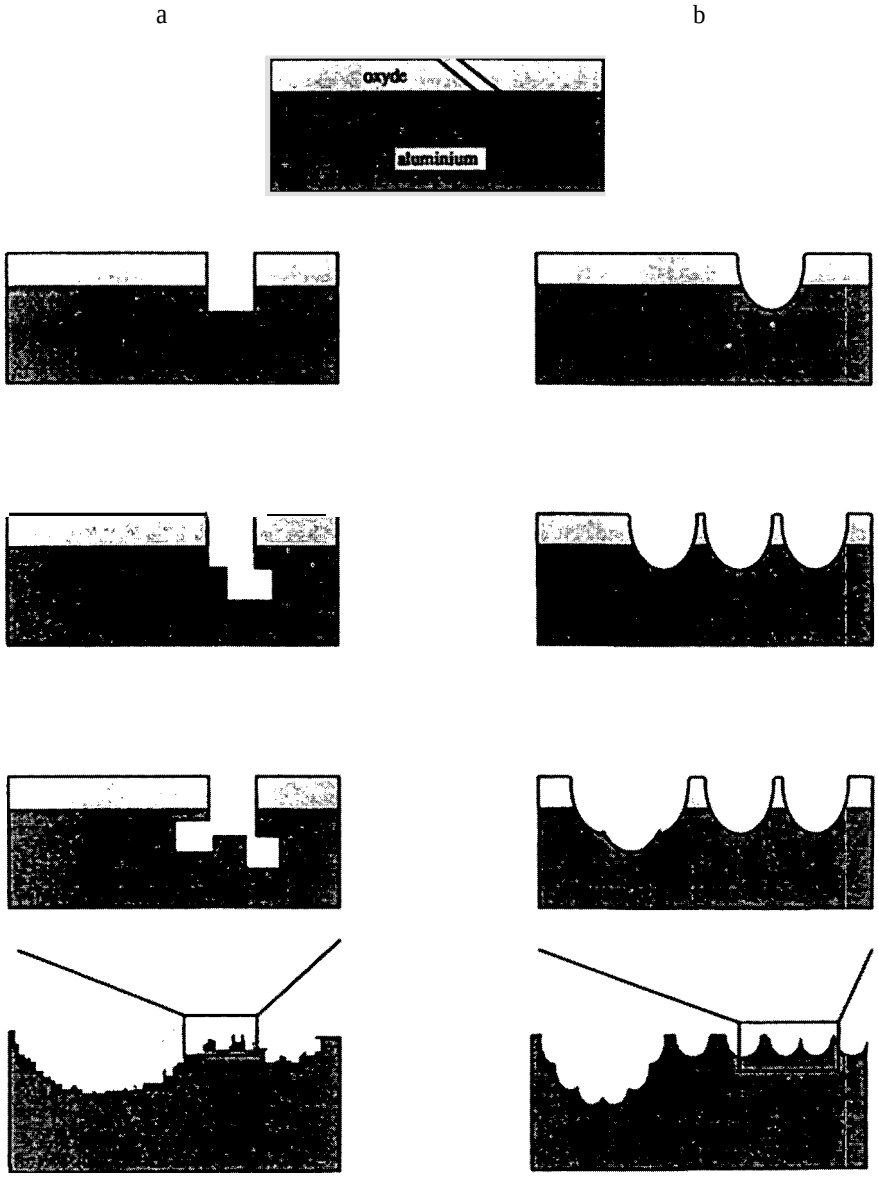


Fig. 4-7. Illustration of the ordering of the morphological building element for treatment in hydrochloric (Fig. 4-7a) and nitric (Fig. 4-7b) acid, leading to the eventual electrograined morphology"'

There is also a difference during the negative half cycle as the etch products are deposited differently. In the case of hydrochloric acid electrolytes the surface is covered with a non-uniform thin film, but with nitric acid electrolytes the etch products are deposited preferentially as a belt around the rim of the pits. In effect all this means that higher voltages and current densities are necessary in nitric acid electrograining than in hydrochloric acid electrograining, but it is possible to produce finer electrograined surfaces in the former electrolyte.

Work on the effect of second phase constituents[109] showed that their role was also different in the two electrolytes in that, in nitric acid, pitting of the alloy started with the dissolution of these second phase particles, whereas in hydrochloric acid they dissolved more slowly than the matrix. In nitric acid the cavities produced promoted pit propogation over the whole surface, so the population density and uniformity of the second phase particles was important, particularly in the case of Mn containing alloys.

The earliest suggestion of nitric acid as an electrograining electrolyte was by Jestl[110] who used it in conjunction with waste sulphite liquors and aromatic aldehydes. Since then many acid combinations, often involving film forming components, have been examined.

Alcan[111] used mixtures of hydrochloric acid and phosphoric acid, and claimed that electrolytes with 2-20 g/l hydrochloric acid and 1.5-15 g/l phosphoric acid reduced sensitivity to sulphate ions and produced more finely electrograined surfaces. Kodak[112] used mixtures of hydrochloric acid and boric acid, and claimed that an electrolyte of 2-2.5% (vol) hydrochloric acid and 1.5-4% (wt) boric acid produced uniform graining at high current densities, particularly on the manganese containing alloy 3003. Hoechst[113] and Depiereaux[114] also claimed processes based on mixtures of nitric acid and boric acid, and Hoechst covered mixtures of nitric acid and fluoride,[115,116] and nitric acid or hydrochloric acid and hydrogen peroxide."' Polychrome[118] and Fuji Film"' again used mixtures of hydrochloric acid and nitric acid whilst Alcoa[120] recommended mixtures of hydrochloric acid and gluconic acid. In the latter case, an electrolyte of I-5% (vol) hydrochloric acid and I-3% (vol) gluconic acid is said to allow the treatment of 1100 and 3003 material at a wide range of current densities, and with reduced sensitivity to aluminium build-up. A similar electrolyte described by Polychrome[121] contains 0.75-3.5% (wt) hydrochloric acid and 0.2-1% (wt) tartaric acid. This electrolyte is unusual in that it only operates satisfactorily at relatively high temperatures (45-75°C). Vickers[122] have used a range of hydrochloric acid and monocarboxylic acid mixtures using acids such as formic acid, propionic acid, butyric acid and acetic acid. Again the benefit of the additions is the production of fine grained surfaces on the higher strength alloys. In a similar development Hoechst[123] have claimed the use of hydrochloric acid with trichloroacetic acid and other organic acids such as hydroxy-ethane-phosphonic acids.[124] Double electrograining treatments have been claimed by Fuji Film[125] and Kodak.[126]

Whilst most electrograining processes use conventional single-phase a.c. power supplies, benefit from rather more complex electrical arrangements has been claimed by several authors. Thus N.K.K.[127] have shown that independent control of the anodic and cathodic parts of the cycle can lead to more effective electrograining. In particular the anodic voltage should be higher than the cathodic voltage, the anodic half cycle should be equal to or less than the cathodic cycle, and the ratio of cathodic to anodic coulombic input should be in the range of 0.3-0.8. In similar work Fuji Film have shown the benefits of controlling the time of the positive and negative periods,[128] and of an assymetrical waveform,[119] and N.K.K. and Fuji Film have claimed use of a current bypassing technique using an auxilliary anode and a diode.[129] In other work Polychrome[130] have used d.c. superimposed with a.c., and Hoechst[131] have used pulsed d.c., which is said to give tube-shaped cavities. Hoechst[132] have also used biased waveforms with a superimposed anodic potential. United Chemi-Con[133] found benefit from a special wave shape, whereas Fuji Film,[134] in a continuous electrograining operation, described a process with variable coulombic inputs along the length of the strip, and another with deliberate pause times of 1-30 seconds.[135] In a different direction Polychrome[136] claim a reduction in smut during electrograining by the use of a.c. of higher frequency than normal in the range of 140-400 Hz.

In most cases, material for lithographic purposes is anodized to a thickness of 0.5-3 microns after electrograining. As might be expected, conventional d.c. sulphuric acid anodizing has been widely used, but other electrolytes have been shown to have benefits and are employed. Thus Howson-Algraphy[137] have tested a 5-50% (vol) phosphoric acid electrolyte, and Kodak[138] claim the use of 15-30% (vol) phosphoric acid at 25-50°C, 50V and a current density of 2.5A/dm^2 to produce a 0.5 micron coating. Kodak,[139] Vickers[140] and Fuji Film[141] all show the benefit of phosphoric acid treatment after sulphuric acid anodizing. Hoechst[142,143] cover the use of a sulphuric acid- phosphoric acid anodizing electrolyte, or double anodizing first in a phosphate containing electrolyte and then in sulphuric acid,[144] and Vickers[145] cover double anodizing first in phosphoric acid and then in a mixture of phosphoric acid and sulphuric acid. Hoechst[146] also describe anodizing in phosphoric acid containing additions of sodium or potassium phosphate. Other work by Hoechst[147] describes the use of a treatment in hexametaphosphate and hydroxy-carboxylic acid after anodizing, and there are numerous claims for silicating after anodizing.[148,149,150,151] Fuji Film[152] have worked with combinations of aliphatic phosphonic acids and aromatic phosphinic acids. Yet another variant is the use of a.c. rather than d.c. anodizing, and Van der Grinten[153] claim a.c. anodizing in sulphuric acid and Fuji Film[154] cover a.c. anodizing in phosphoric acid.

Most plants produce lithographic plates on a continuous, rather than on a batch, basis, and this is true of all the larger plants. Japanese workers[155] have described such an installation and a typical electrograining cell is shown in Fig. 4-8.

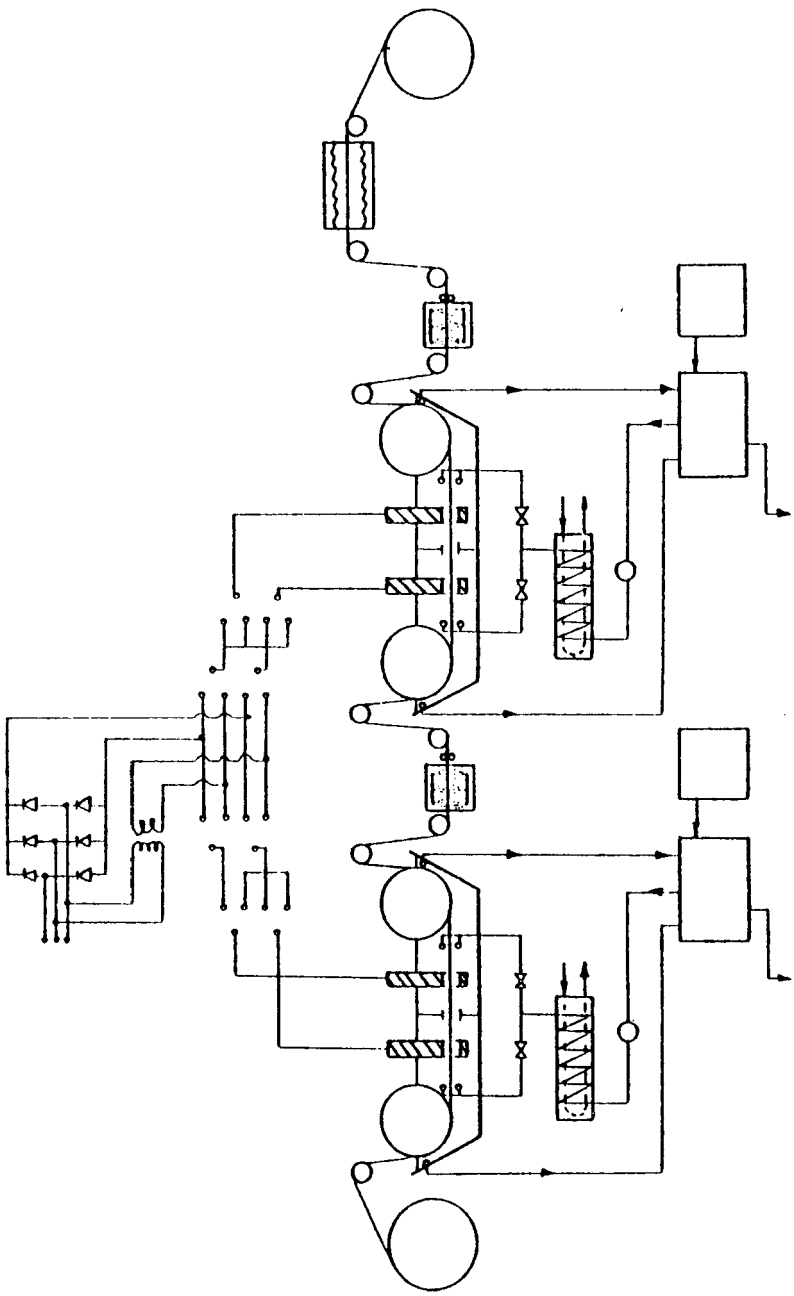


Fig. 4-8. Schematic illustration of an arrangement of electrolytic etching and anodizing plant

The plant shown here consists firstly of an a.c. electrograining cell and then an anodizing cell. Strip is uncoiled and passes over guide rolls into the first cell. This is provided with two electrodes of opposite polarity made of material such as graphite or lead. The cell is partitioned down the centre and an orifice allows the strip to pass freely through. After electrograining, the strip passes through guide rolls into a rinsing chamber where it is thoroughly washed, before passing to a second electrolytic cell where it is anodized under either d.c. or a.c. conditions. The grained and anodized strip is then rinsed again, dried and recoiled.

The electrolyte in each cell is fed from a storage tank, via a pump, into a heat exchanger (to cool or heat the electrolyte), and is then sprayed onto the strip surfaces. Excess electrolyte in the cell passes over an overflow system and is returned to the storage tank, where fresh electrolyte is added to maintain the appropriate concentration.

The plant described uses a 'liquid contact' cell for both electrograining and anodizing. With this system no direct contact is made to the strip and it is described in greater detail in Chapter 7, part 8. Numerous continuous techniques and operations have been patented, and these include special power supplies and anodizing conditions[156,157,158,159] and special cell designs,[160,161,162,163,164,165,166,167] most of them from Fuji Film.

Whilst 1100 and 3003 alloys are most commonly used for lithographic purposes special alloys have also been developed, particularly to provide a higher strength material that is readily grained. Thus Alusuisse[168] disclose an alloy containing 0.1-0.75% Mg, 0.45-0.7% Cu, 0.1-0.7% Fe and up to 0.3% Si, and V.L.W.[169] describe an alloy 0.7-1.3% Mg, 0.7-1.3% Si, 0.4-1.0% Mn and up to 0.1% Cu, and Alcoa[170] cover an alloy containing 0.2% Cu max., 0.055-0.085% Si, 0.55-0.75% Fe, 0.2% Mn max., 0.4-0.7% Mg and 0.25% Zn max. Many other alloys have been suggested including Al-Fe-Mn alloys,[171,172,173,174] Al-Mg-Fe alloys[175,176] and Al-Mg alloys.[177] In a completely different direction, British Aluminium[178] cover the use of an aluminium-calcium alloy containing 0.1-4.5% Ca and up to 2.0% Mn. The benefit of this alloy is that it can be etched in a conventional sodium hydroxide based solution, and gives an etched surface which is suitable for lithographic applications. Alcan[179] has described alloys containing Hg, Ga, In, Sn, Bi, Ti, Cd, Pb, Zn or Sb, or having these elements in the electrograining solution, in order to speed up the electrograining process, whilst Fuji Film[180,181] has looked to the future in covering the use of continuous roll casting for the production of litho materials.

Dowell[182] has discussed the effect of metallurgical factors in the electrograining of 1100 type alloys, and Laevers et al.[183] have described the effect of manganese.

Acid etching for PTFE adhesion

The application of the non-stick polymer polytetrafluoroethylene (PTFE, Fluon, Teflon) to aluminium can be carried out by means of primers comprising emulsions

containing chromic and phosphoric acids, but this system has not been widely employed in the food industry and the problem of attaching the pure polymer to an aluminium substrate demands the production of a deeply etched surface with undercut cavities to provide a mechanical keying effect.

This type of etched surface has usually been obtained chemically in dilute hydrochloric acid of about 5-10% by volume used at 50-70°C for about 15 minutes. The deep undercutting mode of attack is a unique interaction between aluminium and chloride and has found various applications over the years for nickel and chromium plating, anchoring selenium to aluminium base plates of rectifiers, or increasing the surface area of electrolytic capacitor anodes. Its usage for attaching PTFE to aluminium was however covered in two French patents in 1954 in time to secure a substantial stake in the rapidly increasing market for non-stick kitchenware. The first[184] suggests 10% hydrochloric acid with nitric acid used for from 8 minutes at 75°C to 2 hours at 20-25°C, and the second[185] proposes an etchant of hydrochloric acid 20 volumes, water 79 and 40% hydrofluoric acid 1 volume used for 10-15 minutes at 20°C. The requirement is that the surface should be etched with cavities less than 30 mm across.

Japanese workers have used electrolytic treatments to provide a basis for PTFE coating. Sumitomo Electric Industries propose roughening the aluminium surface in a 4% potassium chloride solution under electrolytic conditions and then anodizing the roughened surface in oxalic acid or sulphuric acid to give a harder surface beneath the PTFE coating,[186] whilst in another patent[187] they **claim** the benefits of anodizing in an alkaline bath. Sumitomo Chemical Co.[188] suggest d.c. electrolysis in a 0.1-1% (wt) chloride solution at 20-90°C and others suggest d.c. treatment (aluminium anodic) in a nitric acid/sodium chloride electrolyte,[189] which is claimed to produce small bulbous pores. Pechiney propose anodizing in a sulphuric acid electrolyte containing chloride.[190]

Many attempts have been made to produce a harder surface beneath the PTFE coating, and anodizing, as indicated above, has been a popular choice, but Matsushita Electric Industries[191] suggest the use of an Al-14-25%Si alloy which is etched to leave the silicon particles exposed and these strengthen the PTFE layer, and Boeing[192] use a flame-sprayed alumina coating. Improved adhesion is claimed from adding a silane coupling agent to the resin[193] and by use of a special Al-Mg-Mn alloy.[194] Hard anodizing over an aluminium surface of closely defined roughness has been used as a substrate for PTFE coating by Fissler.[195] Alluflon[196,197] have used a water-based polyamide/imide resin and dimethylamine/ethanol mixture to improve adhesion of PTFE to aluminium surfaces, and Alcoa[198] claim a continuous process for producing highly reflective surfaces using a thin film produced by phosphoric acid anodizing coated with a light permeable fluoropolymer. Workers in Japan[199] have compared the adhesion of Nylon 6 on phosphoric or sulphuric acid anodized surfaces and on an etched surface produced in a 20%(vol) sulphuric acid / 150 g/l ferric sulphate solution. They found that the acid etching treatment produced the best results.

Etching of foil for electrolytic capacitors

The etching process applied to aluminium foil for use in electrolytic capacitors is a specialised technique for achieving the highest practicable increase in surface area, because the capacity of the final product is directly proportional to the surface area. Since this may be increased from 7-10 times or considerably more in the case of low voltage components, the benefit in reduction of size, weight and cost is considerable.

The traditional etching medium was dilute hot hydrochloric acid and this functioned tolerably well with the 99.8% foil purities originally used, but with the advent of 99.99% aluminium the etching **was** both slow and almost impossible to control. Chemical etching has however been used in Germany for many years by using two or more baths in sequence of decreasing aggressivity.[200] **A** typical composition is HCl 400 ml, HNO_3 100 ml, $FeCl_3$ 100 g, water 1 litre used at 30°C for 2 minutes.

The practically universal method in current use is to employ an electrolyte of aqueous sodium chloride and etch with direct current in a continuous process using from 1-25% sodium chloride at 20-110°C. Capacitor foils are of 80-100 μm thickness and the etching process removes about 30% of the foil weight, which in the case of the thicker foil requires 4,300 coulombs/dm^2 or a current density of 24 A/dm^2 for 3 minutes.[201,202,203] The object of the etch is to produce a very rough surface with a finer cubic surface superimposed.[201,202,204] It is also important to achieve uniform ubiquitous etching of the surface without any passive areas, which form so readily on high purity foil. A structure suitable for etching is produced by heating the foil for several hours at a temperature of 450-600°C, a procedure which is believed to orient the (100) and (110) planes parallel to the rolled surface.[203,205,206] With commercial purity aluminium a small grain size and a fine constituent distribution increases capacity by 15-20%, and the presence of fine Al-Cu precipitates can increase it still further.[207] Sumitomo workers[208] have described the benefit of 5 ppm of tungsten in the high purity foil, and Showa Aluminium[209] have claimed a foil containing 50-500 ppm of magnesium. With this alloy they propose a two-step process, using in the first stage a 3-10% (wt) HCl and 10-40% (wt) H_2SO_4 electrolyte used at 70-90°C with a current density of 10-40 A/dm^2. This is followed by treating in a further bath containing 3-10% HCl at 70-95°C and 0-10 A/dm^2.

Although a steady smooth direct current supply gives the most uniform etching, a controlled fluctuation may increase the surface area[210,211,212] and in fact remarkably effective etching can be obtained with pulses of high density current, as Thomas discovered by using successive condenser discharges for etching.[213] Quite a number of patents have introduced variations on this theme.[214,215,216,217,218,219,220] It is possible to increase the area substantially by increasing the current density as the treatment proceeds.[221] More recently Matsushita Electric have used interrupted a.c. cycles[222] and biased electrical supplies,[223] and other Japanese workers[224] have claimed the benefit of two half waves having different waveforms, amplitudes and applied times with a pause period between.

Chloride is essential in some form for this type of anodic etch and such improvements as have been claimed in the electrolyte composition relate to additions to the basic type. These have included 25% sodium chloride with 5% sodium sulphate used at 95°C,[225] or with sodium bisulphate,[226] or sodium thiosulphate;[227] 1% sodium chloride with 1.6% chromic anhydride used at 50°C;[228] sodium chloride with ammonium sulphate;[229] and sodium chloride with tartaric acid or tartrates[230] or boric acid.[231] Hydrochloric acid-nitric acid electrolytes containing chromic acid,[232] citric acid and ammonium acetate,?" or phosphoric acid and sulphuric acid[234] have been suggested by Japanese workers. Sprague Electric, who have numerous patents in this field,[235] claim the use of 1.4-2.3 mole/l of an anodizing acid, 1.1-1.7 mole/l of HCl and 10-2000 mg/l of transition metal ions.[236]

The benefits of a number of these additions have been investigated by Russian workers,[237] who conclude that the addition of acids that do not dissolve the anodic coating, such as boric acid, does not lead to an increase in specific capacitance. On the other hand addition of acids such as sulphuric acid, oxalic acid and tartaric acid or their salts improves etching characteristics. They also found that the addition of nickel or cobalt salts to the etching electrolyte significantly accelerates the etching process and increases the specific capacitance. Many workers describe the 'tunnel etching' that is desirable for high capacity. These are typically 1-2 microns in diameter and 10-100 microns in length[238] and they are formed rapidly, with a much slower and more controllable widening of the tunnels taking place subsequently. A Japanese patent[239] describes a 2-stage treatment to achieve tunnel etching of this type, initially the tunnels being produced by d.c. treatment in an HCl-HNO_3-H_3PO_4 electrolyte, and then a.c. treatment in the same electrolyte causing etching of the side walls of the tunnels. Tunnel etching has increased in importance and Alwitt et al.[240] have described the process in detail. They found that anodic dissolution of aluminium in hot chloride solutions produce a high density of fine etch tunnels that extend along the 100 directions. Tunnels evolve from cubic etch pits when all but one of the pit wall surfaces become passivated. Dissolution then occurs at the one active face at a rate that may initially be as high as 20 A/cm^2. Tunnels have square cross-sections with sides of approximately 1 micron and aspect ratios as high as 100:1. Tunnel growth may be considered as a unique form of pitting corrosion in which dissolution and passivation occur simultaneously with a sustained balance between the two processes. Russian workers[241] studied the effect in a hydrochloric acid / aluminium chloride electrolyte, and Sumitomo[242] have established the importance of the current density used.

3. ALKALINE ETCHING

The most frequently used method for etching aluminium is in aqueous solutions of caustic soda, with or without other additives. It is used for general cleaning

purposes where oxide, grease or sub-surface detritus must be removed, with more prolonged etching to produce satin or matt finishes for nameplates or decorative architectural work, or for deep engraving and chemical milling. It is a fairly cheap and easy method of etching but the details can be exceedingly complex.

Solutions for decorative etching may contain from 4-10% or more caustic soda, used at 40-90°C with perhaps a wetting agent to disperse grease and give a light foam blanket, and sometimes other additions which will be referred to later. The normal operating temperature for cleaning and decorative work is at about 60°C. Fig. 4-9 gives the rate of metal removal at various strengths and temperatures during a 5 minute etching period in the case of 99.5% purity aluminium sheet.[243] These curves refer however to newly prepared solutions and lower values will apply after aluminium has been taken into solution. Springe and Schwall have also published information on the etching rate of 99.5% sheet and 6063 extrusions in caustic soda solutions of 10, 15 and 20% concentration at temperatures between 40 and 70°C.[244] Chatterjee and Thomas have made detailed studies of caustic soda etching of 6063 extrusions,[245] and of 5005 and 3013 sheet.[246]

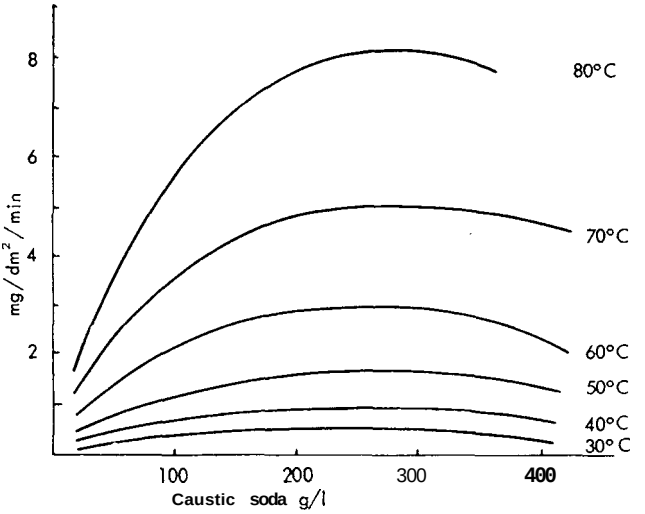


Fig. 4-9. Rate of etching of 99.5% aluminium in caustic soda

Aluminium dissolves in caustic soda with the release of hydrogen to form the compound aluminate which exists only in alkaline solution. The reaction has been written in both of the following ways:

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

$$2Al + 2OH^- + 6H_2O \rightarrow 2(Al(OH)_4)^- + 3H_2$$

The available or uncombined caustic soda decreases as this reaction proceeds and with it the etching rate drops, the electrical conductivity of the solution decreases and the viscosity increases. If no caustic soda is added the bath action becomes very sluggish, but eventually the clear or brownish solution will turn to a milky white and at this point the etching rate will suddenly increase again to a value which may not be very far below the initial etching rate. The reaction at this point is:

$$NaAlO_2 + 2H_2O = Al(OH)_3 \downarrow + NaOH$$

The alumina hydrate or Gibbsite which forms is in a suspension and more free caustic is made available for etching.

The structure of the aluminate ion in solutions of high pH is a question of considerable complexity, and fortunately one that need not concern the practical operator. Moolenaar, Evans and McKeever[247] have examined both the infra-red and Raman spectra of sodium aluminate solutions in water and deuterium oxide (heavy water), and also examined the nuclear resonance spectra of ^{23}Na and ^{27}Al. For aluminium concentrations below 1.5 M they observed four vibrational bands, two of them infra-red active at about 950 and *725* cm^{-1}, and three Raman bands active at *725, 625* and *325* cm^{-1}. There was a narrow resonance line for ^{27}Al. These facts are interpreted as consistent with the existence of the tetrahedral $Al(OH)_4^-$ as the predominant aluminium bearing species in solution. When the aluminium concentration exceeded 1.5 M, new vibrational bands appeared at 900 cm^{-1} for the infra-red, and Raman spectral bands at *705* and 540 cm^{-1}, while the ^{27}Al nuclear resonance band was considerably broadened but without any change of position. These observations are interpreted in terms of the condensation of $Al(OH)_4^-$ with increasing concentration to form $Al_2O(OH)_6^{2-}$, so that in solutions of 6 M sodium aluminate the two forms coexist.

It has been found that a caustic soda solution in continuous use will take aluminium into solution until the uncombined caustic soda is approximately one quarter of the original total soda, and thereafter it will continue etching with the uncombined caustic fluctuating about this level with an amplitude which depends on the temperature, rate of usage and resting periods. The hydrate will slowly settle or crystallise onto the tank bottom and sides to form a very hard rock hydrate which can be difficult to remove, and it shows an unfortunate preference for the surface of heating coils. This represents a third reaction, that of dehydration of the aluminium hydroxide to form alumina:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

The nature of this transformation is shown in Fig. 4-10 where various amounts of aluminium have been dissolved in a 5% (wt) caustic soda solution and measurements were made of the uncombined caustic soda immediately after each addition and also after an interval of three weeks.[243] Up to 15 g/l the aluminium

remains completely in solution with no change in the uncombined caustic soda, but as soon as alumina deposition has taken place, which is a short while before the easily visible deposit, the free caustic begins to recover to 4%, i.e., 80% of its original value. In continued use such a solution will fluctuate between about 1 and 1.5%, rising remporarily to about 2.5% if idle for a few hours. Similar ratios apply to the higher concentrations of caustic soda and these values are practically independent of temperature.

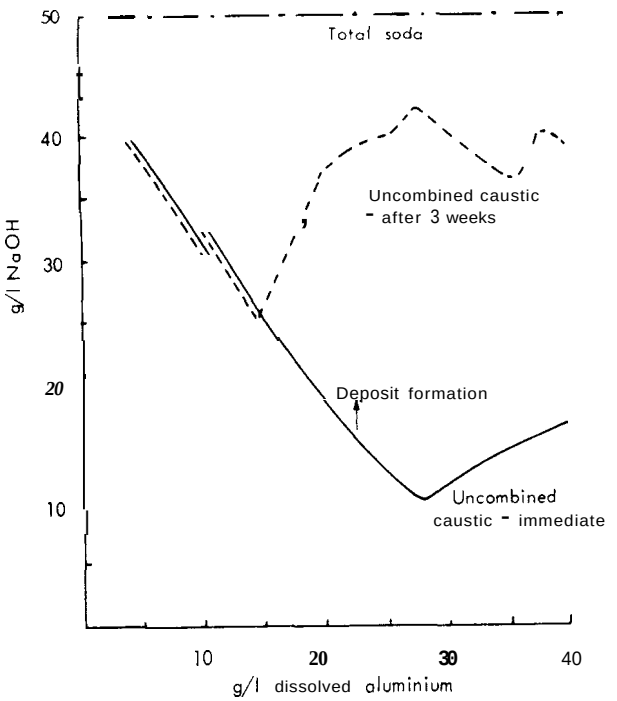


Fig. 4-10. Effect of dissolved aluminium on uncombined caustic soda

Another important effect of aluminium is that increasing aluminium content decreases the etch rate very significantly, and this is shown in Fig. 4-11. In practice this means that if a constant etch rate is required, the free caustic content of the solution needs to be increased as the aluminium content of the bath rises.

The nett reaction is therefore between aluminium and water to give hydrogen and alumina. In theory the solution will continue to etch for ever without consuming caustic soda other than by drag-out losses. It is in fact quite possible to operate an etching tank in this manner provided one is prepared to deal with the deposits of

rock hydrate by periodic removal, and tanks have been operated in this manner for up to two years. Filtering of caustic soda solutions has been less successful, because of the tendency of the very fine deposit to clog the filter very quickly, but there is no compelling reason why it cannot be done.

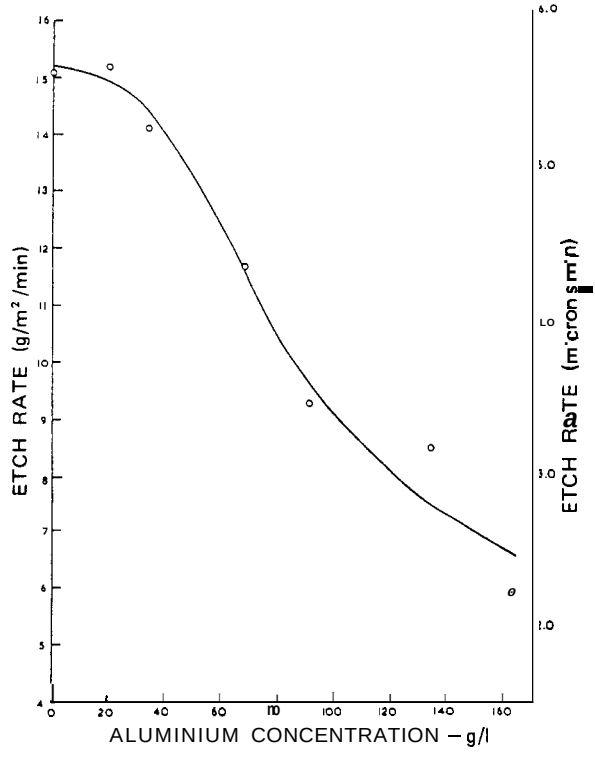


Fig. 4-11. Etch rates in 50 g/l sodium hydroxide-40 g/l sodium nitrate etch at 60°C as a function of aluminium concentration

The chemical control of a solution used before the deposition point or in the steady state after deposition involves a determination of the total soda and the uncombined caustic soda. The latter may be obtained with sufficient accuracy for practical purposes by titration with hydrochloric acid until a phenolphthalein indicator turns colourless. The total soda may be obtained by titrating with phenol red indicator. Alternatively simple potentiometric titrations may be used.[248] It is sufficient to maintain the total caustic soda at a fixed level to make up for drag-out losses, since one can exercise little control over the fluctuations of the uncombined

caustic soda. An accurate determination, which would have to take into account carbonate and dissolved aluminium, is considerably more complicated and a method is given in Table 4-3.

One problem occasionally encountered with caustic soda etches is a sudden tendency to cause pitting or 'burning' of part or all of the work accompanied by an increase in etching rate of some 300%. This may occur in heavily worked solutions which are given no chance for recovery, when hydrate crystallises onto the work followed by increased local etching, a local temperature rise and perhaps grain boundary attack having the characteristics of an acid etch. It is sometimes very difficult to strip anodic films in such a solution without pitting. The temperature should be lowered when this occurs. (See **p.** 443 for effects of intermetallic constituents.)

It can thus be seen that, although nominally the etching process is a very simple one, in practice there are many competing reactions which must be understood if consistent etching is to be achieved. Major factors controlling etching response are the free caustic content of the solution, the presence and level of bath additives (discussed in later sections of this Chapter), the solution temperature, and the aluminium content of the solution. The effect of solution composition has already been discussed, but it can be seen from Fig. 4-9 that solution temperature has a strong effect on etch rate. Whilst nominally this should be easy to control, in practice the fact that the etching reaction is exothermic means that etch baths often need cooling facilities to keep the temperature down when they are in continuous use. Most etch baths are operated in the range of 55-65°C, as higher temperatures can lead to transfer etch staining, particularly on sheet products.

TABLE 4-3

Analysis of caustic soda etching baths

Principle

Free soda, carbonate and alumina are determined by titration with standard acid making use of the complexes formed between aluminium and (a) sodium gluconate and (b) potassium fluoride.

Reagents

Hydrochloric acid, 0.2 N accurately standardised
Potassium fluoride, 50% $KF.2H_2O$ (= 30% KF) filtered and stored in polythene (see Note 1)
Sodium gluconate, 20% solution
Sodium hydroxide, 0.2 N standardised against hydrochloric acid.

Method

1. Determination of Free Soda plus ½ Carbonate

Take an aliquot of solution containing not more than *250* mg sodium hydroxide and 50 mg aluminium. Add 15 ml sodium gluconate solution *(20%)* and 3 drops phenolphthalein and dilute to approximately 100 ml. Titrate with 0.2N hydrochloric acid to a colourless endpoint. **Let titre** = A ml.

2. Determination of Total Soda and Aluminium

Take a similar aliquot to 1. Add 3 drops of phenolphthalein and add an excess of standard hydrochloric acid **(B ml)** (see Note *2).* Boil the solution gently for 10 minutes, cool, add *15* ml sodium gluconate solution *(20%)* and back-titrate the excess acid* against standard 0.2 N sodium hydroxide solution. Let titre = **C ml.** Add 10 ml potassium fluoride solution (50%), mix, titrate the liberated hydroxide immediately with *0.2* N hydrochloric acid to the change point of phenolphthalein and add 10 ml acid excess (total = **D ml).** Back-titrate with *0.2 N* sodium hydroxide solution **(= E ml)** until the solution is permanently pink.

Note 1:

Adjust the potassium fluoride solution with acid or alkali so that the addition of 10 ml of fluoride solution to a solution of 15 ml gluconate in a volume of 100 ml, previously adjusted to neutrality to phenolphthalein, will not require more than 1 drop of 0.2 *N* acid or alkali to restore the original colour.

Note 2:

Indication of excess acid present is given by the solution becoming almost clear.

* This represents free acid **plus** acid ≡ to AI.

Calculations

(i) % Total soda as NaOH $= \dfrac{(B - CF_1) \times 0.8 \times F_2}{V}$

(ii) % Na_2CO_3 $= \dfrac{2(B - CF_1 - A) \times 1.06 \times F_2}{V}$

(iii) % Free soda as NaOH $= \dfrac{[2A - (B - CF_1)] \times 0.8 \times F_2}{V}$

(iv) or % Free soda $=$ % Total soda − % Na_2CO_3 x $\dfrac{40}{53}$

(v) % Aluminium $= \dfrac{(D - EF_1) \times 0.18 \times F_2}{V}$

(vi) % Uncombined NaOH $= \dfrac{12A - (B - CF_1) - 1/3(D - EF_1)]X0.8 \times F_2}{V}$

(vii) or % Uncombined NaOH $=$ % Free soda - % AI x $\dfrac{40}{21}$

where

F_1 = factor to convert NaOH to equivalent HCl
F_2 = HCl factor
V = volume of solution taken

1st titration:

$$NaAlO_2 + nGl + 2H_2O = Al(OH)_3Gl_n \downarrow + NaOH$$

2nd titration.

1a $NaAlO_2 + NaOH + Na_2CO_3 + 7HCl = AlCl_3 + 4NaCl + CO_2 + 4H_2O$
(+ xs HCl) (+ xs HCl)

1b $AlCl_3 + nGl + 3NaOH = Al(OH)_3Gl_n \downarrow + 3NaCl$

2 $Al(OH)_3Gl_n \downarrow + 6KF = K_3AlF_6 + 3KOH + nCl$

Of all the factors, it is the aluminium content of the etchant that provides most problems. It is build-up of aluminium that controls the life of the solution, and it is variation in aluminium content that leads to the greatest variations in etch rate and etched appearance. It can be seen from Fig. 4-10 that more than about 20 g/l of aluminium in a 50 g/l sodium hydroxide solution (about 40 g/l in a 100 g/l NaOH etchant) leads to precipitation of aluminium hydroxide, and this level is rapidly achieved, as typical etching conditions remove about 100 g of aluminium per m^2 of surface etched; each 100 g of aluminium will then produce about 300 g of aluminium hydroxide. Much work has therefore been centred on reducing the effect of aluminium build-up or dealing with it once it has been formed. For example suggestions have been made to prevent any deposit forming by the addition of powdered sodium oxide,[249] and also by the addition of an alkali metal silicate to form a precipitate of aluminosilicate.[250]

Another approach to dealing with the aluminium build-up problem is to continuously dump small amounts of the etch bath, so that a particular aluminium level or range is maintained. In effect this is achieved with even greater control by the etch recovery systems which are widely used in Japan.[251] Whilst the main reason for using such a system is to produce a more crystalline alumina precipitate, and hence to make the aluminium hydroxide effluents much easier to deal with, the fact that the etchant is continuously regenerated means that the aluminium content is maintained within close limits (usually in the range of 30-40 g/l of aluminium). With such a system sequestering agents can no longer be used, as they hinder precipitation of the alumina, and the level of aluminium in the etchant must therefore be limited to prevent precipitation in the etch bath itself.

Chelating agents

The main method to prevent or slow down the rate of deposition of alumina is the use of sequestering or chelating agents. Tartrates or citrates[252] were commonly used for this purpose, but the introduction of sodium gluconate and sodium heptonate has provided much more effective agents for retaining aluminium in alkaline solution.[253,254] A relatively small amount of sodium gluconate will completely prevent the formation of rock hydrate.[255] In this case however the uncombined caustic soda continues to decline as also does the activity of the etch, and one must continue to add fresh caustic soda to keep it functioning. There is of course a limit to these additions since the solution becomes very concentrated and viscous and must be discarded after it reaches about 250 g/l of total caustic soda.

Gluconates may also be added in much smaller amounts to delay but not prevent the deposition of alumina, and it is claimed that the deposit then forms as a soft non-adherent sludge which can be much more readily removed than the troublesome rock hydrate.[253] This will be the case if the removal of the deposit is not delayed too long, but in time it will settle on the tank bottom and form a cement-like deposit quite as adherent as with the simple caustic soda solution. More recently sorbitol has become widely used as an alternative to gluconates or heptonates, as it is claimed to be more effective at high aluminium contents.

The addition of sequestering agents also reduces the formation of a visible grain structure on alloys containing heavy metals[256] as does the use of triethanolamine or other additives.[257]

Long-life etches

The need for a consistent etch rate resulting from a reasonably constant aluminium content has led to a different approach in the case of the so-called 'long-life' etches. These rely on the fact that the viscosity of the etch bath rises considerably as the aluminium content of the etchant increases. With the increased viscosity, the amount of solution dragged-out with the work increases also, until at an equilibrium point of about 120-150 g/l of aluminium, the amount of aluminium lost by drag-out is equivalent to the amount of aluminium removed from the work during etching. In theory, at this stage, provided that the free caustic soda level of the solution is maintained, the bath can continue to be used without limit. In practice this result cannot be achieved without making special additions to the etchant to cope with the build-up of other impurities, particularly zinc. The presence of only a few p.p.m. of zinc in an etching solution can lead to a defect on 6063 extrusions known as 'galvanizing' or 'spangling'. This is illustrated in Fig. 4-12 and is a preferential grain etching effect. It is prevented by making additions of such things as sulphides[258,259,260] or chromates[261,262] to the etch. Addition of oxidizing agents such as persulphates, chlorates or peroxides,[263] or dithionites,[264] are claimed to give similar benefits.

Use of such long-life etching solutions has been described by Smith and Carroll,[265] and they point out some of the hazards, as well as the benefits, of the long-life systems. For example the high viscosity of the solution can lead to rinsing problems and use of appropriate surfactants[266] in the solution is important. It also leads to a high rate of drag-over of free caustic soda and this may increase chemical costs and effluent disposal problems. The very high aluminium content also means that the solution must not be allowed to go cold, even when not in use (minimum recommended temperature 50°C), or it may precipitate out and solidify. Nevertheless such systems are increasingly used, particularly in architectural anodizing plants.

A long-life etch is really a continuous dumping system, and therefore, an amount of aluminium equivalent to the average amount removed on each load treated in the etch solution, is dumped every time a load is processed. This is normally dumped by drag-over into the post-etch rinse, the outlet from which will be treated to remove the aluminium in the rinse water effluent treatment system (see Chapter 16).The greater the amount of aluminium removed per load, the larger will be the volume of solids that has to be removed and subsequently dumped on some approved waste site.

The amount of aluminium removed in any etch is generally governed by the need to produce a uniform appearance on the final product. In general, aluminium extrusions need *to* be etched for longer times than aluminium sheet to obtain a similar degree of smoothing. This is because the former tends to have a rougher surface due to die lines on the surface. Reducing the amount of aluminium removed in the etching solution will reduce the demand on the effluent treatment system and the cost of dumping the solids that it generates. Therefore, any etching solution or technique that will provide a satisfactory appearance with less metal removal has certain environmental and perhaps economic benefits. Although the rate of etching in a caustic etch solution decreases as the aluminium content increases (see Fig. 4-11) its smoothing power tends to improve. In etches having very high aluminium contents (150 to 170 g/l), a good matt finish can be obtained with the removal of 50 to 70 g/m^2 of metal. The finish is usually as good as that obtained in an etch with an aluminium content of 120 to 130 g/l, where it is necessary to remove 100 to 120 g/m^2 to obtain the same degree of mattness. Such high aluminium contents are not practical with a normal long-life etch, because the viscosity of the etch results in too much solution being dragged out with each load for the aluminium to build up to the desired level. Almetron markets an etching system[267] where they use a static, post-etch, rinse that is used to top up evaporative losses from the long-life etch. The net result is a build up of the aluminium content to levels much higher than normally obtainable with a conventional running water rinse after the etching solution. To keep this higher aluminium level in solution it is normally necessary to add much higher levels of sequestering agent or a purpose designed additive.[268]

Table 4-4 illustrates the potential reduction in consumption of caustic soda and generation of solids per square metre of aluminium surface treated for different etch systems.

TABLE 4-4

Consumption of NaOH and generation of solids for various etch systems

Etch system	*Metal removed* g/m^2	*Free NaOH* g/l	Al^{3+} g/l	*NaOH used* g/m^2	*Solids generated as 25% Al(OH)₃* g/m^2
Periodic dumping	100	75	*25-15*	298	1156
Long-life	100	100	120	231	1156
Long-life with static rinse	100	100	150	215	1156
Long-life with static rinse	80	100	150	172	924

The calculations in Table 4-4 indicate that using the long-life etch system with a static rinse feed back and, assuming that the metal removal required is reduced from 100 to 80 g/m^2, there are potential savings to be made. The above figures show a reduction of 25% on the usage of caustic soda, as well as a reduction of 20% in the weight of solids generated, by the etch, in the effluent treatment system. The financial benefits of such savings will depend on the local costs of caustic soda and dumping solid waste, compared to the cost of the extra additives required to keep the higher aluminium level in solution in the etch.

Nitrate-accelerated etches

Gluconates and similar additives are also found in another popular group of caustic soda based etches which are accelerated with sodium nitrate or sodium nitrite.[244.269] In this case the nascent hydrogen released by the primary reaction of aluminium with caustic soda converts the nitrite ion to ammonia:

$$NaNO_2 + 6H \rightarrow NH_3 + NaOH + H_2O$$

The overall reaction between aluminium and caustic soda in the presence of nitrate may be represented by the equation:

$$3NaNO_3 + 8Al + 5NaOH + 2H_2O \rightarrow 8NaAlO_2 + 3NH_3$$

The chemistry[270] and control of these solutions is more complicated, but they are attractive because of lower caustic soda consumption, less effervescence, less spray and they tend to give a more matt etch. The nitrate reaction forms the basis of some proprietary etches,[271.272] and added to them may also be the chelating agents sodium gluconate[273] and sodium boroheptonate.[274]

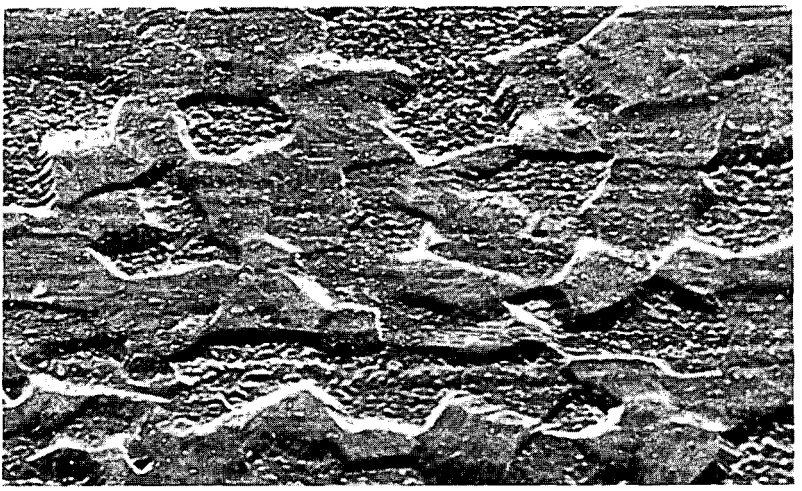


Fig. 4-12. Spangling or galvanizing effect on etched 6063 extrusion (x 150)

Sodium fluoride has also been added to caustic soda in order to obtain a whiter and more uniform etch. A composition such as 5% caustic soda with 3% sodium fluoride can give surface appearances varying from lightly etched to a matt frosted finish similar to finely etched glass, depending on the period of immersion and the alloy composition. The analytical problem in the presence of fluoride is greater even than for the nitrite-containing solutions.

Etch regeneration

Changes in environmental legislation and the general awareness of the need to conserve resources have focussed attention on methods of regenerating process solutions in most chemical or electrochemical processes. Alkaline etching has been no exception and techniques, based on the principle of the Bayer process, originated in Japan in the late 1960's and early 1970's, where Fujisash and NLM developed the continuous recycling of the etch solution.

These recovery systems are well documented in the literature[275,276] and have resulted in a process that continuously regenerates the etch solution through a special plant, in which the aluminium, precipitated as hydrated alumina, is filtered, and the reclaimed NaOH returned to the etch tank.

Such systems work well with simple caustic etching solutions and the aluminium content of the solution is kept consistent and fairly low. The process cannot be used with etches containing sequesterants or other forms of scale inhibitor. The Zn contamination, associated with long life systems, is removed with the aluminium hydroxide during precipitation.

The etched finish produced is generally less matt than the typical European finish. The plant required is relatively expensive, and a large plant, with a high throughput of work, is necessary if the capital investment is to be economically justified. However, with increasingly tighter effluent restrictions in all countries, and the difficulties experienced in transporting and dumping sludges, such plants will inevitably become more common in the future.

The etch recovery system does not completely eliminate the aluminium from the rinse waters, but because the etching solution is relatively low in aluminium concentration, and hence lower in viscosity, the drag out into these rinses is small. There is a considerable saving on the consumption of NaOH with the recovery system, and because of the lower aluminium content of the etch and the high solids content of the hydrated alumina by-product, the total volume of solids produced per square meter processed is relatively small.

As an example, in an etch solution containing 100 g/l free NaOH and 30 g/l Al^{+++} operating with a recovery system, for 100 g/m^2 metal removal the NaOH consumed would be 58 g/m^2 compared to 231 g/m^2 for a conventional long-life etch. Likewise, the solids generated would be 139 g/m^2 of 25% filter cake compared to 1156 g/m^2 for the long-life etch.

In addition, the recovery system would produce 299 g/m^2 of crystalline hydrated alumina recovery by-product, having a solids content of 85%. Although it may be claimed that this by-product is commercially saleable, it is not universally so, and its value, if any, varies from country to country.

These facts would suggest that caustic recovery systems are the direction the industry should take. To do this and still meet the desired "European Matt Finish" some improvement in the mattness of the finish obtained by this system needed to be achieved.

Eco-tec with their Alrec process[277] and Brodalla[278] with the Gartner patented system[279] both claim to have overcome the problem of producing the "European Matt Finish". There are now a few architectural anodizers in Europe who are using recovery systems on their caustic etch solutions but they are still in the minority.

Mechanical etching

Another innovation aimed at reducing chemical costs and effluent solids was developed in the mid 1990'sby Italtechno, who claimed a method for producing a very fine etched finish on extrusions, based on a mechanical treatment followed by a short immersion in a caustic etch solution. The process was claimed to produce a typical 'Matt European Finish' with a 75% saving in caustic soda consumption and a reduction in effluent solids. Strazzi and Finessi presented data[280], based on the production of a batch of 4000 m^2 , that showed a reduction in overall cost of 56%. However, this did include a significant allowance for the value of the aluminium that had to be removed from the extrusion surface by the two processes to obtain the desired finish. Without this allowance the cost saving was 6%.

Marcucci reported similar findings in his paper,[281] which indicated that the process is essentially shot peening with steel balls. The payback time for the necessary equipment was said to be two years but, again, it was based on a significant contribution in cost saving from the value of the metal removed from the surface in the respective treatments. Unless aluminium extrusions are produced with a reduced wall thickness for treatment by this process it is difficult to justify the cost savings claimed. However, the reduction in effluent solids that may be obtainable could be of significance in the long term.

Other additives

The effect of additives to caustic soda solutions on the etching rate and behaviour of aluminium is a very complex subject and no detailed or comprehensive study has been published. Quite small additions of certain compounds, particularly those containing heavy metals, can exercise a profound influence on the etching rate, and these may sometimes be derived from the impurities which the aluminium contains. Table 4-5[243] lists the effects of several compounds on the etching rate of 99.99% and 99.5% aluminium in little-worked solutions and after the deposition of alumina. The effect on very high purity aluminium is generally very much greater than on the lower purities, and this is particularly noticeable in the case of the soluble cobalt compounds where the etching rate can increase by over six times.[243] Kape has examined the effect of quite substantial additions of a variety of compounds to 50 g/l caustic soda at 60°C and listed the accelerators and inhibitors.[269] In later work[282,283] he described the effect of complexants of many different types on etch rate, smut formation and scale production, showing how additives can both accelerate or slow down the etching reaction as the aluminium content rises (Table 4-6).

TABLE 4-5

Effect of various additives on etching rate of 2% caustic soda solution used at 28°C for 10 minutes[243]

Addition 0.014 g/l	*Form*	*Etch rate, 1 g/l Al* 100% (=6.3)	*99.5% Al Satd.* 100% (=5.2)	*Etch rate, 1 g/l Al* 100% (=2.2)	*99.99% Al Satd.* 100% (=1.6) mg/dm² /min
none					
chromium	sod. chromate	104%	118%	217%	–
molybdenum	sod. molybdate	123	168	171	131
vanadium	sod. vanadate	110	94	194	–
tungsten	sod. tungstate	100	103	85	77
titanium	sod. titanate	100	105	96	92
iron	ferric chloride			274	
	ferrous chloride			160	
	sod. ferrate			293	

Addition 0.014 g/l	*Form*	*Etch rate, 1 g/l Al* 100% (=6.3)	*99.5% Al Satd.* 100% (=5.2)	*Etch rate, 1 g/l Al* 100% (=2.2)	*99.99% Al Satd.* 100% (=1.6) mg/dm² /min
none					
copper	cuprammonium hydroxide	–	145	211	184
cobalt	sodium-cobaltinitrite	–	–	253	–
	hexammine-cobalt nitrate	160	165	450	465
	tetramminecarbonato cobaltic chloride	190	173	550	505
	pentammine chloro cobaltic dichloride	192	185	580	540
	trans dinitrito tetrammine-cobaltic chloride	202	150	425	635

The inhibiting effect of chromates and silicates is well known but it is not generally realised that chromate at low concentrations can increase attack in alkaline solution. Molybdates and vanadates also have this dual action according to the quantity present.[243]

Organic inhibitors which are effective in reducing attack of aluminium in sodium hydroxide solution include (in decreasing order of efficiency) gum acacia, agar agar, dextrin and glue.[284]

Other etching solutions proposed have included additions to caustic soda of acids from the iminodiacetic group;[285] potassium-sodium tartrate along with dissolved zinc;[286] 1-4% carboxymethyl starch and gluconates;[287] and lithium hydroxide;[288] reaction products of propylene oxide with aliphatic amino or aliphatic polyalcohols;[36] and gluconate with ethylene glycol or ethanolamine.[37]

TABLE 4-6

Effect of various additives to 50 g/l caustic soda etchant operated at 60°C for 5 minutes, using 3003 alloy

Additive	*Weight loss* *Fresh soln, mg/dm²*	*Soln contg 100 g/l Al, mg/dm²*	*Type of smut produced*	*Scale and/or sludge formation*
Nil	612	1300	light grey	scale; lumpy sludge
Sodium borogluconate	1300	936	black	no scale; light sludge
Trisodium N hydroxy-ethyl ethylene diamine tri-acetate	2275	1750	grey	scale
Sodium glucoheptonate	1963	910	yellow-grey	no scale, porridgy sludge

Additive	Weight loss: Fresh soln mg/dm²	Weight loss: Soln contg 100 g/l Al, mg/dm²	Type of smut produced	Scale and/or sludge formation
Trisodium nitrilo-triacetate	1142	1157	light grey	scale
Sodium dihydroxy-ethyl glycine	1000	1105	grey	scale
Disodium malate	195	1040	light grey	no scale or sludge
Sodium gluconate	1755	1183	black	no scale, little sludge
Disodium **EDTA**	1027	1255	black	scale
EDTA-triethanolamine complex	1629	1521	black	scale
Citric acid	104	286	light grey	white sludge
Tartaric acid	104	546	very slight	gel-like sludge
Sodium formate	104	1638	light grey	slight scale, lumpy sludge
Sodium benzoate	494	819	light grey	slight scale, lumpy sludge
Succinic acid	520	1118	very slight	slight scale, lumpy sludge
Phthalic acid	329	152	very slight	slight scale, lumpy sludge
Diglycollic acid	312	1105	very slight	slight scale, lumpy sludge
Fumaric acid	325	–	very slight	slight scale, lumpy sludge
Proprionic acid	341	924	very slight	slight scale, lumpy sludge
Sodium acetate	533	1053	very slight	slight scale, lumpy sludge
Phytic acid	1085	533	grey	scale, cryst precipitate
Oxalic acid†	846	–	grey	scale
Maleic acid	494	152	light grey	scale
Sulphosalicylic acid	286	806	grey	sludge
Salicylic acid	273	533	grey	sludge
Tannic acid*	612	312	dark grey	slight sludge
Gallic acid*	452	364	dark grey	porridgy sludge
Hydroxyacetic acid	143	311	light grey	scale, lumpy sludge
Silico-tungstic acid*	1053	832	grey	sludge
Tungsto-phosphoric acid*	1196	923	grey	scale and sludge
Sulphamic acid	819	858	grey	scale and sludge
Methane sulphonic acid	850	850	grey	scale
Cyanoacetic acid	616	910	grey	scale
Malonic acid	559	653	light grey	scale and sludge
Itaconic acid	622	1053	light grey	scale and sludge
Mandelic acid	390	492	light grey	scale and sludge
Mucic acid*†	1170	1040	black	sludge
Benzilic acid$	403	819	light grey	sludge
Cyanuric acid$	598	936	grey	lumpy sludge
Mannitol	590	1105	grey/black	hardly any sludge

* Solutions tended to foam during etching
† Material did not entirely dissolve
‡ Oily layer in solution during etching

4. CHEMICAL MILLING, ETC.

An important application of both alkaline and acid etching is found in the development of chemical contouring or 'chemical milling' processes which are used mainly in the aircraft industry. Developed in the U.S.A.,[289 290 291] these processes have also come into use in Britain.[292] In practice, the aluminium plate or sheet is cleaned and deoxidized and a suitable maskant is applied and cured. A template of the design to be etched is placed in position and the design is scribed through the maskant which is then stripped off the areas to be etched. The normal operating sequence in chemical milling is shown in Fig. 4-13.

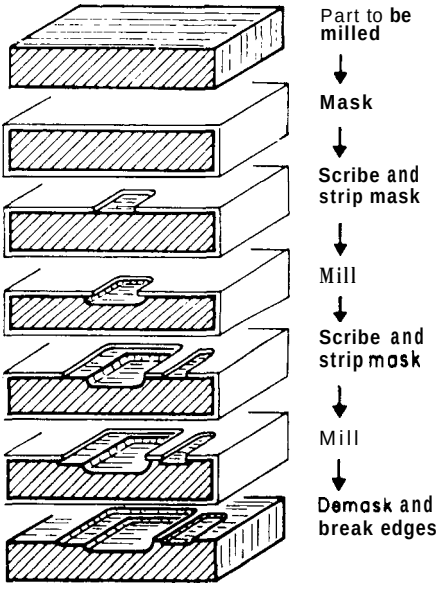


Fig. 4-13. Masking and chemical milling sequence"?

Maskants for alkaline baths, which are frequently operated at around 90°C (195°F), must be chosen with care. Neoprene, acrylonitrile, styrene elastomers, chlorinated or butyl rubber, p.v.c. and polyvinylidene chloride, polystyrene and polyethylene (polythene) as well as lead or polyester tapes have all been used for this purpose. Dipping or flow coating is suitable for a number of these materials while neoprene may also be sprayed. Heat curing is essential only for butyl rubber.[294]

More complex maskants are also used in chemical milling, e.g., a composition described by Hermann[295] contains;

neoprene A.C.	9.6%
neoprene KNR	6.6%
chlorinated rubber	4.5%
phenolic resin	7.1%
soot	9.1%
phenyl-a-naphthylamine	0.4%
toluol	62.7%

Photosensitive maskants have been used and it has also been proposed to electroplate with nickel followed by copper.[296]

Alkaline chemical milling solutions

The first and simplest chemical milling solution is the plain caustic soda bath which is normally used at a concentration of 100-150 g/l (16-24 oz/gal) sodium hydroxide[292] and, at the temperatures used (70-90°C), the rate of metal removed is normally adjusted to between 12 and 37 μm (0.5 and 1.5 mil) per minute by closely controlling the temperature. In the U.S.A., slightly more dilute solutions, containing 75-105 g/l (12-16.8 oz/gal) sodium hydroxide, have also been used at similar temperatures; wetting agents, sequestering agents or inorganic salts may also be added to improve the surface finish. Frequently the bath is worked-in by adding about 6 g/l (1 oz/gal) aluminium scrap to the bath.[256]

The bath is normally discarded when the aluminium concentration reaches about 30 g/l (about 5 oz/gal). When high-strength alloys are chemically milled, the copper and zinc from these alloys may cause irregularities by redeposition on the surface. This may be controlled by addition of sodium cyanide or by precipitating these metals from the solution as sulphides.[258] The latter is achieved by adding sodium sulphide or elemental sulphur to the solution.[65] A solution containing an addition of this type is made up from 110 g/l (1.1 lb/gal) of a mixture containing 86% NaOH and 3% Na_2S together with organic wetting and reducing agents. This solution is regenerated by adding the same mixture until the aluminium content reaches 75-85 g/l (12-14 oz/gal).

An alternative method of preventing immersion deposition is to make the aluminium anodic, using only just sufficient current to remove about 2% of the metal electrolytically. This method has been claimed virtually to eliminate rejects.[297]

More recently, complexing or sequestering agents have been recommended for the purpose. One patent[253] claims the use of such materials as sodium gluconate, sorbitol, mucic acid and gum arabic and another uses carboxymethyl cellulose, gelatin or agar added to caustic soda and cyanide.[298,299]

After alkaline chemical milling, the plate is rinsed, deoxidized in dilute nitric acid, which also helps to neutralize any remaining alkali, again rinsed and dried.

The extent to which lateral etching taker place under the maskant edge is given by the 'etch factor' (see Fig. 4- 14).Better results in chemical contouring are usually obtained on fully heat-treated than on solution-treated aluminium alloys and the initial surface should be smooth and free from cracks and pinholes.

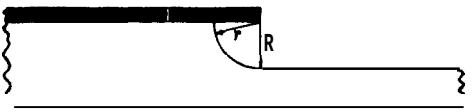


Fig. 4-14. r/R = etch factor. Ideally. the etch factor is equal to one

Acid chemical milling solutions

A number of acid chemical milling solutions are in use. The simplest of these is hydrochloric acid while nitric-hydrofluoric acid mixtures have also been used.[300]

A more complex solution, used in the Boeing process,[256,301] contains, e.g.:

nitric acid (40" Bé)	18 gal	I8 litres
hydrochloric acid (20" Bé)	7.5 gal	7.5 litres
hydrochloric acid (60%)	6 gal	6 litres
acetic acid (glacial)	2.5 gal	2.5 litres
oxalic acid	2.4 lb	24 g
disodium phosphate	1.2 lb	12 g
water	to 100 gallons	to 100 litres

As in chemical polishing, the nitric acid acts as an oxidizing agent and also helps to dissolve any copper or nickel in the alloy. The hydrochloric acid is used to maintain a satisfactory rate of attack while the hydrofluoric acid also controls the rate of attack and dissolves silicon and magnesium silicide. The function of the acetic acid is to reduce evaporation of hydrofluoric acid, while phosphates and oxalates are added to produce a smooth surface. Surface-active agents may also be present.

Aluminium is precipitated as oxyfluoride from this solution. This may be delayed by adding a little titanium to the bath or oxalates or citrates. As in alkaline solutions, this also improves the texture of the precipitate. An alternative method of removing dissolved metals is to seed with the metal salt and 'freeze out' overnight in a settling tank.

A British Aerospace patent[302] describes a technique for keeping any precipitates in the chemical milling solution in suspension, and a facility for bleeding off controlled volumes of the solution for filtration, by means of an external filter, before returning it to the main tank.

The Boeing process removes 0.3-1.5 mil (8-38 μm) per minute and is used at up to 130°F(55°C), though the temperature chosen should be controlled to within ± 5°F (± 3°C) or preferably ± 2°F (± 1°C).

Chromic-sulphuric acid chemical milling solution

A solution containing:

chromic acid	42 lb/100 gal	420 g/100 l
sulphuric acid (conc).	12 gal/100 gal	12 l/100 l

can be used for chemical milling at a rate of 0.3-2.5 mil (8-65 μm) per hour at 90-190°F(30-90°C).[303]

Acid versus alkaline solutions

In practice alkaline solutions are rather cheaper to operate than acid solutions and also require less expensive equipment. On the other hand they leave a rougher surface (see below) and result in a slightly inferior fatigue life. Moreover, optimum conditions vary to a greater extent with alloy composition, i.e., the rate of dissolution increases more rapidly with impurity content in alkaline baths, and acid solutions are therefore more versatile.

The roughness of aluminium after chemical milling in caustic soda solution increases with the concentration of the solution, as well as with increasing temperature and immersion time. In acid solution this effect is less marked.

Dimensional control in chemical milling

The thickness tolerance of the process is shown in Fig. 4-15, and this must be added on to the original tolerance of the part thickness. It is important to remember that after chemical milling the milled line will deviate to some extent from a true straight line. A commercial value for 'line definition' is normally $\pm 1/32$ inch (0.031 inch; 0.79 mm).[293] The adhesion of surface films and variations in surface structure may also affect dimensional changes in chemical milling; e.g., on rough material more metal is removed in the direction perpendicular to rolling than in the direction parallel to rolling.[304]

When the entire edge of a part is to be milled, it is important to keep the reduction down to 25% for a round edge and 15% for a square edge. Any excess should be mechanically trimmed. Any holes should be drilled after chemical milling to cut down the expense of masking.

A controlled degree of taper can be obtained in chemical milling, either by removing the rotating part from the solution at a calculated rate or by repeated immersion and removal.

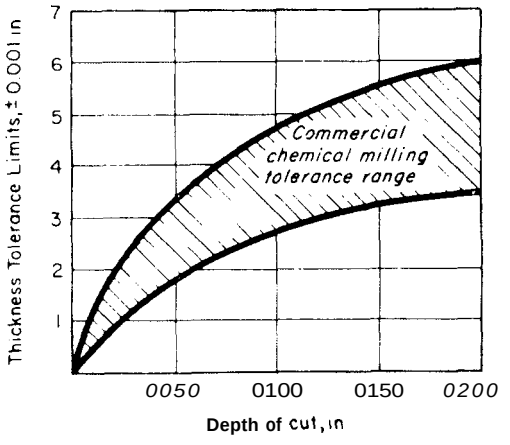


Fig. 4-15. Thickness tolerance in chemical milling at various depths of cut[294] (1 inch = 25.4 mm)

Narrow grooves and other surfaces which reduce solution flow should be avoided in parts which are to be chemically milled.

Lockheed Aircraft Corporation machine aluminium components to tight tolerances using either a horizontal chemical milling tank 20 ft (6 m) long or a vertical milling tank 30 ft (9 m) deep. The etchant is caustic soda used at 90 ± 2°C with the bath agitated, and metal is removed at the rate of 2.5 μm per side per minute.[305] The following points have been emphasised:

1. Warpage from stresses in metal before etching can occur when the process is done on only one side of the component.
2. Thick parts with stiffeners, and stress-relieved parts resist the revealing of residual stresses when both sides are etched.
3. Welded parts can be etched if preferential attack is shown not to occur in the weld zone.
4. Avoidance of traps or bends which could retain processing solutions, or gases produced during etching, is necessary.
5. Cuts on opposite surfaces should be spaced from 0.31-0.63 cm (⅛ - ¼ inch) apart.
6. Different etch rates, due to variations in grain structure and direction in forgings, are dependent mainly on forging geometry, small simple forgings having a narrower chemical milling tolerance than large very complex forgings.
7. For cuts of depth less than 0.63 cm (¼ inch). minimum width should be (2 × depth) + 0.15 cm (+ 0.06 inch). Deeper cuts require an additional 0.63 cm (¼ inch).

8. Minimum land width should be 2 x depth of the deepest cut next to it, but not less than 0.63 cm (¼ inch).
9. Outside radii decrease, and inside corners increase, in proportion to the depth of the cut.
10. Pocket cuts on masked parts have sharp outside corners but radiussed inside corners. Conventional milling may be required if a specific radius of close tolerance is needed.
11. Depths of cut are limited, being for aluminium extrusions not more than 0.63 cm (¼ inch) on a side.
12. Tapers less than 30 cm (12 inches) long and more than 0.5 cm per 0.3 m (0.2 inch per foot) require special considerations.
13. Grid patterns should be cut at 45" to the metal grain direction.
14. The surface finish produced depends largely on the original surface finish, stock, alloying constituents, depth of cut and temper condition.

Surface finish obtainable by chemical milling

The surface finish values obtained by chemical milling in alkaline and acid solutions given in Table 4-7 are due to Cotton.[256]

TABLE 4-7

Surface finishes obtainable by chemical milling

Alloy	*Typical drawing specification, RMS or RHR (micro inches)"*			
	Acid solution		*Alkaline solution*	
	Minimum	*reconnnended*	*Minimum*	*reconnnended*
1100	40	63	80	125
2014t	125	160	250	250
2020	63	125	–	–
2024	40	63	160	250
2219	63	63	160	250
3003	40	63	160	250
5052	40	63	160	250
6061†	40	63	250	250
7075	40	63	160	250
7079	40	63	160	250
7178	40	63	160	250
356	250	500	–	–

* 1 pinch = 0.0254 ym.

† The acid solution is preferred to avoid stress raisers

Effect on fatigue properties

In common with other chemical dissolution treatments, chemical contouring may reduce the fatigue strength of the aluminium alloy. While the fatigue resistance of chemically milled aluminium with cuts less than 0.04 inch (1 mm) deep is about equivalent to that of machined parts of the same surface finish, deeper milling in alkaline solution slightly reduces fatigue resistance below this level, as the sharp end grain boundaries act as stress raisers. Deep milling in acid solution is less harmful and may even improve fatigue properties.[256]

Where fatigue resistance is important, one of the following stress relieving treatments may be applied:[304]

(i) Grit- or shot-blasting (see Chapter *2)* with non-metallic abrasive, e.g. alumina, glass beads, or vapour blasting. Any ageing treatment on solution heat-treated alloy should be carried out before blasting.

(ii) Heat-treatment at 130°C (± 5°C) for at least one hour. This method applies to sheet or plate contoured on one side only.

Cleaning before and after welding

For many purposes, prior to spot welding, the surface must not only be freed from oil, grease and dirt, etc., but the oxide film must be removed, and the surface given a uniform low electrical resistance. This may be achieved either mechanically, by sand- or shot-blasting, or scratch brushing or, more easily, by chemical means. Several solutions are available for this purpose:

(1) **A** chrome pickle of the D.T.D.915 type'' is used, after degreasing and alkali cleaning, as follows:''''

phosphoric acid	9 oz/gallon	(56 g/l)
chromic acid	2.75 oz/gallon	(17 g/l)

after which it is given a hot water rinse and dried.

(2) A sodium bisulphate solution[289] may be used with or without organic additions, e.g., wetting agents, oxalic acid, etc. This method is economical, and is not critical in its operating conditions. The work tends, however, to smut up in the bath, and the solution does not remove silica-containing inhibiting films remaining from the alkaline cleaner. The solution must also be operated hot and requires special tanks.

(3) Cold phosphoric acid may be used with or without organic additions. This method is lengthy, requiring about 20 minutes to achieve the lowest possible electrical resistance, as well as smutting and leaving silica on the surface.

(4) Chromic acid alone or with mineral acids or acid salts is satisfactory for removing the oxide film from Duralumin-type alloys but gives poor

results with pure aluminium. The solutions may be used hot or cold, require lead-lined containers, and do not smut, but they also leave silica untouched on the surface, as well as a chromate film which may interfere with subsequent processing.

(5) Fluorides and fluosilicate solutions are also used. Fluosilicic acid is useful for removing the oxide film from aluminium or aluminium-clad alloys, and will remove silica films. It has been used for spot welding due to the fact that it leaves a surface of extremely low contact resistance. Its disadvantages are that it is somewhat difficult to control, however, due to **the** low concentrations (1%) in which **it** is used, and it smuts badly. It may, however, be used cold. Large quantities of aluminium quickly deplete the acid and build up the insoluble aluminium salt. Buffering does not help, as sodium salts precipitate the insoluble sodium fluosilicate, the solution therefore having to be constantly replenished. Hydrofluoric acid or its salts act rapidly but are not to be recommended as the time of immersion is short and extremely critical. Also the solution smuts readily and the work requires hand scrubbing.

(6) Diluted acetic acid or vinegar is occasionally used for removing the oxide film from aluminium-clad Duralumin-type alloys.

(7) Mixtures of nitric and chromic acid have also been reported to be satisfactory.[290]

(8) The work may also be cleaned by immersion in 5% sodium hydroxide solution and/or a cold 2-5% nitric acid dip. Alternatively, articles may be cleaned with live steam and rinsed in clean water.

Cleaning before spot welding must be adequate in removing all traces of oxide film. In the presence of any non-uniformity, variations in welding heat will be caused by differences in the contact resistance, and the extent of the fusion will be affected.

More recently work by Alcan[307,308,309] in the automotive field has shown that high quality spot welds can be produced with surfaces having a thin controlled pretreatment layer. Such surfaces have a significantly higher contact resistance than a cleaned surface, and the spot welding conditions need to be adjusted accordingly. Their benefit is that they have a good shelf life, so, on sheet surfaces, they can be provided in coil form by the aluminium supplier, and the car company does not need to prepare the surface before spot welding. The pretreatment can be in the form, for example, of a conversion coating, or a thin anodic coating such as that produced by phosphoric acid anodizing. Such material is particularly useful in the production of weld-bonded automotive structures.[310]

In flame and arc welding, fluxes are employed to dissolve the oxide layers, which float on the surface of the fused metal. They also help to provide a continuous protective layer over the melt, and prevent or minimise oxidation,

dissolving any oxide that may form, and preventing oxide inclusions in the weld. After welding, the fluxes must be removed as the same factors on which their efficiency depends will cause trouble later on.

Fluxes are mainly alkali chlorides which are corrosive to aluminium. Their removal is complicated by the fact that basic salts are formed with the aluminium, and these are hydrolysed in the presence of water to acids and bases,[291] e.g.:

$$AICI_3 + 3H_2O = Al(OH)_3 + 3HCl$$

$$6HCl + 2AI = 2AlCl_3 + 3H_2$$

In addition, the alkali metals in fluxing form aluminates, the acid radical being taken up by the aluminium:

$$3NaCl + 2Al_2O_3 = 3NaAlO_2 + AICI_3$$

These reaction products should be washed off as soon as possible, as they are water soluble only in the condition shown in the last formula.

A minimum quantity of flux should, therefore, be used in welding and the work cleaned immediately after the operation.

Pretreatment for adhesive bonding

With the increasing use, particularly in the aircraft industry, of adhesive joining rather than mechanical fixing or welding, much work has been carried out to optimise the surface preparation methods for chis application. Both initial bond strengths and bond durability are important, and it has been established"' that the required surface preparations should produce an even oxide layer on the surface of the aluminium with the following characteristics. It must adhere strongly to the basis metal, and must be cohesively strong, wettable by the adhesive, receptive to the formation of adhesive bonds and be environmentally stable.

The simplest method of surface preparation involves mechanical treatment by conventional methods but although giving high initial bond strength, bond durability in corrosive or humid environments is often low. Work by 3M, however, has shown that use of Scotch-Brite brushes can produce satisfactory durability,"' though in this case the samples were phosphoric acid anodized after mechanical treatment.

Chemical cleaning, for example in inhibited alkaline solutions, is another alternative, but again poor durability is often experienced.[313] As a result special chemical etching treatments have been developed to provide increased bond durability. The best known of these is that developed by the Forest Products Laboratory and known as the FPL etch. The solution contains sodium chromate and sulphuric acid and the recommended preparation procedure is as follows:

1. Remove surface grease or oil with a suitable solvent.
2. Immerse in mild alkaline degreasing agent.

3. Rinse in hot water.
4. Immerse in FPL etch for 15-30 minutes at 60°C.

H_2SO_4 (98%)	16.3% (vol)
$Na_2Cr_2O_7$	6% (wt)

5. Rinse in running water for 20 minutes.
6. Dry in warm air (20 minutes).
7. Bond within 3 hours of pretreatment.

A similar solution used in the UK contains:

H_2SO_4 (98%)	179 ml/l
CrO_3	68 g/l
$CuSO_4$	0.39 g/l
Al powder (stearate free)	1.5 g/l

During treatment in these etchants the original oxide layer is removed and about 1-3 microns of aluminium is dissolved from the surface. A new, more uniform oxide film forms and this is thickened during rinsing.[314] It has been suggested[315] that this oxide has a surface consisting of 'whisker-like' protrusions, and that these are important in ensuring bond strength and durability. Certainly the surface is heavily pitted with many microscopic etch pits within larger pits. The effect of variables in the etching procedure has been studied by Bijlmer[316] and the solution lifetime by McNamara *et al*,[317] and a general survey of this type of pretreatment has been carried out by Moloney.[318]

Because of the presence of hexavalent chromium in the FPL type etch, alternative chromium-free systems have been developed, particularly based on solutions of sulphuric acid and ferric sulphate.[319] Such solutions have been studied in detail by Russell and Garnis[320] and by Rogers,'" and they conclude that an etch containing 370 g/l of concentrated H_2SO_4 and 150 g/l of ferric sulphate (75% by wt), used at 68°C for 16 min. gives results at least equivalent to those of the FPL etch.

In many cases such etchants are used as a pretreatment before chromic acid or phosphoric acid anodizing, and the benefits of these additional anodizing treatments have been studied particularly by Boeing[322] (see also Chapter 7). A comparison between the bond durability obtained with the optimised FPL etch and phosphoric acid anodizing has also been reported by McMillan,[323] and a typical result is shown in Fig. 4-16.

A detailed comparison of phosphoric and chromic acid anodizing, as pretreatments for bonding and painting, has been reported by Thompson and Heaton.[324] They concluded that the phosphoric acid treatment was superior and that this was particularly true when using epoxy-based adhesives. This field was reviewed by Kozma and Olefjord,[325] and a very broad ranging review of pretreatments for bonding purposes has been produced by Critchlow and Brewis.[326] In another study the same authors[327] confirm the superiority of phosphoric acid anodizing with epoxy adhesives.

Alcan has carried out a great deal of work on the production of material for structural adhesive bonding in the automotive industry.[328 329 330] Their work concentrated on AI-Mg alloy sheet material, prepared in coil form, with an applied conversion coating or anodizing pretreatment. This material has a forming lubricant applied, and both the pretreatment and the forming lubricant are compatible with the structural epoxy adhesive used. There is now an enormous amount of work in the field of structural adhesive bonding of aluminium, and a book by Kinloch[331] summarises much of the current knowledge.

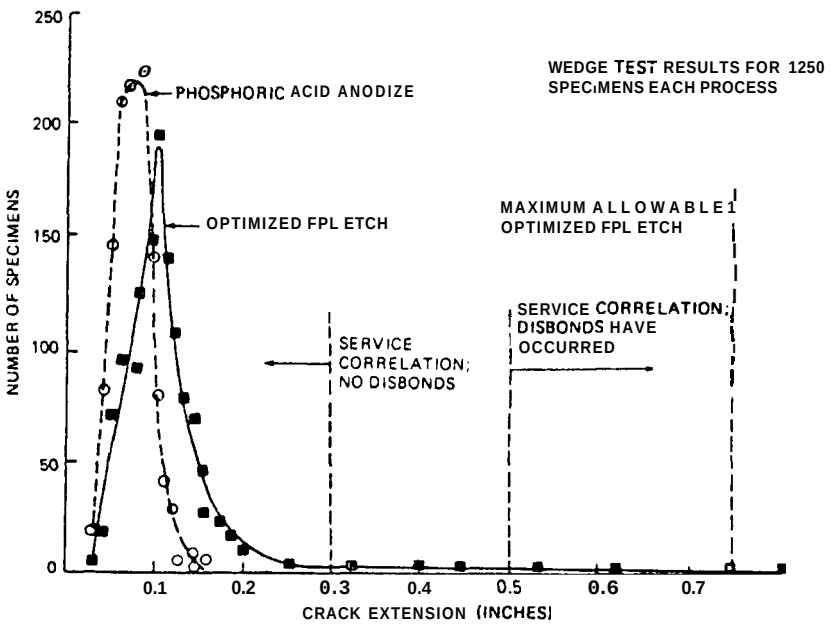


Fig. 4-16. Wedge test result comparison[323]

Cleaning cycles

With the large variety of alloy compositions, as well as varying shapes and forms of contamination that may be encountered, it is not possible to prescribe cleaning cycles for every individual operation. Thus, cases have been reported in which aluminium alloys are anodized directly after fabrication, while surface scale has been known to provide an adequate paint base. These are exceptional.

The care taken in the supervision of pretreatments will be amply repaid by the economy gained in the finishing processes, low rejection figures and the improved appearance and permanence of the finished article.

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CHAPTER 5

Chemical Conversion Coatings and Pretreatment Films

1. INTRODUCTION

Methods of chemically treating aluminium and its alloys to produce surface films **that** protect metal surfaces against corrosion and provide a suitable base lor organic coatings are of considerable industrial significance. Coatings are of two types; chemical conversion coatings are formed as a result of reaction of the metal surface with a wide range of different solutions, and 'no-rinse' coatings are formed by drying a variety of solutions on the metal surface. Of these, no-rinse types have gained steadily in importance at the expense of the chemical conversion coatings particularly for the treatment of metal in coil form. Both types of process are used mainly as proprietary solutions, and a large variety of these is available on the market.

Functions and advantages of conversion coatings

The main functions of conversion coatings are to improve the adhesion and corrosion protection of organic finishes and adhesives under wet and dry conditions and to provide corrosion protection of uncoated metal surfaces. Corrosion protection and resistance to wear and abrasion are inferior to the much thicker films produced by anodizing. Conversion coatings can also act as substrates for dyes but the effects are not competitive with those obtained by dyeing anodized surfaces.

The main advantages of chemical conversion processes are economy and speed. Pretreatment involves plant of relatively simple construction, and the

coating speed reduces costs to a fraction of those incurred by most anodizing processes. Because of the speed of many processes, they can be employed on modern high speed, continuous paint and lacquer coil coating lines.

Properties of pretreatment films

The natural oxide film present on all aluminium surfaces is responsible for the comparatively high corrosion resistance of the metal. The thickness of the oxide film varies, depending on alloy composition and processing or exposure conditions, but is normally in the range of 0.005-0.015μm. It will withstand corrosive attack but can only be used as a basis for paints or lacquers in cases where the coated products are not subjected to severely corrosive environments. For example, in many foil products the metal is only cleaned prior to lacquering or printing. By suitable chemical treatment, however, films can be formed that increase corrosion protection and provide an effective substrate for organic coatings. The ideal pretreatment film possesses the following properties' :–

(1) It should be continuous and impervious to gases and liquids.
(2) It should be inert or almost insoluble in its environment
(3) It should not electrolytically accelerate the attack on the basis metal.
(4) It should be resistant to mechanical damage such as abrasion or scratching or, if weak and thin, it should be self-repairing.
(5) It should bond readily with paints and other organic finishing materials.

2. HISTORY OF PRETREATMENT PROCESSES

The possibility of strengthening the natural oxide coating on aluminium was first suggested in 1857 by H. Buff? and C. Pollack[3] but it was not until 1915 that the first chemical pretreatment method was developed. Suggested by O.Bauer and O.Vogel,[4] the method involved the oxidation of the metal in a solution containing potassium carbonate, sodium bicarbonate and potassium dichromate. The process was used successfully on pure aluminium and on aluminium-zinc (7-10% Zn) alloys. Improvements in the process were achieved by adding an aluminium containing accelerator to the Bauer-Vogel solution.' A number of other processes were developed between 1922 and 1930, but it was not until 1930 that a rapid, simple and economical process was devised.[6] Closely related to the original Bauer-Vogel process it employed a solution containing sodium carbonate and sodium chromate. Known as the M.B.V. process (Modifizierter Bauer-Vogel Process) it only required a pretreatment time of 3-5 minutes and, depending on alloy composition, gave coatings suitable as a basis for organic finishes. Improved corrosion protection could be achieved by sealing the films in a water-glass solution. The process was applied to aluminium and alloys low in copper. Later

developments of the M.B.V. process were the E.W.[7] and L.W.[8] processes developed by the Vereinigte Aluminium Werke A.G. These allowed the production of colourless coatings and the effective protection of copper-containing alloys. The corrosion protection of the films was higher than those formed in the M.B.V. process but they were not suitable as a basis for paint. The solutions employed were based on the M.B.V. solution, but also contained sodium silicate or disodium phosphate. The Alrok process, developed in the U.S.A. and operated under patents held by the Aluminum Company of America, produces coatings similar to those produced by the M.B.V. process. The solution consists of potassium carbonate and sodium dichromate. The Pylumin processes were patented by the Pyrene Co. Ltd. in 1936[9] and like the L.W. process employ additions of disodium phosphate or a heavy metal carbonate to the M.B.V. solution. Modifications to processes of this kind have continued up to the present day and the most recently patented solution involves additions of trivalent chromium salts and complexing agents to alkaline chromate solutions. The presence of the complexing agents greatly enhances the solubility of trivalent chromium and results in solutions capable of rapidly forming protective coatings with good paint performance on aluminium, zinc and aluminium-zinc alloys.[10]

Phosphating processes originally developed for the pretreatment of steel surfaces and patented by T.W. Costlett in 1906" were adapted for aluminium in the mid 1940's.[12] Developed by the Parker company and known as Bonderizing, the process is similar to the ones used for steel and zinc pretreatment. Formulations contain a metal acid phosphate solution, an oxidizing agent, and a complex fluoride accelerator. Crystalline coatings are formed by immersion in a solution containing an acid phosphate and a salt of a metal which forms an insoluble phosphate." The metal salts used are normally iron, manganese, zinc, cadmium or nickel. An amorphous form of the pretreatment has been developed. Zinc phosphating[13] is one of the most promising pretreatments for the rapidly developing painted aluminium car component business. Phosphating pretreatments are now being used extensively for the pretreatment of aluminium components for vehicles in Europe, Japan and the United States.[14] Amorphous iron phosphate and crystalline zinc phosphate treatments can also be used prior to powder coating.[13]

Pretreatments based on the oxidation of aluminium by acidic chromates were first described in the mid 1940's and their use has increased in parallel with the considerable increase in the use of coil coating for the continuous painting and lacquering of aluminium sheet and foil products. The processes are equally effective as batch pretreatments for extruded sections and castings. They can also be applied to all alloy types. Pretreatment involves the reaction of the metal surface with acid solutions containing hexavalent chromium and fluoride ions. Chromium containing products of the reaction are deposited on the metal surface to form the film. Known as the Alodine processes, they were developed by the American Chemical Paint Company in 1945, and were introduced in Britain by I.C.I. Ltd. as the Alocrom processes. Some of the first commercially useful versions of the conversion coating were the amorphous phosphates[15] (the 400 Series), and these are produced by reacting aluminium and its alloys with a

combination of the primary solution and phosphates.[16] Because of the non-toxicity of the films formed and the ease of paint coverage, the pretreatments are particularly useful for extrusions and containers, and they continue to be used on modern or recently built plants.[17,18] They are also an effective base for powder coatings[19] and electrocoated products." Neutralisation of alkaline cleaners and additional cleaning give the pretreatment particular advantages.[15]

Amorphous chromate coatings became popular because of their simplicity and excellent uncoated corrosion resistance. All that was required for this type of pretreatment were the primary acid solution of hexavalent chromium and a source of fluoride. Because of their higher corrosion protection, the most widely used conversion coatings for painted products were the accelerated chromates (the 1200 series). In these formulations, potassium ferricyanide was added to the primary solution in order to increase the rate of film growth. In general, thinner pretreatment films give superior coating adhesion and thicker films more effective corrosion resistance. In addition, a rapidly forming, brush-on version of the 1200 series of accelerated chromate pretreatment was developed,[20] and a range of other compounds have been used as accelerators, including molybdates,[21] vanadates and tungstates.[21,22]

Although chromate conversion coatings have been used successfully for many years, and continue to be used to the present day, particularly for extrusions and in the aircraft industry,[23,24] environmental considerations[25,26] and the cost of the disposal of the highly toxic effuents have led to the increased use of three main groups of alternative processes. However, it has been claimed that none of the non-chromate alternatives satisfy all the requirements of the aircraft industry[27] and very few are capable of giving surfaces that can meet the very stringent requirements of the specification MIL-C-5541.[28]

The first series of alternative processes are the dry-in-place or no rinse pretreatments. Such pretreatments are particularly effective for sheet coating lines where they can simply be rolled on to the metal surface. Effluent problems are minimised because of the considerable reduction in the total amount of effluent from the processes. It is more difficult to apply no-rinse pretreatments to complex shapes often encountered on extruded sections. and, although some no-rinse formulations for extrusions have been described,[29,30] widespread use has not been reported. Some no-rinse formulations contain chromium, but others are based on a wide range of different chemistries. One of the most widely used and successful formulations is based on a solution of partly reduced chromates and colloidal silica. The first and best-known system of this type is Accomet C, developed by Albright and Wilson Ltd.[31] in the late 1960's. Partial reduction of the chromate solution is effected by reaction with organic reducing agents such as sugars, starches or alcohols.[31] Bonderite 6010 manufactured by Henkel has a very similar composition.[32,33] In Gardabond 4918/2 developed by Chemetall chromates have been incorporated into an advanced organic polymer pretreatment system.[34] Other chromium containing formulations that have been developed are hexavalent chromium free, so are fully acceptable as pretreatments for the canning and food packaging industries. For example, NR6207,[35] developed by Henkel in the mid 1970's, is currently one of the most widely used formulations, and it is of interest

because it can be regarded as a no-rinse version of the original chromate/phosphate pretreatment. The formulation comprises chromium trifluoride, phosphoric and polyacrylic acids, and results in a pretreatment film of similar composition to the chromate phosphate process.[36]

In the second series, interactive chemistry with non-chromium containing solutions is used to form films on the metal surface. Such pretreatments are available in both rinse and no-rinse forms. A range of formulations based on fluozirconates and titanates have proved to be amongst the most popular. Originally developed for pretreating for beverage cans,'' a number of such formulations is now available that are capable of meeting the exacting requirements of the architectural industry,[38] and as a result commercial paint pretreatment lines have started to successfully make the transition to non-chromium formulations.[25,39,40] Incorporation of recently developed polymers, usually based on acrylic acid copolymers, has led to the consistency in paint performance. Various modifications to the inorganic component of the formulation, usually in the form of anodic or cathodic corrosion inhibitors, has led to corrosion resistance of painted products claimed to be comparable to that achieved by chromate conversion. However, the operating window of such formulations appears to be more critical than chromate pretreatments.[38] They are more sensitive to coating weight and continue to be more sensitive to the cleanliness of the incoming metal, but for certain applications more consistent performance than chromate pretreatments has been claimed.[39]

The third series of alternative pretreatments involve electrolytic processes usually used at high temperatures. AC anodizing in sulphuric[41,42] and phosphoric[43] acid can be used to pretreat aluminium for both paints and lacquers. Effuents from such lines are readily disposable or recyclable, so do not present the environmental problems of chromate pretreatments. These processes have been described in Chapter 4.

Finally, replacement of a chromate process with abrasive blasting has also been found to be possible for armour plate alloys.'''' The potential of physical vapour deposition, PVD, processes for paint pretreatment has also been explored.[45]

In todays world a combination of all types of pretreatment is in use, depending on the type and scale of the application. To appreciate the total volume of material being pretreated, it is of interest to note that in 1992 European production of batch coated aluminium was estimated as 448,000 tonnes and coil coated material as 282,000 tonnes.[46]

3. HYDRATION PRETREATMENT

Oxidation in hot water

The interaction of aluminium and water has been extensively reviewed.[47] From room temperature to 90°C the hydroxide overlayer is a duplex film, consisting of pseudoboehmite adjacent to the metal substrate, and a layer of bayerite crystals at

the outer surface. The bayerite crystals are not embedded in the surface or attached to the pseudoboehmite layer so can be removed mechanically or by adhesive taping. The crystals have the appearance of cones, wedges or rods and have been referred to as somatoids.[47] The pseudoboehmite of the film occurs in the form of platelets, so can be readily identified.

Pseudoboehmite is an aluminium oxyhydroxide similar to boehmite (AlOOH), but containing more water, and bayerite is a form of aluminium trihydroxide [$Al(OH)_3$].

Above 90 to 100°C the hydroxide layer is a relatively well crystallized pseudoboehmite film. At 1 atm. pressure no bayerite has been observed, but at increased pressure bayerite has been shown to be present up to 120°C. However at normal pressure above 100°C boehmite is the only oxide reported. The interrelationships of chemical structure and physical properties of the oxide/hydroxide of aluminium have been reviewed.[48] It has also been shown[49] that for reactions at 100°C there is no difference between the hydration products formed on an aluminium foil substrate and an anodic oxidation film. The calculated water contents of the hydrated film vary between 20 and 27%, with a specific gravity of the film of 2.4, as compared to 3.0 for pure boehmite.

On the air-formed oxide film and on anodized surfaces, film growth proceeds in three stages. During an induction period[50] little change in the initial surface is observed (Fig. 5-1).

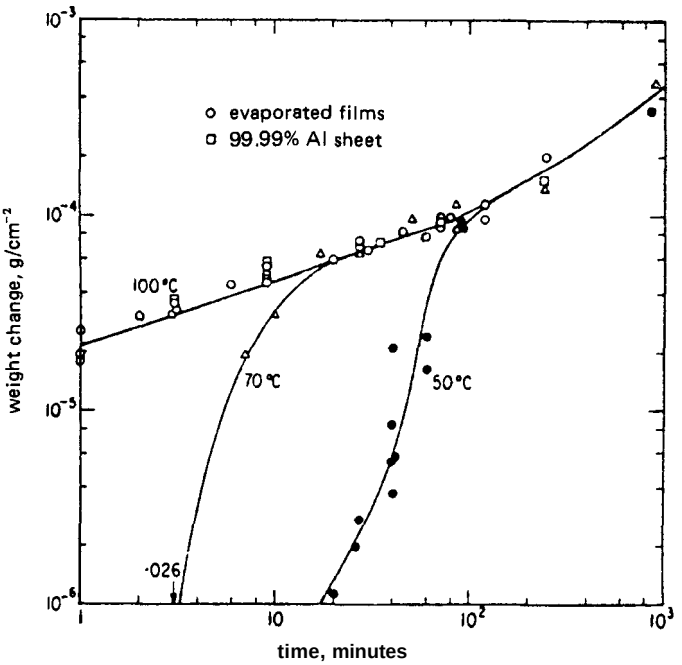


Fig. 5-1. Weight changes of aluminium specimens exposed in water[49]

The second stage of the reaction is the formation of the pseudoboehmite layer, and the final stage is the crystallization of bayerite. These last two stages may overlap.[51]

Mechanism of film growth

When aluminium reacts with water the driving force for film growth is provided by an electrochemical process. The anodic and cathodic half-cell reactions can be written[47] as:

$$\text{Anodic} \qquad Al + \left\{ \begin{array}{ll} 3(H_2O) & Al(OH)_3 \\ 2(H_2O) & \rightarrow \ AlOOH \\ \frac{3}{2}(H_2O) & \frac{1}{2}Al_2O_3 \end{array} \right\} + 3H^+ + 3e$$

$$\text{Cathodic} \qquad 3H_2O + 3e \rightarrow \frac{3}{2}H_2 + 3OH^-$$

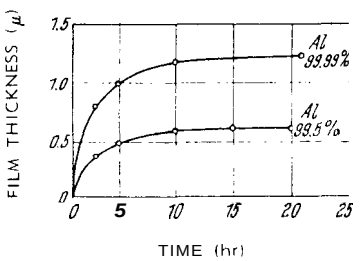


Fig. 5-2. Growth of oxide film on 99.99% and 99.5% Al in distilled water at 100°C[52]

The anodic reaction occurs over almost all of the surface, whereas the cathodic reaction takes place at preferential sites such as impurities and grain boundaries.[50] The standard potential for the overall electrochemical reaction depends on the composition of the hydroxide formed, but has values in the range -1.47 to -1.55V.[53]

Hydrogen evolution occurs at 80-100°C and commences after an induction period at separate points. During the early stages of reaction with water vapour saturated air, hydrogen induced blistering of the amorphous oxide film occurs. Hydrogen generation is localised at grain boundary-surface intersections.[54]

A model for film growth suggests that during the induction period the oxide film thickens and is penetrated by either protons, hydroxyl ions or water, until conditions for hydrolysis are established and a soluble aluminium species is

produced. Dissolution is accompanied by the simultaneous precipitation of hydrous oxides which can transform to pseudoboehmite. Film growth continues by diffusion through this layer at a rate probably determined by the inward diffusion of water and not the outward migration of Al^{3+}.[55] Under such conditions, new film growth occurs beneath the existing film.[49] The mode of bayerite formation is uncertain, but could be analogous to the ageing mechanism in a colloidal suspension,[56] where dissolution and reprecipitation of the pseudoboehmite is thought to occur in contact with water.

Hydrous film growth is affected by temperature.'' Metal purity also affects film growth with thinner films being formed on lower purity material (Fig. 5-2).[52] Inhibition of diffusion of aluminium ions due to the presence of impurities at the grain-boundaries,[57] or the presence of thicker barrier layers on the less pure metal, may cause the changes in film growth..

Alloying constituents and solution impurities also affect the colour of films formed in boiling water. On high-purity AI-Cu or AI-Ti alloys, dark films, varying from brown, blue and purple to grey and black, can be obtained, while still darker shades are formed when sodium metasilicate and carbonate or sulphate are present.[52]

Hydration processes

Steam treatment films

Coatings with improved overlying coating adhesion and improved corrosion and abrasion resistance can be produced by treatment of aluminium metal or alloy surfaces in **a** swirling flow of steam generated from deionised water.[58] The swirling action of the steam prevents the crystallisation of the oxide layer in definite or ordered patterns. The resulting high quality finish is said to comply with the US military specification MIL-C-554 1.

Boehmite coatings

Dense and protective films can be obtained on aluminium by boiling in distilled water, as previously described, but reaction is normally too slow for growing protective films for industrial use. However, the process has been used in the production of electrolytic capacitors from aluminium foil. Because they have a pronounced effect on film thickness and structure, water purity and temperature must be strictly controlled. Films of between *0.06-0.3* μm thickness can be grown in a few minutes in water at 75-120°C.[59] Chlorides and silicates must be rigorously excluded. Films formed in water containing as little as 1 ppm SiO_2 are up to 50% thinner, unstable, and are unsuitable for electrolytic capacitors. Optimum films are formed at pH *5-6* (Fig. *5-3).* Most hydrated films are used for the protection of capacitor foils in storage and are formed after the foil has been etched. For high

and medium voltage d.c. capacitors, thick hydrated oxide films are preferable. Such films are best applied immediately before forming because delay decreases the barrier layer thickness after forming. Thin, hydrated oxide films are the most suitable for low-voltage capacitors. The barrier layer at the base of the hydrated oxide film gives a voltage drop of approximately 1 volt for every 1.4nm thickness[59] and this is ideal for such capacitors.

A water treatment process has also been used for colouring aluminium flake. The flake is oxidized in a boiling mixture of alcohol with 30-35% (wt) water. The rate of the reaction and the thickness of the film depend on the water content of the mixture. An anhydrous oxide is formed at 35% water, but the degree of hydration of films formed in solutions containing 20% water is believed to correspond to boehmite[60] i.e., the degree of hydration increases with decrease in water concentration.

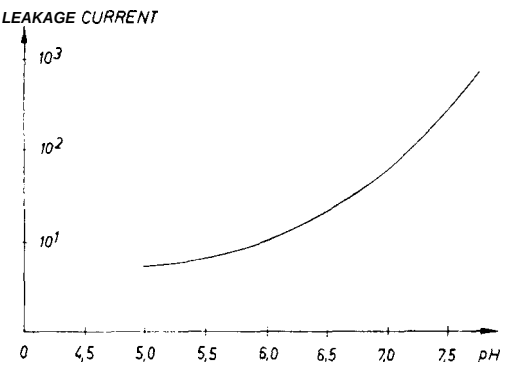


Fig. 5-3. Effect of pH of water on leakage current of foil oxidized by immersion in hot water[59]

Films formed by chemically assisted hydration

The oxidation of aluminium in the presence of water stops after a certain thickness is reached, because the film formed is substantially non-porous and will not allow the passage of the solution to the metal surface. To obtain thicker films, it is necessary to include in the solution reactants which will continue to penetrate through the growing film, or will result in the formation of a film which remains sufficiently porous to allow film growth to continue. Maintenance of these conditions requires careful control of the pretreatment solution pH. If pH is too high or too low, the material formed by reaction with the surface will simply dissolve in the solution and no further film growth will take place. Because of this, commercially suitable solutions are usually inhibited alkaline solutions or weak or

dilute acids, such as hydrofluoric, fluosilicic, chromic or tartaric acids, which form complex ions. Lithium hydroxides also have potential as film forming agents on aluminium.

Hydrotalcite films

In lithium hydroxide/lithium carbonate solutions a polycrystalline film comprised predominately of hydrotalcite $Li_2[Al_2(OH)_6] . CO, . 3H_2O$ is deposited on aluminium surfaces.[61 62] Films are formed by a coprecipitation reaction involving aluminium as aluminate ions $Al(OH)_4$- and lithium carbonate.[61] SO_4^{2-}, Cl^-, B r salts of lithium and LiOH alone also result in the deposition of films with similar properties.[62] Films formed by a 10 min immersion in a 1% lithium carbonate or 2% lithium hydroxide solution at 70°C have been claimed to have superior corrosion and alkali resistance to that obtained from anodized surfaces.[63] Subsequent treatment in sodium silicate and sodium fluoride can be used to increase the thickness of the deposited film.

Boehmite films formed in aqueous ammonium and organo-nitrogen compounds

Most of the boehmite films used for protecting aluminium surfaces are formed by treating the metal in a solution of an organo nitrogen compound. For example the staining and discolouration of aluminium sterilisation vessels can be prevented by coatings 0.05 microns or thicker formed by treatment in hot water containing an organic amine or amide.[64]

Boehmite coatings 5-200 μm thick are also believed to be formed on aluminium by treatment for 5-15 seconds at 85-100°C with deionised or distilled water containing 0.001-0.03% hydrazine or other organic amine.[65] Other patented processes use 0.1-10% (wt) triethanolamine or 0.5-15% (wt) hexamethylene tetramine at 70-100°C;[66] or an amine, such as hydrazine or hydroxylamine which has a reduction potential at least 30 mV higher than water, at a concentration of 0.1 M to saturation, pH 7.2 or above, temperature 75°C to boiling point.[67] Improvements are also claimed in the production of boehmite films in amine containing solutions by the addition 0.025-0.25 mole of a lithium salt[68] or 5-20 g/l of glycerol.[69] Use of quaternary ammonium salts has also been claimed,[70] and the addition of Mg, Ca or Co salts is said to overcome silicate sensitivity.[71]

Coatings formed by reaction with aqueous solutions of metal salts

A hydrated calcium-aluminium oxide film is formed on aluminium by immersion in a hot calcium hydroxide solution containing dissolved aluminium. Applying a small anodic potential greatly increases the rate of film formation.[72]

A protective coating is claimed to be formed on aluminium by immersion in a solution containing 4% alkali metal molybdate at 160-200°C (325-400°F) under pressure for at least 4 hours.[73]

Corrosion resistant, bacteria and fungi proof coatings suitable for heat exchangers can be produced by reacting aluminium surfaces with a solution of an alkali or alkaline earth metal sulphate or nitrate and a reactive or weakly basic organic compound[74] such as sodium mercaptobenzothiazole, oxine, triethanolamine or sodium benzoate. Coatings formed are comprised of basic double salts of aluminium and the cations used in the pretreatment solutions. At room temperature production of a 2 μm coating requires a treatment time of 3 hours, but at 90°C treatment time is reduced to a few minutes.

4. INHIBITED ALKALINE PRETREATMENTS

The basic reaction in inhibited alkaline solutions (eg the M.B.V., E.W. and Alrok processes and various other modifications), is probably the reaction of water with aluminium. Reactions also depend to a lesser extent on the type of inhibitor and alkali. In solutions containing chromate, secondary reactions of the chromate with aluminium may also result in the production of hydrous aluminium oxides in addition to chromic oxide[75]

$$Al + Na, CrO_4 + H_2O = Al, O_{(3\ x/2)}(OH)_x + 2NaOH + Cr, O,$$

However, the process is only a secondary one.[75]

Sodium carbonate in an M.B.V. solution may also be involved with the overall reaction **via** the formation of **a** sodium aluminate intermediate:[76]

$$2Al + Na_2CO_3 + 3H_2O = 2NaAlO_2 + CO_2 + 3H_2$$

that is subsequently hydrolysed:

$$2NaAlO_2 + H_2O = Al_2O_{(3-x/2)}(OH)_x + 2NaOH$$

but this is unlikely to be of significance,[77] and the main role of carbonates is likely to be as a source of OH- ions.

The m.b.v. and e.w. processes

The original M.B.V. solution contains:

sodium carbonate (anhyd.) 2-5% (opt. 3%)
sodium chromate (anhyd.) 0.5-2.5% (opt. 1.5%)

and is operated at between 90 and 100°C for 3-5 minutes. After treatment, the pretreated metal is rinsed in hot or cold water and dried. Constituent concentrations are not critical, but they do influence treatment time. Because the solution also acts as an alkaline cleaner, initial precleaning of the metal surface may also be unnecessary.

The E.W. process[78] is a patented modification of the M.B.V. process where the reaction is partially inhibited by the addition of silicates or fluorides to the pretreatment formulation. The recommended bath composition using sodium silicate is:

sodium carbonate 47 g/l
sodium chromate 14 g/l
sodium silicate (pure, dry) 0.06-1 g/l

Full details of both the process and a range of modifications including the paste process have been described elsewhere.[79] Typical corrosion performance of metal pretreated with the processes is given in Table 5-1.

Coatings can also be dyed to a variety of colours using solutions of metal salts[80] but the colours are much inferior to those obtained by anodizing. Improved corrosion protection may be obtained by sealing in waterglass.[81] Chemical and mechanical resistance of the sealed M.B.V. films can be improved further by annealing.[79]

Other modifications to the basic process include the L.W. and Pylumin process, where disodium phosphate is added to the M.B.V. solution.[8,9] A heavy metal carbonate may also be substituted for the phosphate in the Pylumin processes. The Alrok process produces coatings similar to those produced by the M.B.V. process. The solution consists of potassium carbonate and sodium dichromate and the coatings are sealed in potassium dichromate solution. Other modifications to the MBV process can be found in earlier editions of this book.[79]

Filiform corrosion testing (CIN 65472) of organic coatings on an AlMg substrate has shown that M.B.V. pretreated metal can significantly outperform chromate or zirconium oxide pretreated material over periods of up to 4500 h.[82] Despite the fact that the pretreatment film was only 1-2 μm thick, it also outperformed a much thicker coating of 5-6 μm formed by the Alrok process.[82]

Later modifications to the process include the addition to alkaline chromate solutions of:

(a) 0.01-10 g/l of a zirconium compound and a complexing agent such as a gluconate or heptonate[83]

(b) an alkali metal salt, a complexing agent such as EDTA, an oxidizing agent (eg peroxide) and a betaine surfactant.[84]

Effective pretreatment for aluminium, zinc and aluminium-zinc alloys is possible using such formulations, because complexing agents increase the solubility of the trivalent chromium in the pretreatment solution.''

Table 5-1

Effect of alloy composition and casting skin on appearance and corrosion resistance of M.B.V. and E.W. coatings[85]

Alloy composition %	Coating*	Casting skin not removed: Appearance	Casting skin not removed: Corrosiori resistance after 60 days in artificial fog	Casting skin removed: Appearance	Casting skin removed: Corrosion resistance after 60 days in artificial fog
Al 99.2	A	–	Local corrosion	–	Local corrosion
Si 0.36	B	Metallic,green	Unchanged	Light grey	Unchanged
Fe 0.41	C	Uniform, slightly matt white	Unchanged	Iridescent	Unchanged
Al 99.5	A	–	Local C	–	Local C
Si 0.16	B	Metallic,green	Unchanged	Light grey	Unchanged
Fe 0.27	C	Uniform, slightly. matt white	Unchanged	Iridescent	Unchanged
Al 99.8	A		Matt, white,		Matt, white.
Si 0.088			spotty, no		spotty, no
Fe 0.11			deep attack		deep attack
	B	Light grey,	Unchanged	Light grey	Unchanged
	C	Uniform, slightly matt white	Unchanged	Iridescent	Unchanged
Al 99.98	A	–	Matt,white,		Local small
Si 0.0030			spotty		holes
Fe 0.0048	B	Metallic, slightly milky	Unchanged	Grey white	Unchanged
	C		Unchanged	Slightly iridescent	Unchanged
Silumin	A		Occasional		Local strong
Si 12.05			small holes		
Fe 0.18	B	Spotty, light	Occasional	Uniform dark	Occasional
Al remainder		& dark grey	spots	grey	spots
	C	Metallic,light, slightly iridescent	Occasional spots	Metallic,light. slightly iridescent	Occasional spots
Al-Mg 3	A	–	Local corrosion	–	Local corrosion
Mg 3.21	B	Metallic, Slightly	Unchanged	Spotty, metallic	Unchanged
Si 0.17		greenish		light, slightly green	
Fe 0.13					
Al remainder	C	Unchanged	Unchanged	Unchanged	Unchanged
Al-Mg 7	A	–	Local corrosion	–	Local corrosion
Mg6.57	B	Metallic, slightly	Unchanged	A little spotty,	Unchanged
Si 0.22		matt white		otherwise	
Al remainder				unchanged	
	C	Unchanged	Unchanged	Unchanged	Unchanged

– *A = *Without treatment*
B = *M.B.V. treatment and waterglass seal*
C = *E.W. treatment*

5. CHROMATE PRETREATMENT

Film formation

Chemical and detailed XPS studies[86,87] have established that two components of the chromate and chromate phosphate pretreatments are of importance in the reaction of the pretreatment solution with aluminium surfaces. Fluorides in solution remove or thin the oxide film originally present on the metal surface.[88]

$$Al_2O_3 + 6HF = 2AlF_3 + 3H_2O$$

Fluorides also maintain a thin oxide at the interface between the growing pretreatment film and the metal substrate by removing any oxides or hydroxides formed.

Reduction of chromate ions occurs at the metal or thinned oxide surface according to:–

$$8H^+ + 2HCrO_4^- + 2A1\ (metal) = 2Al^{3+} + Cr_2O_3H_2O + 2H_2O$$

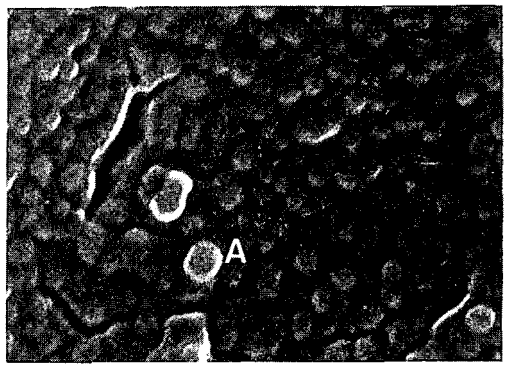
Initiation of the reaction can occur at flaws or grain boundary intersections in the surface.[89] Electron tunnelling at flaws, or cathodic sites thinned by the interaction of fluorides, provides a mechanism for reduction of the chromate ions to form the trivalent species.[89,90]

At low temperatures, ferricyanide accelerated pretreatment can result in the rapid coverage of the surface with discrete fairly uniformly sized rounded nodules approximately 50nm diameter and 10nm in thickness.[91] Elongation of these nodules occurs with increased pretreatment time. Reaction products formed on the surfaces pretreated at more conventional temperatures can precipitate in the form of gelatinous spherically shaped particles[91] of a size varying from <3 to 30nm in diameter. (Fig. 5-4.).

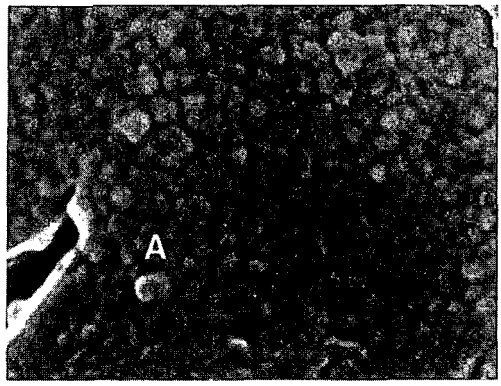
Such particles closely resemble those found in chromium hydroxide sols.[93] The size of particles varies considerably depending on a number of parameters, including surface topography and the presence of surface intermetallic particles.[91,92,94] During the early stages of film formation coverage of intermetallic particles can occur at different rates to that found on the metal matrix surface.[91] On thicker films the particles can deposit in layers[92,94] (Fig. 5-5).

In such structures surface particles can be of smaller size than those beneath. (Fig. 5-5). As film thickness increases, a tendency for the film to crack and form a "mud crack" structure increases[92,95] (Fig. 5-6).

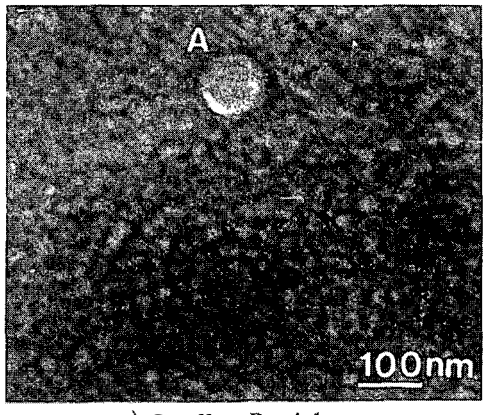
Mud-cracking occurs as a result of shrinkage of the film as the large amounts of water trapped between the particles in the gel deposited on the metal surface is removed during drying. Cracking of the films and surface texture can increase during ageing.[96]



a) Largest Particles



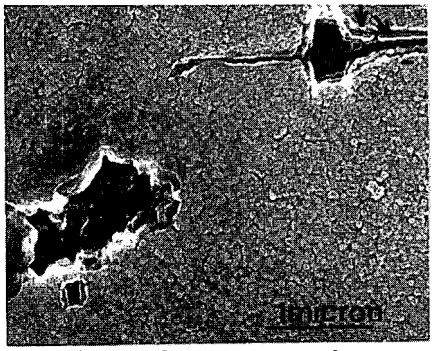
b) Intermediate Particles



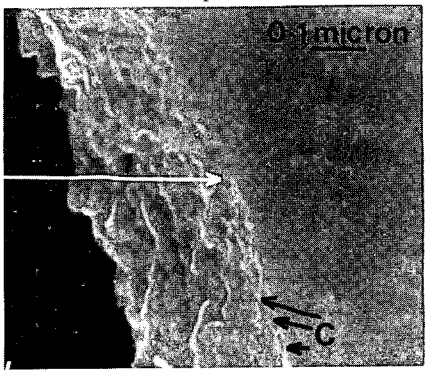
c) Smallest Particles

A: Larger particles randomly distributed across surface

Fig, 5-4 Particulate structures of ferricyanide accelerated chromate pretreatment film deposited on aluminium[92]



a) Layer Structure near Fault in Film on Electropolished Substrate



b) Layers of Particles on Surface of Thick Film on Normal Substrate
C: Layers of film near defect



c) Larger Particles beneath Surface

Fig. 5-5. Layer- Structures of Chromate Conversion Coatings i) uniform layers of film deposited on electropolished substrate ii) layers of fine particles deposited on thicker particles beneath[94]

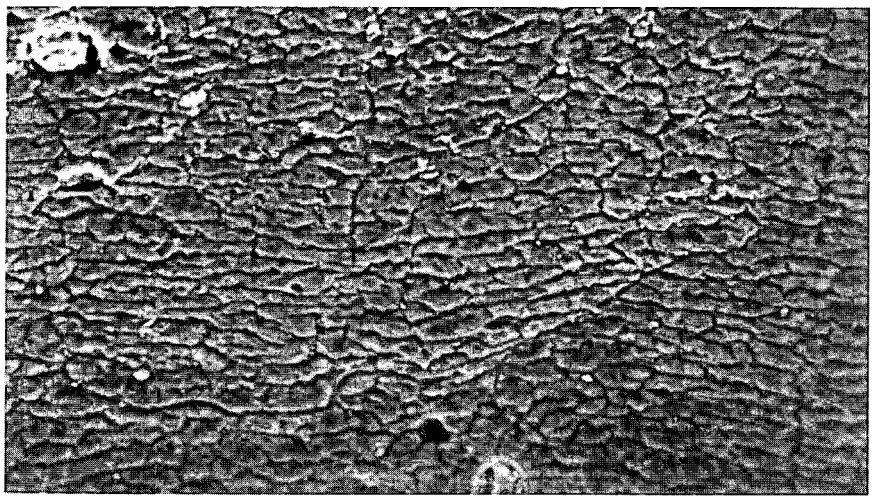


Fig. 5-6. Mud Crack Pattern of Alocrom I200

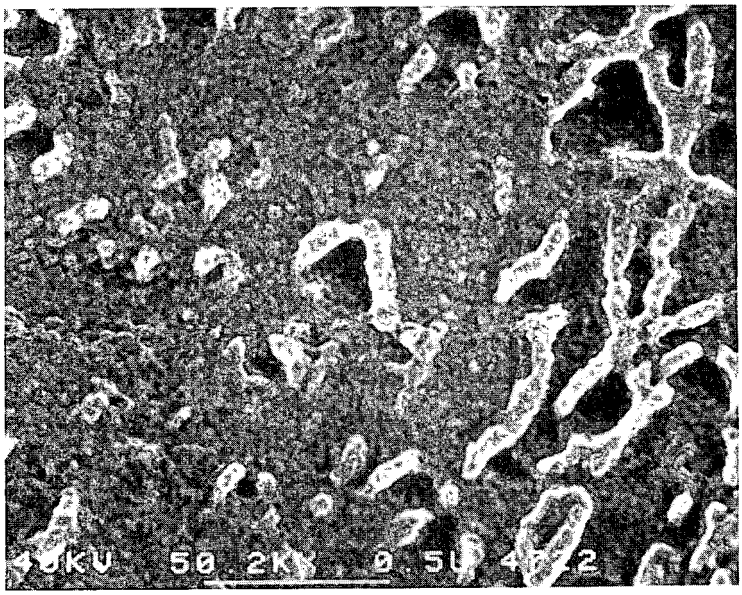
Chromate phosphate pretreatment can also result in the formation of films with a "mud-crack" topography."

The process can also lead to films with a filamented structure.[98,99]. The particles that make up the filaments are approximately 30-60nm in diameter." The types of filaments formed and particle distribution are dependent on surface preparation and the pretreatment time. On acid cleaned surfaces, filaments can be several particles in diameter (Fig. 5-7) but, on electropolished surfaces, filaments a single particle in width can be formed (Fig. 5-8).[99] On both substrates, low pretreatment times tend give films comprised mainly of discrete particles[99] (Fig. 5-7 and Fig. 5-8). Decrease of the phosphate content of the pretreatment solution can result in the deposition of very large (1-2 μm particles) on the metal surface."

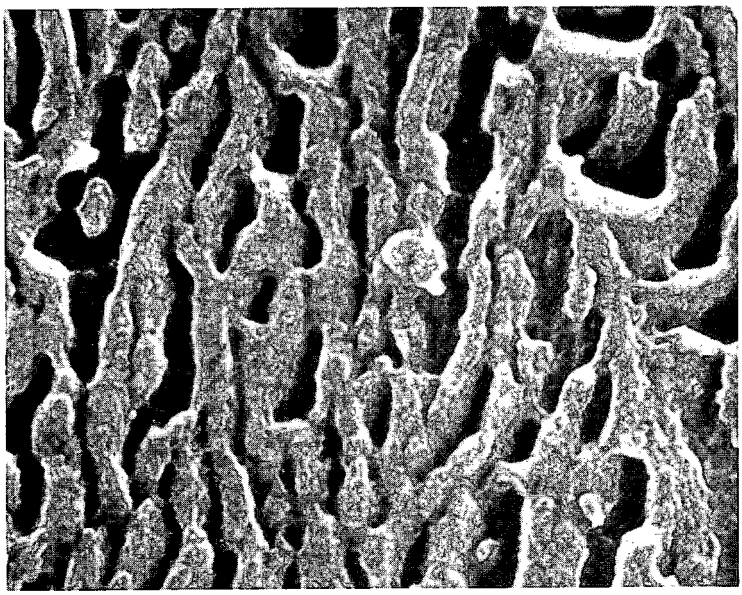
Diffusion of the reactants through the gelatinous growing film provides a mechanism for the continuation of film growth on surfaces already covered with a layer of reaction products.

Although topography may vary, the surface composition and the general distribution of elements throughout ferricyanide accelerated and chromate/phosphate films show little dependence on pretreatment time (Fig. 5-9 and 5-10). Concentrations of iron and nitrogen in surface regions of the film[87] (Fig. 5-9), and the similarity of XPS analyses of mechanically exposed subsurface regions of the film[94], suggest that the ferricyanide accelerator is deposited in the form of a monolayer on all of the particles of the film.

In chromate/phosphate pretreatment films, phosphates are concentrated on the surface of the particles in the film but in this case they also form a surface rich layer of chromium phosphate.[99] Heating of the film at 200°C gives changes in the infrared spectrum consistent with loss of water of crystallisation from the chromium phosphate.[98]

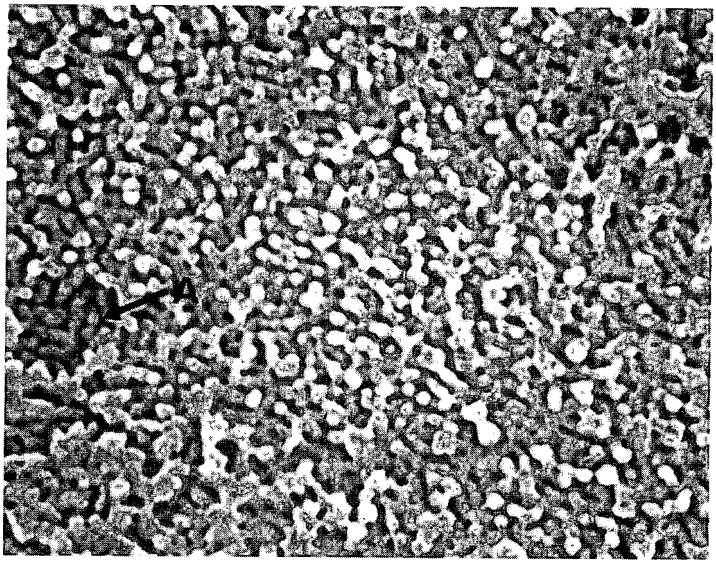


a) 5 Seconds Treatment

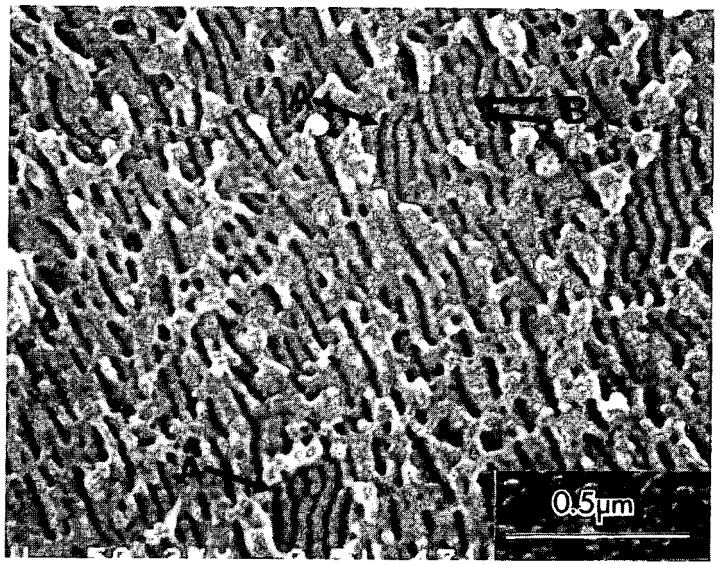


b) 10 Seconds Treatment

Fig. 5-7. Filamented and non-filamented areas of chromate phosphate films deposited on electropolished substrate"



Area of Particulate Topography



Area of Filamented Topography

A : Circular areas of Thinner Pretreatment
B : Particles lined end-to-end

Fig. 5-8. Growth of filamented structures in chromate-phosphate films"

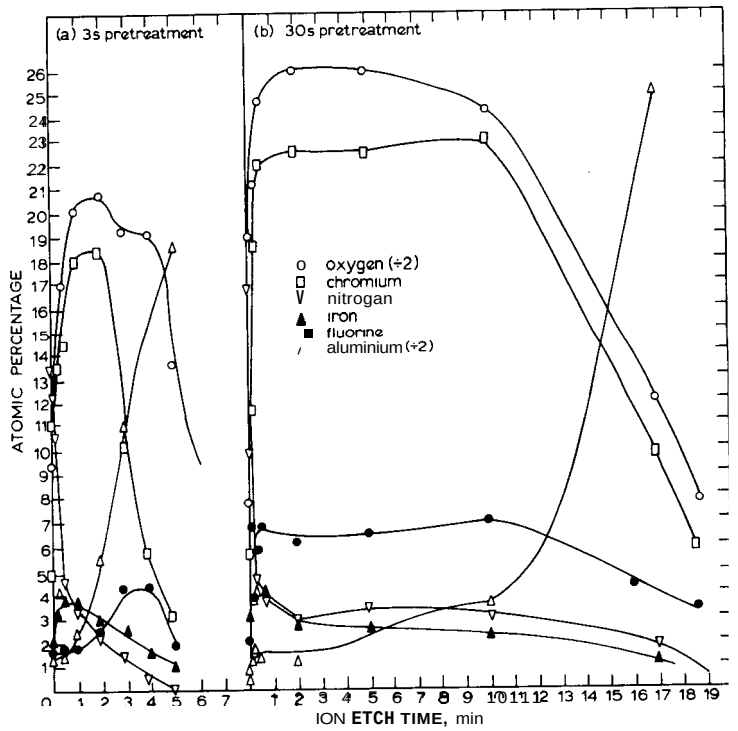


Fig. 5-9. Effect of film thickness on XPS depth profiles of ferricyanide accelerated films[95]

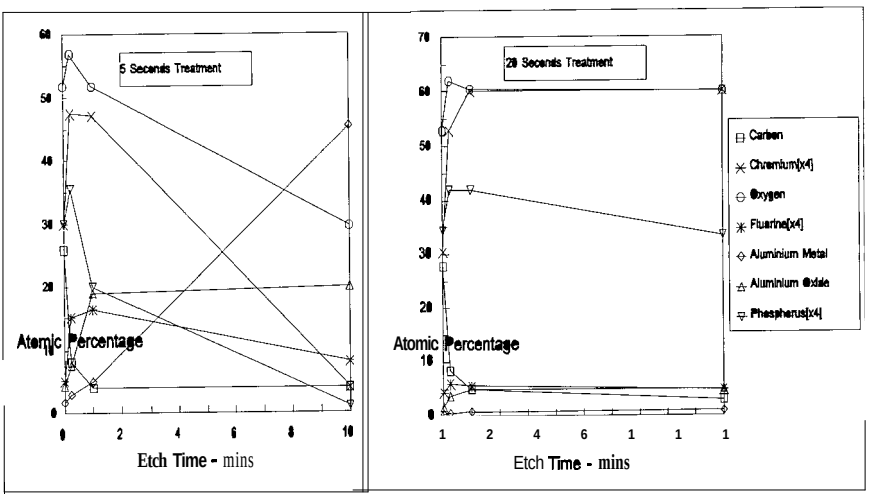


Fig. 5-10. Effect of film thickness on XPS depth profiles of chromate phosphate films

All chromate ions in solution are reduced to Cr^{3+} during chromate phosphate pretreatment.[99,101] However chemical,[101] X-ray Absorption Near Edge Spectroscopy (XANES),[102] X-ray absorption spectroscopy (XAS)[103] and XPS[87,96] studies have all shown that various amounts of chromate compounds can remain within the surface, or bulk, of ferricyanide accelerated pretreatment films. XAS studies[103] indicated that up to 23 ± 2% of the total chromium within the film can occur as tetrahedrally coordinated Cr^{6+}. The presence of the chromate ions within ferricyanide accelerated films is responsible for their superior corrosion inhibition. Improved corrosion protection from pretreatment films containing Cr(VI) compounds is believed to originate from the partial release of such compounds when the films are exposed to moist or corrosive environments. Released material can repair defects in the film by reaction with aluminium metal at the defect site. Released Cr(VI) compounds may also protect areas where the metal substrate has been exposed because of stressing during fabrication of painted material. However, levels of Cr(VI) compounds remaining in the film can be insufficient to counter the developing network of cracks that are formed during aging.[96] Impedance measurements and polarisation studies of the corrosion behaviour of chromate pretreated Al (99.995%) and Al (5050) substrates in neutral solutions have shown that, especially at high anodic potentials, chromate ions migrate from the film and this results in the formation of a less protective layer. In addition the porous conversion layer is converted to a thinner and more compact oxide layer.[104] Chromates can be removed from freshly formed films by treatment in boiling water,[105] and the levels also decrease during salt spray corrosion testing."" Loss of trivalent chromium can also occur during salt spray testing."" Chromate levels within unaccelerated conversion coatings are higher than found in the accelerated versions.[101]

A summary of the physical and chemical structures of ferricyanide accelerated chromate and chromate phosphate films is included in Fig. 5-11.

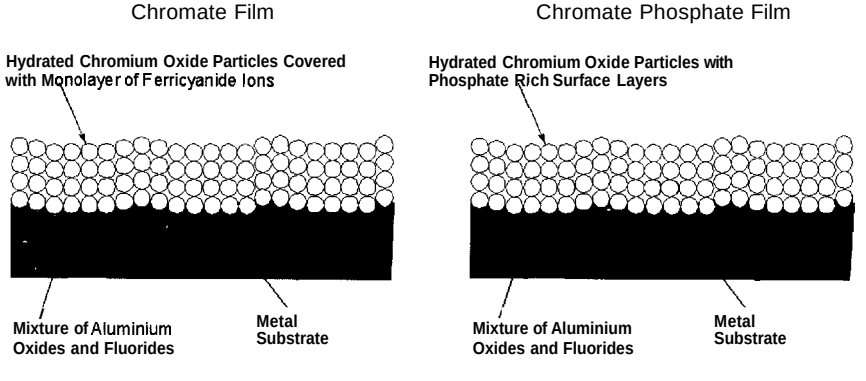


Fig. 5-11. Structures of pretreatment films

Formation of a surface layer of phosphates or ferricyanides provides a mechanism for the acceleration of film growth. Such layers will prevent the interaction between the chromates within the growing film and the surface of the hydrated chromium oxide particles that are first formed as a result of reaction with the metal surface. **As** a result, a higher concentration of chromate ions is available for reaction with the metal substrate. Molybdates and other accelerators may also act in a similar manner. Ferricyanide ions may also block sites within the gelatinous particles from reaction with chromate ions.[96]

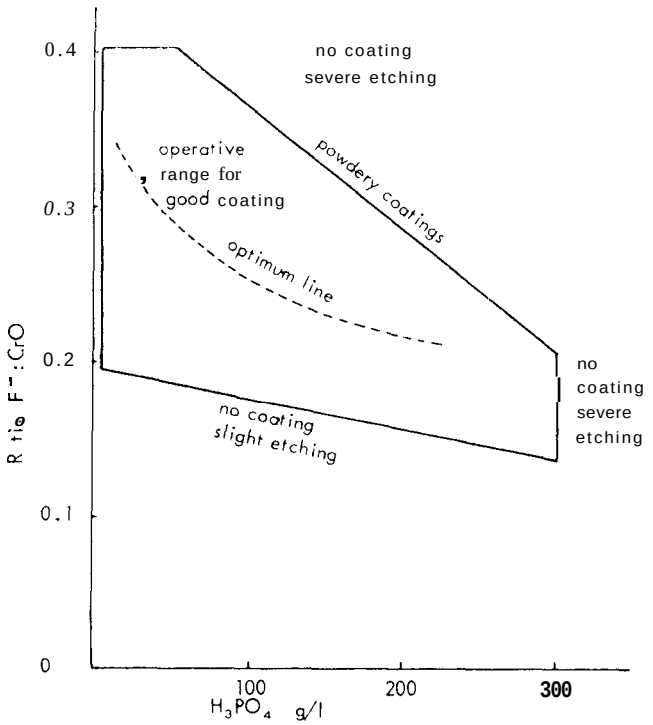


Fig. 5-12. Operating range chart using alkali fluoride chromic acid and phosphoric acid (Alodine/Alocrom process)''

Chromate-phosphate processes

Chromate phosphate pretreatments continue to be the preferred choice for many pretreatment lines, including a number of recently built lines for painting or powder coating of extrusions.'' Chromate-phosphate pretreatments use an acid solution containing chromates, phosphates, and fluorides within the range shown in Fig. 5-12.[16]

The optimum range of the solution is:

	g/l
PO_4^{3-}	20-100
F^-	2.0-6.0
CrO_3	6.0-20

and the ratio of fluoride to chromic acid (F^-/CrO_3) should lie between 0.18 and 0.36, with an optimum value of 0.27. If the phosphate content is too low (below 6 g/l), the concentration of fluoride and chromic acid becomes critical and control of the solution is difficult. If the fluoride: chromic acid ratio is too high, the coating is non-adherent and the surface is etched. No coating is formed if the ratio is too low.

The total acidity should not exceed 3N. (For this purpose, all polybasic acids where the second ionisation constant is less than 10^{-7} have been considered as monobasic.) If the acidity is *too* high, powdery, non-adherent coatings are formed or the metal may be etched. Reliable pH measurement is not possible due to the oxidizing effect of the dichromate ion on indicators or hydrogen or quinhydrone electrodes, and the effect of fluoride on glass electrodes. A commercial pH meter with a glass electrode can be used for control, however, and the final 'nearly-steady' pH reading, or the lowest value indicated within the first 10 minutes, is taken. This should be preferably between pH 1.7 and 1.9. The fluoride may be included in the form of a complex acid such as fluosilicic or fluoboric acid.[106]

The cations present in the solution are important only as buffers. Aluminium, trivalent chromium, zinc, copper, manganese, iron, nickel, cobalt, calcium, barium, strontium, tin, sulphate, nitrate, acetate and chloride may be present in reasonable quantities without harm to the coating. Reducing agents are harmful as they cause loss of dichromate by reduction to trivalent chromium (though this can be done deliberately in strip coating lines *to* produce a chromate-rinsed phosphate coating).'"' Many of the commercial alloys have been coated satisfactorily.

Examples of solutions given in the patent specification are shown in Table 5-2.

The consumption rates of the ingredients per sq ft (i.e. per 9.3dm^2) are approximately:

F^- (gm)	1.0
CrO_3 (gm)	0.7-1.4
Acid (gm equivalents replaceable hydrogen)	0.06-0.14
PO_4^{3-} (gm)	0.5-1.0

During processing, concentrations of acid, phosphate, fluoride and chromate decrease as a result of the reactions involved in film formation.

The coating loses 40% of its weight on heating and becomes increasingly corrosion resistant as a result of the dehydration.

Table 5-2

Alodine and Alocrom solutions, patented compositions

	A	*B*	*C*	*D*	*E*	*F*
	(gm per litre)					
Phosphoric acid (75%) (H_3PO_4)	64	12	24	–	–	–
Sodium dihydrogen phosphate ($NaH_2PO_4 \cdot H_2O$)	–	–	–	31.8	66.5	31.8
Sodium fluoride (NaF)	5	3.1	5.0	5.0	–	–
Aluminium fluoride (AlF_3)	–	–	–	–	–	5.0
Sodium acid fluoride ($NaHF_2$)	–	–	–	–	4.2	–
Chromic acid (CrO_3)	10	3.6	6.8	–	–	–
Potassium dichromate ($K_2Cr_2O_7$)	–	–	–	10.6	14.7	10.6
Sulphuric acid (H_2SO_4)	–	–	–	–	4.8	
Hydrochloric acid (HCI)	–	–	–	4.8	–	4.0

Coating weights of freshly formed films can be determined by stripping the film in 70% nitric acid solution. Following heating, or after standing for more than about 24 hours, the coatings cannot be stripped using nitric acid but they can be removed using molten salt.[108] X-ray fluorescence is the basis for the most effective method of assessing coating thickness. Secondary fluorescent radiation from samples irradiated with X-rays is characteristic of the elements present in a coating, so with a suitable detector, both qualitative and quantitative assessment of coating composition and thickness can made. A particular instrument developed for pretreatment evaluation is the Portaspec (Fig. 5-13). A typical relationship between Portaspec measurements and coating weight for a chromate-phosphate coating is shown in Fig. 5-14.

For corrosion protection, the chromate-phosphate coating can be several microns in thickness, but when used as a pretreatment for organic coating it is normally less than 0.25 micron (0.01 mil). **A** combination of chemical analysis, infra-red and thermo-gravimetric analysis showed that the coating contains[109]

Al	9.41%
Cr	19.7%
PO_4	32.8%
H_2O	26.1%

As mentioned earlier the coating also contains chromium oxide and fluorides.

After pretreatment, the coating is rinsed in cold water for 10-15 seconds; counter-flow rinsing has been recommended.'"' Subsequently it is immersed for 10-15 seconds in a 0.05% solution of chromic acid or phosphoric acid ('Deoxylyte' rinse) which is kept at 40-50°C. The coatings are dried at 40-65°C.

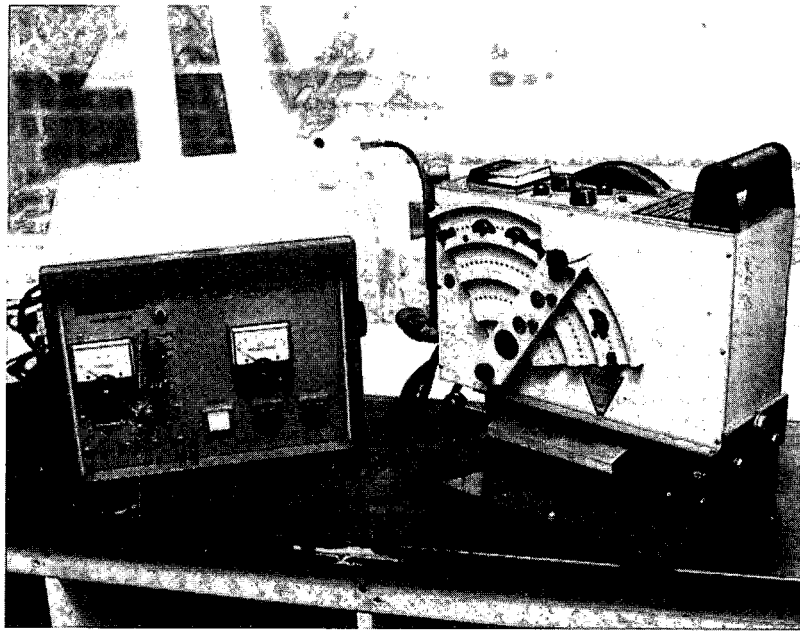


Fig. 5-13. Portaspec X-ray spectrograph

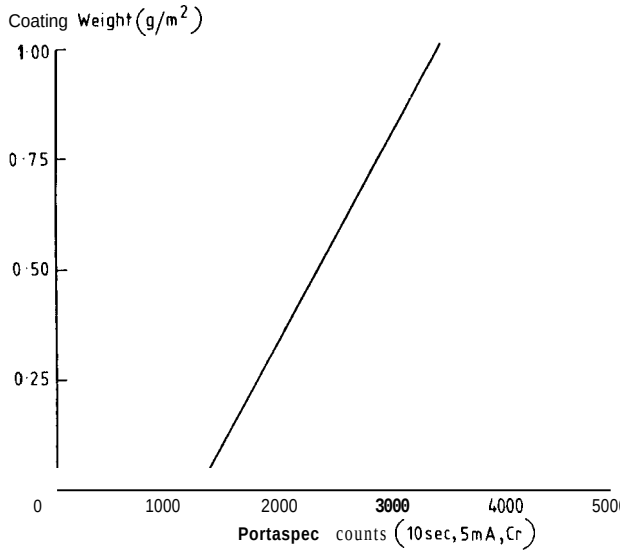


Fig. 5-14. Calibration curve for Portaspec with chromate-phosphate conversion coating

As an alternative to chromic or phosphoric acid in the final rinse, sodium bisulphite in distilled water is claimed to promote better paint adhesion.''' Other patented processes employ oxygenated sulphur compounds, which act as reducing agents for hexavalent chromium, together with metal ions such as those of beryllium, boron, calcium, aluminium, etc.[112,113] The effect of temperature on the growth of the coating is seen in Fig. 5-15. An alkaline rinse (pH 9-11) has been recommended on chromate-phosphate coatings on aluminium, where these are to be followed by a water-based paint.[114]

There is a reversal in the rate of growth between 55 and 60°C for which there is no satisfactory explanation, and this is parallelled by a similar decrease in the rate of dissolution of aluminium in the solution. The time required to produce a coating of satisfactory thickness (approximately 20 mg/dm^2; 200 mg/sq ft) is longer in the immersion than in the spray process. Coatings obtained by spraying are usually thinner and more compact than those obtained by immersion.

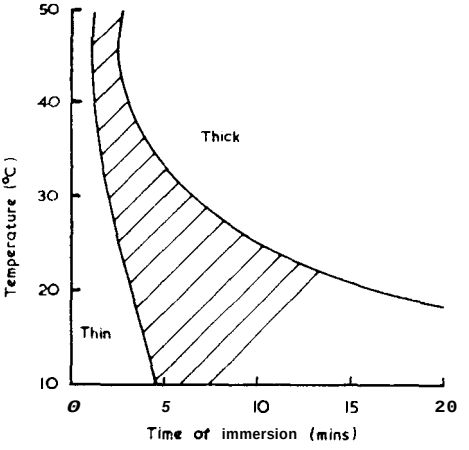


Fig. 5-15. Effect of operating time and temperature on coating thickness in the Alocrom process

Advantages of the process include the pretreatment time (five minutes) and the low temperature of application (room temperature, 17°C). Operating time can be cut to approximately 1 minute if the temperature is raised to 50°C. Application of solution by power spraying can decrease the pretreatment time to a few seconds. For the pretreatment of continuous strip, a solution containing 7-45 g/l CrO_3 and a 0.5-3 times excess of H_3PO_4, is metered over the surface of the strip to obtain a final coating weight of 2-12 mg/dm^2 (20-125 mglsq ft) after which the strip is heated to 165-330°C for 3-8 seconds to produce an amorphous coating.[115]

Problems connected with the concentrations of highly toxic chromate ions in the effluent can be largely overcome by the use of low concentration solutions.[116] Waste water from such processes only contains a small concentration of chromate ions and this can be reduced to an acceptable level with minimum processing. Any chromates remaining in the waste from the pretreatment can be removed with the minimum amount of treatment.[116] Despite the fact that such solutions are of considerably lower concentration than conventional chromate-phosphates, excellent paint performance and corrosion resistance of aluminium container and coil stock in a number of tests has been recorded.[116] Such solutions are normally made up from concentrates containing the individual components in the correct proportions eg.

CrO_3	1.0g/l
H_3PO_4	3.9g/l
HF	2.0g/l

The pretreatment solutions that can be used can vary in the range

CrO_3	0.005-0.2g/l
H_3PO_4	0.02-0.4g/l
HF	0.015-0.04g/l

with a pH of less than 3.5.

The optimum formulation contains about 0.1 g/l CrO_3, 0.09 g/l H_3PO_4 and 0.02g/l HF. Used solutions can contain 0.005-20g/l of aluminium. Effective coatings can be obtained using a pretreatment time of 2-40 seconds at temperatures of between 15 and 65°C, but the preferred pretreatment conditions are times of 2-40 seconds and a temperature of between 30 and 40°C.[116] Because additional cations can interfere with the process and reduce the effectiveness of the coating formed, use of salts of the acid components is not recommended. Tap water can be used to make up the formulation but care must be taken to ensure that the pH of the solution is not increased above 3.5, so deionised water is preferred. During operation of the pretreatment, free fluoride concentration must be maintained between 0.005 and 0.04g/l and preferably between 0.015 and 0.030g/l. Any loss of fluoride through complexing with aluminium and other alloying elements eg Ca and Mg must be compensated. Pretreaments of this kind can be applied by spray, immersion or roller coating techniques.

Equipment

Chromate-phosphate solutions are contained in stainless steel tanks, and racks, hooks or baskets should also be of stainless steel. Alternatively, racks can be of aluminium, in which case they are replaced from time to time. Heating is by stainless steel steam coil or by means of a gas-heated waterjacket. The temperature should not exceed *50°C* and a thermostat should be used. If heated, the tanks should be fitted with exhausts, as in all solutions containing highly toxic chromic acid. Unlike alkaline processes, work must be cleaned before the Alocrom treatment.

A vapour degreasing stage or solvent immersion type cleaner is sufficient. During operation a sludge forms and settles to the bottom of the tank. This is removed when necessary by decantation.

Colour of coating

The coating produced by the treatment is thin and hard and is an attractive light bluish-green colour with slight iridescence on copper-free alloys, and an olive-green colour on copper-containing alloys. The colour is dependent on the operating conditions. If the coating becomes too light in colour, however, this can be corrected by raising the temperature, lengthening immersion time or making the bath more concentrated.

The fluoride ion concentration of the solution is probably the most important factor in determining the colour of the chromate-phosphate-fluoride type coating If it is controlled within fairly narrow limits, uniform colours are obtained.[117] However, the optimum fluoride content increases as the bath dissolves more aluminium. In one particular bath,[118] it increased from 2.5-10 g/l F-at a concentration of 1 g/l Al^{3+} to 114-123 g/l F^- at the maximum Al^{3+} content of 55 g/l.

The colour of the coating can be maintained by circulating the solution continuously through cation exchange columns. Maintenance of colour can also be achieved[119] by rinsing the work in hot water before chromating. Rinsing in an alkaline solution of pH 9-13 can result in the production of green chromate coatings.[120]



Fig. 5-16. Aluminium body panels and components of Land Rovers and Range Rovers are Alocrom treated to provide corrosion resistance and good paint adhesion

A colourless coating can be formed on aluminium assembled car radiators, etc., by treatment in a solution containing CrO_3 0.1-1.9 g/l, HF 0.1-1.5 g/l, H_3PO_4 1-15 ml/l.[121] When assemblies are treated, a methanol rinse before chromating has been recommended instead of the normal caustic soda etching.

Powdery surfaces are obtained if

the work is not properly cleaned
traces of alkali remain on the work
the solution is too hot or too concentrated
the treatment time is too long
the acid rinse is contaminated or its temperature is too high.

Thick coatings or drying at high temperatures can cause 'mud-cracking' of the coating (Fig. 5-6) and this can lead to break-up of the coating and failures in service (Fig. 5-17).

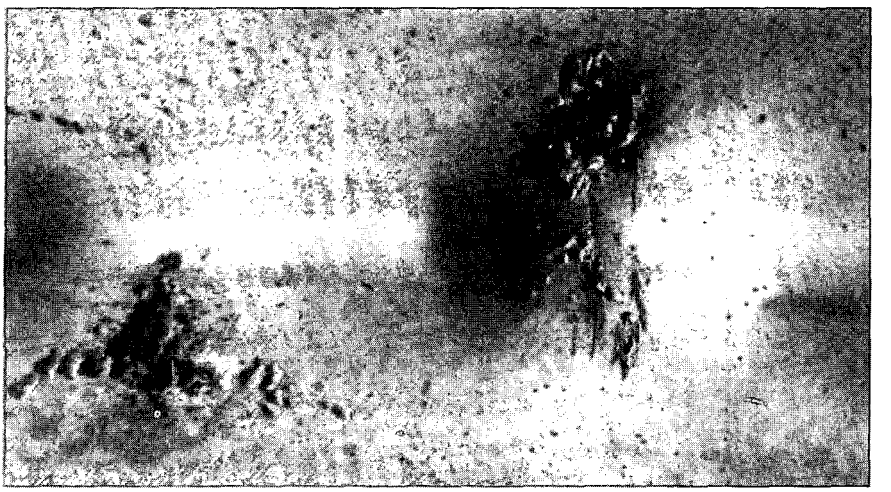


Fig. 5-17. Paint failure in the weather, resulting from poor quality conversion coating.

Solution control

Titration against standard sodium hydroxide solution, using bromo-cresol green as indicator is used as a solution control.

To maintain the solution at optimum concentration, replenishment concentrates of different composition to the basic solution are used. eg, a solution containing CrO_3 6-12 g/l, CrO_3:P_2O_5 ratio 0.3-0.6 and F:CrO_3 ratio 0.075-0.45 is replenished

by the addition of a solution of 15% higher CrO_3:P_2O_5 ratio.[122] Chromate-phosphate solutions can also been regenerated by passage over a cation exchanger, where the addition of sodium or potassium ions results in precipitation of aluminium as a fluoaluminate, if the solution concentration exceeds 1 g/l.[123]

It has been claimed that accurate control of the film thicknesses of coatings formed in fluorine containing acidic conversion treatments baths can be made using the Effective Fluorine Concentration (EFC).[124] This is determined by titrating the solution against an aqueous solution containing a metal ion (Al, La, Y, Zr, Ga Ce or B) using a selective ion electrode to determine the end point.

Boric acid addition

Addition of boric acid to the chromate-phosphate bath decreases the rate of film formation but gives films with good appearance and corrosion resistance (see Fig. 5-18). Contact resistance is also low so the films formed can be spot welded. The S.T.C. modified chromate-phosphate solution[125] contains:

chromic acid	2 g/l
sodium fluoride	5 g/l
phosphoric acid (d. 1.74)	12.5 ml/l
boric acid	2 g/l

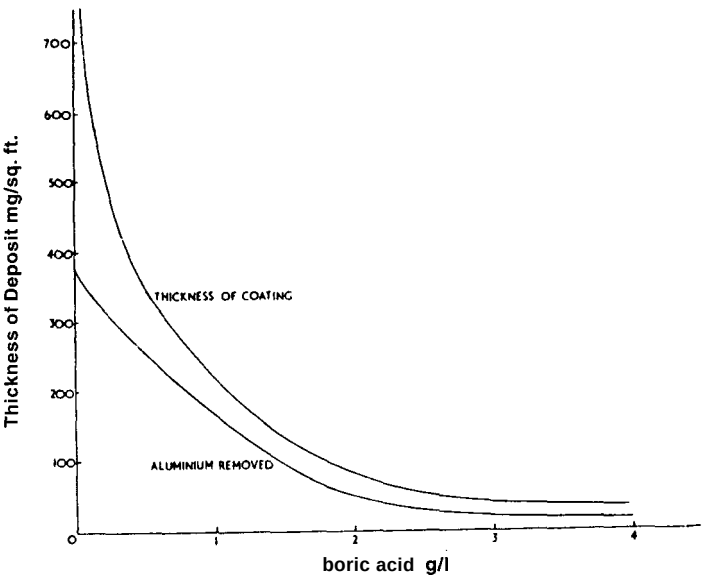


Fig. 5-18. Effect of boric acid addition on chromate-phosphate coating thickness on AI 1¼ Mn alloy.[125] (Conversions: 100 mg/sq ft = 10.7 mg/dm^2)

At 22°C, 10 minutes pretreatment in the solution gives a 70 mg/sq ft (7.5 mg/dm^2) coating, which has a very low contact resistance and is resistant to fingermarking. The solution can treat 120 sq ft per gallon (250 dm^2/l). Due to its low thickness, this film has marginally lower corrosion resistance than the more conventional type of coating. In addition an etch primer must be applied before painting in order to obtain good adhesion.

Two other boric-acid-containing chromating solutions are:–

Solution 1[126]	CrO_3	3-5 g/l	Solution 2[127]	CrO_3	2-12 pt (wt)
	$Na_2Cr_2O_7$	3.5-5 g/l		PO,	0.6-6 pt (wt)
	H_3PO_4	5-12.5 g/l		F	0.6-8 pt (wt)
	NaF	0.8-1 g/l		BO,	0.5-50 pt (wt)
	boric acid	0.1-2-0 g/l		pH	1.0-1.6
	temperature	50-70°C			
	pH	1.1-1.4			

Tungstate and molybdate and other additions

Addition of 0.1-3 g/l of tungstate and/or molybdate ions to a chromate-phospate pretreatment solution (0.5-4 g/l chromate ions; 5-30 g/l phosphate ions; 0.05-2 g/l free flourides) can be used to give accelerated film growth.[128] With such formulations 0.5 to 3 second spray pretreatment at 40-60°C can give a highly corrosion resistant paint adherent pretreatment film.

Corrosion resistance and paint adhesion, particularly of surfaces coated with polyvinyl chloride based paints, is claimed to be improved using a chromate-phosphate formulation containing a minimum concentration of[129]

phosphates: equivalent to 5 g/l phosphoric acid
1 g/l hexavalent chromium
1 g/l fluoride ions

with an addition of a minimum of a complex fluoride selected from:

4 g/l fluosilicate ions
0.5 g/l fluoborate ions
2 g/l fluozirconate ions
2 g/l fluotitanate ions

Additions of hexadecylamine to chromate phosphate pretreatment solutions decrease the rate of film growth but enhance the quality and corrosion resistance of the film formed.[130] An addition of 500 mg/l of hexadecylamine to a solution containing 16 g/l CrO_3, 9.5 g/l NaF, 50 ml/l H_3PO_4 is claimed to give films with optimum performance.

Chromate processes

Chromate (chromate-fluoride) conversion coatings have similar applications to chromate-phosphates. Although the coatings produced are usually thinner (around 0.5 μm: 0.02 mil), corrosion resistance is superior to the chromate-phosphate type.

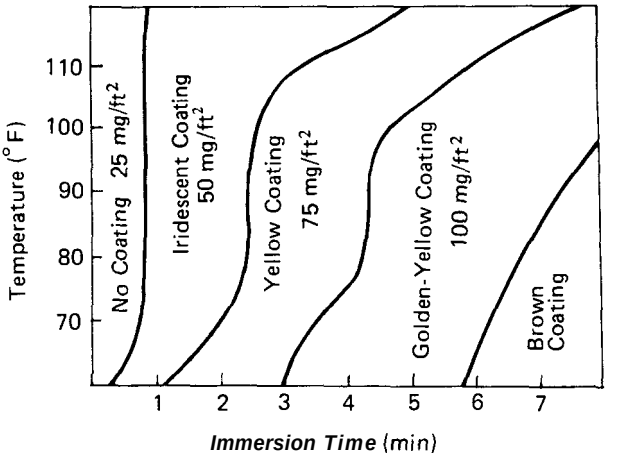


Fig. 5-19. Variation of coating weight and colour of chromate coatings with time and temperature[105]

Because they are thinner, they tend to be iridescent and generally non-uniform in appearance. For this reason, chromate-phosphate films are usually preferred as a pretreatment for clear lacquers. Residual chromates within the film also mean that they cannot be used for any applications involving beverages or foodstuff. However, their higher corrosion resistance means that they are the preferred basis for paint finishes, particularly for external applications. Chromate baths are often more critical to control than chromate-phosphate baths.

The effect of temperature and immersion time on the coating weight and colour of a typical chromate conversion coating is shown in Fig. 5-19. Adequate performance is also obtained by pretreating with a solution (S.T.C.* bath) containing:

chromic acid	3.4-4.0 g/l
sodium dichromate	3.0-3.5 g/l
sodium fluoride	0.8 g/l

at pH 1.5 and at 30°C for 3 minutes.[125] The coating weight of the film formed is about 42 mg/sq ft (4.5 mg/dm²) and during deposition about 24 mg/sq ft (2.6

* Standard Telephones and Cables Ltd.

mg/dm^2) of aluminium is dissolved. pH control of the pretreatment solution is easier if sodium hydrogen fluoride is used instead of the fluoride.

Most chromate conversion coatings are produced from proprietary solutions containing hexavalent chromium and fluorides or complex tluorides, and many contain ferricyanide accelerators. The solutions are normally operated at room temperature. The appearance of the coating varies with the alloy composition, film thickness and treatment time (normally 10 seconds to 6 minutes). As Pretreatment continues the coating changes from colourless to iridescent yellow or brown. Corrosion resistance of coloured coatings is high, as hexavalent chromium is leached out of the film during exposure and protects any bare metal. Because of this, in salt spray tests chromate films have been found to have twice the life of chromate-phosphate and phosphate films,'" but on heating to 60°C, the soluble constituents are rendered insoluble and the protective value is reduced. Colourless films and films prepared by bleaching in acid or alkali have inferior corrosion resistance. Chromate coatings appear to have little or no effect on fatigue life, but may not prevent reduction in mechanical properties through corrosion in service."?

In the aircraft industry, particularly in applications where anodizing is not possible (e.g. where assemblies with other metals are concerned or the parts are too long), chromate treatments are a suitable alternative because they can give adequate corrosion resistance at low cost. In U.S. Military Specification MIL-S-5002D (1994), chromate treatment is suggested as an alternative to anodizing except in cases where components are subject to wear, abrasion, erosion or severe corrosion conditions. In addition all parts subjected to marine environments are required to be anodized. Unpainted chromate films **are** not to be subjected to temperatures greater than *65°C*. In the U.S.A., aircraft components are generally made of high strength aluminium alloys such as 6061, 7075, 2024, 5052 or 5056, and practices for chromating the high strength alloys have been described.[133] For optimum corrosion resistance the following procedure is recommended:

1. Clean in non-etching alkaline cleaner.
2. Rinse for at least 1 minute.
3. Deoxidize using a chromate-sulphate deoxidizer.
4. Rinse for at least 1 minute.
5. Apply a MIL-C-1706, Class 1 A chromate film.
6. Rinse film for at least I minute.
7. Air dry at a temperature below 60°C.

With regards to durability, U.S. specification MIL-C-5541 E(1990) stipulates that an unpainted film must withstand 5% salt spray for 168 hours without significant pitting. Also, the corrosion resistance of painted films should be comparable with that of the same paint system on panels chromic acid anodized to MIL-A- 8625 (Type 1). Two classes of conversion coating are covered. Class 1A

coatings are used for maximum protection against corrosion on surfaces to be painted or left unpainted and Class 3 are used for protection against corrosion where low electrical resistance is required.

The **A.S.T.M.,** in specification B449-93, recognises three classes of chromate conversion coatings on aluminium :

Class 1 – for maximum corrosion resistance and for use unpainted. The coating is yellow-brown in colour and weighs 3.2-11 mg/dm^2 (30-100 mg/ft^2).

Class 2 – for **corrosion protection and use as a paint base. The coating** is iridescent yellow in colour and weighs 1.1-3.8 mg/dm^2 (10-35 mg/ft^2).

Class 3 – for decorative applications (coating colourless) and for low electrical contact resistance coatings (coating yellow-colourless).

In the U.K., DEF STAN 03-18/2 (1995) specifies that unpainted chromate films must withstand 96 hours exposure to neutral salt spray **(B.S.** 7479) without showing any corrosion. These specifications are designed for military purposes and are more than adequate for most commercial applications.[134]

With regards to other properties of chromate coatings, Table 5-3[135] shows that electrical conductivity is low and dependent on the contact pressure.

TABLE 5-3

D.C. electrical surface resistance of chromate coatings

	Contact pressure		*Resistance*	
	p.s.i	*(bar*)*	*(μohm/in^2)*	*(μohm/cm^2)*
Untreated	10	0.7	1,200	7,730
	100	7.0	470	3,100
Chromated	10	0.7	8,000	54,600
	100	7.0	1,900	12,250

* 1 bar = 10^5 N/m^2 = 0.102 kgf/cm^2

As a result the shielded arc method that is normally used to weld chromated aluminium can be replaced with spot-welding (Table 5-4[135]). Machine settings need to be higher than for bare aluminium due to the resistance of the coatings. The contact resistance produced by the chromate-phosphate and chromate type coatings are approximately equivalent.

TABLE 5-4

Spot-welding data for chromated aluminium alloy

Alloy: 5052, 0.064 inch **(1.63** mm) thick
Machine: Peer Inc., Model 5105, 50 kVA

Surface treatment	*Voltage ut welding tips*	*Cycles per weld*	*Shear test, lb to failure*
Etched in alkali,	5.1	13	650
dipped in nitric	5.5	10	700
acid	5.5	15	175
As above, then	5.1	13	650
chromated	5 5	7	425
	5.5	10	500
	5.5	13	650
	6.1	7	525

In both cases, weldability varies with alloy composition and different alloys may well give the best results with different proprietary processes.[136] Such processes may also yield coatings of very different electrical resistance on the same alloy. Values varying from 475 to 5050 microhms have been found on chromated 2024-T3 alloy [131] Electrical resistance rises appreciably during storage, particularly on alloys containing heavy metals. There appears to be no correlation between high electrical resistance and corrosion resistance.

In addition to application by immersion, the chromate processes are often applied by spraying. Degreasing, chromate treatment (1 minute at 20 p.s.i (1.5 bar) spraying pressure at 23°C), cold rinse, hot rinse, oven dry represents a typical pretreatment sequence. On continuous strip lines, acid or alkaline spray cleaning is followed by rinsing and spray application of the conversion coating. The pretreatment film is rinsed and dried before application of the organic coating.

A number of similar processes to those described above are in use employing solutions containing, in addition to chromic acid and fluoride, ferrocyanide or mixtures of ferro- and ferricyanide (hexacyanoferrate (11) and (III)),[137] ferro- and ferricyanide together with, for example, barium fluosilicate or phospho- or silico-molybdic acid.[138] **A** suggested solution for strip lines contains 1.5-6 g/l hexavalent chromium (expressed as chromic acid CrO_3), 0.05-1.5 g/l HF and 0.1-1.5 g/l ferricyanide. Sodium nitro ferricyanide as an alternative accelerator gives a treatment time of 1-10 sec[139] at 32-49°C.[140] Such formulations can be applied by brushing or roller coating in addition to spraying or immersion.[139]

A ferricyanide free solution[141] contains zinc, hexavalent chromium, fluoride and molybdate ions. Molybdenum, uranium, vanadium, tungsten, arsenic

compounds,[142] substituted amino acids,[143] mixtures of nickel and nitrate compounds[144] or mixtures of barium and nitrate compounds[145] have also been used as activating agents. In the Recobright process,[146] an aluminium sulphamo-fluo-citrate film was formed by treatment in a sulphamic acid solution containing citric acid, sodium fluoride and sodium alkyl aryl sulphonate, followed by immersion in a sodium dichromate-bifluoride solution in sulphuric acid.

Cathodic chromating processes have been described. In one process[147] a solution of chromic acid saturated with calcium, strontium, barium, zinc, cadmium, aluminium, iron (III) or lead chromate is used.[148] A dilute solution of chromic acid (50-100 g/1) and sulphuric acid (0.2-5% of the chromic acid content) can also be used.

The adhesion of paints can be improved by treating the chromated aluminium in a 30% nitric acid solution containing 5-20% copper sulphate and 0.5-2% sulphuric acid at 50-70°C,[149] or in a 0.25 g/l or stronger solution of Cr(VI).[150]

A radiographic method for testing the thickness of chromate coatings gives an accuracy of ±15% in routine control of a proprietary process.[151] Radioactive tracer procedures have been used to investigate the leaching characteristics of chromium dissolving from chromated aluminium surfaces.[152]

Performance of chromate pretreatments

Methods of assessment of corrosion performance

Salt spray and SO_2 testing are generally used to asses the corrosion performance of coated and uncoated pretreated surfaces. As mentioned earlier U.S. specification MIL-C-5541 E(1990) stipulates that an unpainted film must withstand 5% salt spray for 168 hours without significant pitting and U.K., DEF STAN 03-18/2 (1995) specifies that unpainted chromate films must withstand 96 hours exposure to neutral salt spray (B.S. 7479) without showing any corrosion. More rapid assessment of pretreatment corrosion performance can be made using electrochemical techniques[153] Potentiodynamic methods and chronoamperometry are available. In potentiodynamic methods current is recorded as the voltage applied to the aluminium electrode of a corrosive cell, which is swept from open circuit potential though the anodic, film forming and cathodic, film thinning, cycles.[153] The electrodes can be pretreated prior to use in the cell. Single potentiodynamic sweeps from open circuit to 2V (Fig. 5-20) show the decrease in current in the active portion of the cycle as the film thickness increases.

Multi-sweep methods are also available. Multisweep methods tend to enhance the differences between protected and unprotected surfaces.[153] For example in a 0.3% chloride solution the observed current increases on succeeding sweeps because the electrolyte is always corrosive in nature. In chronoamperometry,

current is monitored as the voltage on an electrode immersed in a chloride solution is stepped from one value to another. Such techniques can be used to predict the corrosion performance of chromate treatments, so may be used to investigate the potential of many proprietary chromate or other formulations.[153] Computer software is available to control the electrochemical parameters and process the resultant data. The most suitable electrolytes for the corrosion cells are close to the corrosion threshold, and the potentials employed range from open circuit to values just above that of pit formation.[153]

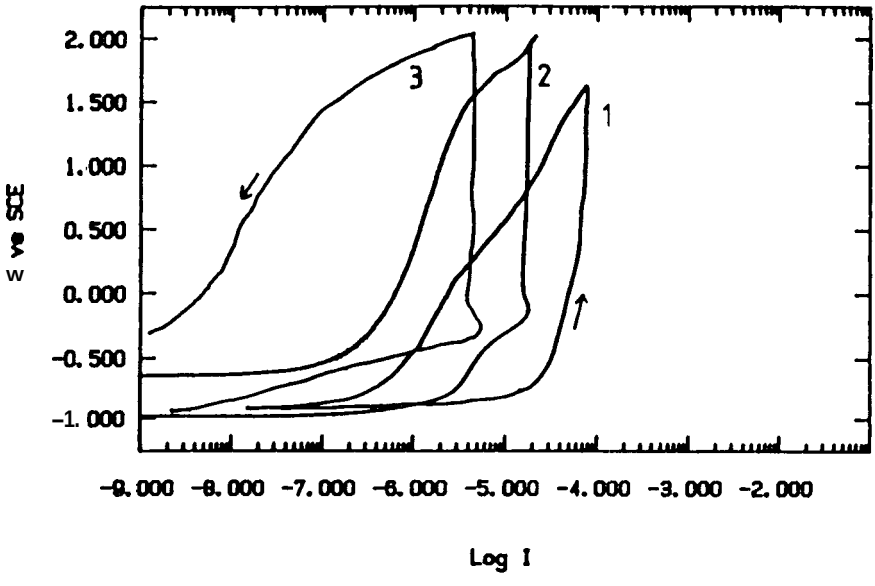


Fig. 5-20. Single Potentiodynamic sweeps from open circuit to 2.0V in 0.1M Na_2SO_4 sln. of samples chromate pretreated for 0 (1), 60 (2) and 180 (3) secs.[152]

Corrosion resistance of uncoated films

There is not a clear correlation between coating weight and corrosion resistance of pretreated metal exposed to 1,000 hours of salt spray testing (Fig. 5-21). Also, the optimum coating thickness for corrosion protection is often somewhat below that giving the best paint adhesion.

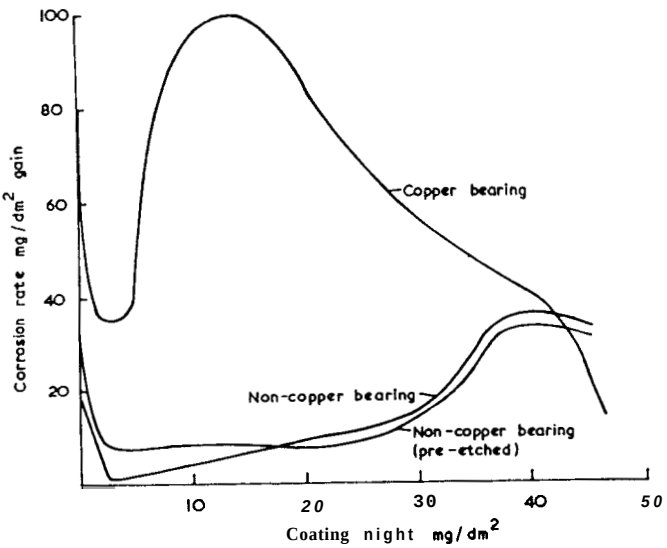


Fig. 5-21. Weight gain of unpainted Alocromed panels after 1000 hours exposure to salt spray. Conversions: 10.7 mg/dm^2 = 100 mg/sq ft.

Corrosion resistance and adhesion of painted films

Using the results of the product of four arbitrary ratings of adhesion[154]

i Bell Telephone Laboratory Adhesion Test
A painted panel was pushed under a hard chromium plated stylus and adhesion measured as the stylus pressure necessary to penetrate the coating to the metal

ii The Impact Test
Adhesion measured as the percentage of paint not removed by a 1 kg-m impact.

iii The Olsen Cup Ductility Test
Adhesion measured as percentage paint left at breakage

iv The Conical Mandrel Bend Test
Adhesion taken as the reciprocal of the diameter of the mandrel at the failure point.

it has been demonstrated that paint adhesion increases with coating thickness up to about 200 mg/sq ft (20 mg/dm^2), but at high thicknesses it gradually decreases (Fig. 5-22).

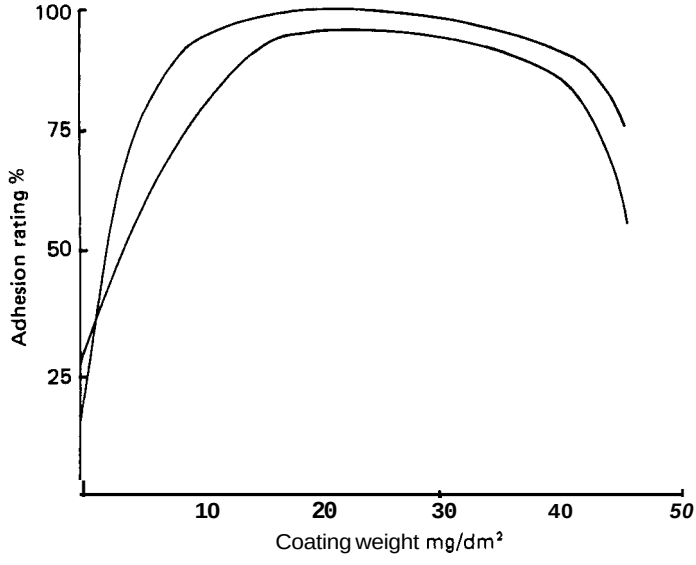


Fig. 5-22. Adhesion of paint systems on Alocrom (chromate-phosphate) coatings

The relationship between organic coating performance and film thickness can also be influenced by the type of application of the coated product (Fig. 5-23).[98] The 180° peel strength of an epoxy phenolic paint has been found to increase with film weight until the coating thickness reaches 7 mg/m^2. However, the maximum feathering resistance of a vinyl organosol paint is not attained until the pretreatment thickness was above 10 mg/m^2 and the adhesion of a vinyl paint in cup drawing adhesion tests reached a maximin when film thicknesses exceeded 5 mg/m^2. In all cases, heat treatment of the pretreatment prior to the application of the coating resulted in a marked deterioration in coating performance (Fig. 5-23). In the case of the adhesion tests the increase in the pretreatment film thickness above 10 mg/m^2 also resulted in a marked deterioration in performance (Fig. 5-23). Feathering resistance is the ability of an organic coating to remain adhering to the edge of the ring pull of a can end when it is opened. If adhesion is poor a considerable amount remains on the inside edges of the opening of the can.

Corrosion resistance testing of similar painted samples using a 1,500 hour exposure to salt spray (Fig. 5-24) shows a generally poorer corrosion resistance of copper-bearing alloys, but corrosion resistance also increased with film thickness in a similar manner to adhesion. Little or no difference between the corrosion resistance obtained from chromate phosphate pretreatment and an unspecified chromic acid anodizing treatment was detected.

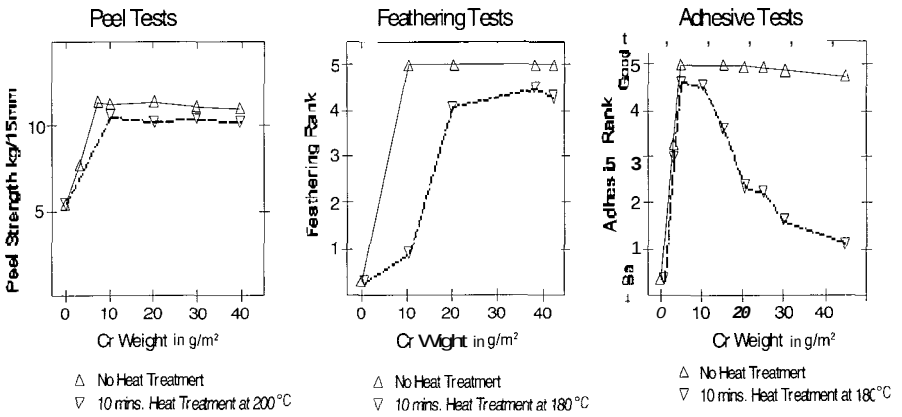


Fig. 5-23. Coating Performance on Chromate Phosphate Pretreated Surfaces[98]

An alkaline rinse (pH 9-11) has been recommended on chromate-phosphate coatings on aluminium where these are to be followed by a water-based paint.[155]

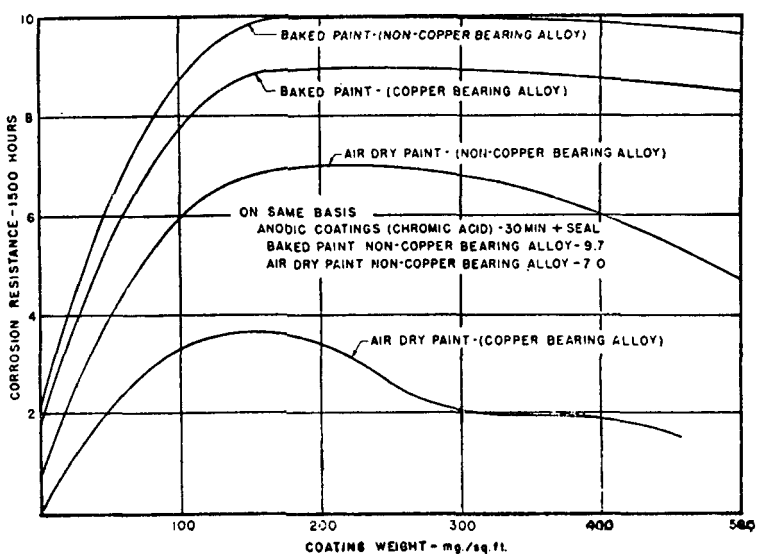


Fig. 5-24. Salt spray resistance of painted Alocrom (chromate phosphate) coatings.
10 mg/sq ft = approx. *1* mg/dm²

Chromate-protein processes

A process involving the addition of proteins to chromic acid solution is claimed to give corrosion-resistant coatings with the hardness of enamel. It is applicable not only to aluminium but also to steel, zinc and brass, and employs a solution containing chromic acid (or a chromate or dichromate), formaldehyde, a protein, e.g. gelatin, casein or albumen, and a bactericide. The work is immersed in the protein solution and, after the film is dry, it is dipped into a chromate solution for 1/2-3 minutes, which both hardens and inhibits the film, after which the work is dried without rinsing. Instead of the dichromates of heavy metals, amines, e.g. diethylenetriamine, may also be employed. The film may be applied as a paint, which is produced by milling an insoluble chromate with a protein solution, and is dried and hardened with an organic reagent or dichromate.

Yellow, transparent coatings of 0.05-0.4 mil (1.2-10 μm) thickness, of good ductility and adhesion, may be obtained by this process. The corrosion resistance is high, due to the slow rate of leaching compared to other chromate films, though it is not suitable for use in very moist atmospheres.

The major problem associated with all forms of chromate conversion process is the handling of the highly toxic chromate containing pretreatment solutions, and the cost of disposal of the effuents that result from spillage and rinsing of the pretreatment films. Such problems could lead eventually to restrictive legislation where the only practical response will be to adopt chromate-free or no-rinse processes.[156]

Trivalent chromium processes

Conversion coatings can be developed on aluminium using baths containing trivalent chromium.[157,158] Light but visible coatings are deposited on the metal surface from solutions of $Cr_2(SO_4)_3$ and Na_2SiF_6 or NaF_3, when the pH is adjusted with NaOH to a point close to or beyond the point where basic compounds are precipitated. In a solution containing 4 g/l $Cr_2(SO_4)_5(OH)_2$, 4 g/l Na_2SiF_6 and 20 ml/l of NaOH, pale tan films are produced by 10 mins immersion. Violet films are produced after 20 mins immersion and pale blue films after 40 mins immersion. Film formation may occur via a similar mechanism to that proposed for the formation of normal chromate conversion coatings. pH changes at the metal/solution interface, resulting from the attack of fluoride ions on the metal surface, lead to the precipitation of the chromium hydroxides.[158] However, electrochemical studies indicate that a more complex mechanism may be operating. Electrochemical impedance spectroscopy and DC polarisation measurements'" showed that the film formed resulted in a 10- to 100-fold increase in the polarisation resistance compared to that obtained from untreated aluminium alloy. Electrochemical results compared well with corrosion behaviour in salt spray tests. **A** treated surface can show no corrosion for up to 200 hours in 5% salt spray. A post-treatment with an

oxidiser improved corrosion resistance further. Post-treatment in peroxide or permanganate solution can give films on 7075-T6 and 2024-T3 alloy substrates capable of withstanding 336 hours in 5% NaCl salt spray.[158]

6. NO-RINSE PROCESSES

No-rinse chromium-based systems

Almost all "no-rinse or dry-in-place'' processes have been developed for use on continuous strip painting or lacquering lines (Fig. 5-25).

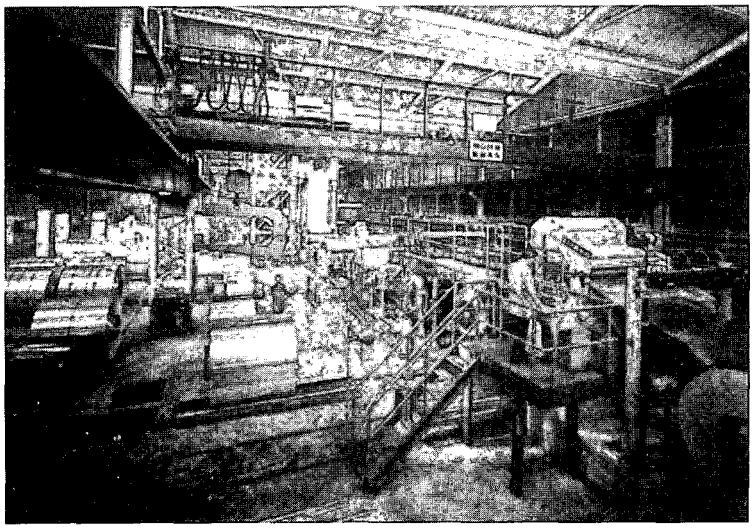
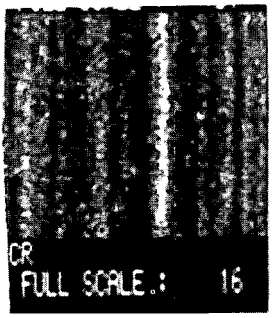


Fig. 5-25. Paint and Pretreatment Line Using No-Rinse Pretreatment

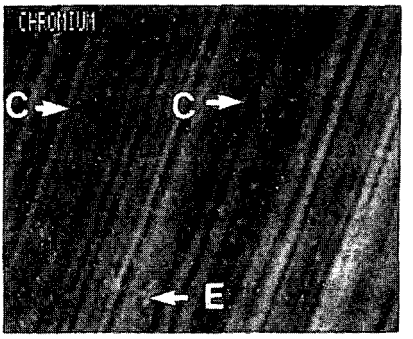
The process involves the application of a conversion coating to the cleaned strip surface, in such a form that subsequent rinsing of the film is unnecessary. The only additional requirement is to dry the deposited film before application of the appropriate paint or lacquer. Because the pretreatment is not rinsed, problems of water pollution are minimised. The coatings can be applied equally effectively to galvanized or rolled steel, so are also suitable for multi-metal coating lines. However, most processes are not suitable for pretreating the complex shapes of extruded sections or castings.

No-rinse formulations range from the highly interactive to the almost totally inert. For example, formulations based on chromium fluoride show a considerable degree of interaction with the aluminium substrate,[36] whereas formulations based on fumed silica and partly reduced chromium interact to a much lesser extent. On commercial pretreatment lines the formulations are normally applied by roller coating. However, in the laboratory such formulations are invariably applied by spin coating. In the case of chromate/silica formulations, differences in the method of application can lead to variations in the composition of the film deposited.[159] As a result formulations which appear satisfactory in laboratory testing may not always be suitable for commercial pretreatment lines.

Irrespective of the chemical reactions taking place or the method of application, most no-rinse formulations deposited on rolled sheet tend to concentrate within the parallel troughs formed on the metal surface during rolling[159,36] (Fig. 5-26).



a) No-Rinse Chromium Phosphate Pretreatment



b) No-Rinse Chromate-Silica Pretreatment

C: Bands of Thicker Pretreatment (Higher Chromium) in the Valleys Formed Between Roll Lines
E: Thicker Pretreatment deposits in defects

Fig. 5-26. Chromium X-ray maps from reactive[36] and less reactive[159] pretreatments showing the concentration of chromium in bands

Partly reduced chromate-fumed silica formulations

As mentioned earlier, Accomet C developed by Albright and Wilson Ltd was one of the first no-rinse systems to be formulated.." The pretreatment is water based and comprised of partially reduced chromic acid and a suspension of silica or a silicate. The pretreatment solution is prepared[3'] by partial reduction of a 100-

500 g/l chromic acid solution, using organic reducing agents such as sugars, starches or alcohols. The ratio of hexavalent to trivalent chromium in the final solution should be in the range 0.5 :1 to 0.75 :1. Silica or silicates capable of forming a homogeneous colloidal suspension are added to the solution, 5-100 g/l of fumed silica being the preferred addition. In order to improve adhesion of the coating to the metal surface, alkali metal salts such as potassium or sodium hydroxide are also claimed to be added, and these are used to adjust the final pH of the solution to 2.5-3.5.[31] However, alkali metals have not been detected in XPS or SIMS analyses of coatings formed from pretreatments of this kind.[159] A number of similar formulations are available on the market, including NR6010 from Henkel,[32] and Alodine NR-2010 and Alodine NR-2375 from Amchem.[160]

Some reaction between the substrate and pretreatment solutions of this type is believed to occur. XPS depth profiles (Fig. 5-27) show an accumulation of chromium between a surface layer comprised mainly of fumed silica and the metal substrate below. Such a layer could occur as a result of partial reduction of chromate ions by the aluminium metal. However, reaction is insufficient to reduce all of the hexavalent chromium in the deposited film[159,161]. The amount of hexavalent chromium remaining in the surface of films deposited by spin coating is random and independent of the pretreatment solution concentration. During deposition and drying of the film the silica particles gel to form the basic film structure. Gelation results in agglomorates of silica particles being deposited on the surface.[159]

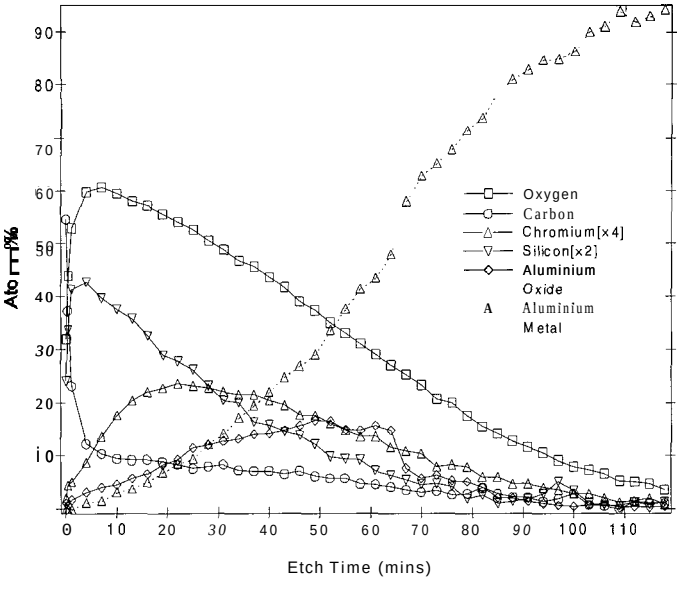


Fig. 5-27. Depth profile of no-rinse, partly reduced chromate, fumed silica pretreatment

At low solution concentration the level of silica is insufficient for the agglomorates to form a continuous film. (Fig. 5-28). At higher solution concentrations the degree of coverage of the metal substrate increases and a continuous film of silica particles is deposited (Fig. 5-28). Gelation of silica and the drying of the chromium containing solution occur independently. On a spin coater, gelation can occur during the spinning operation with the result that silica remains on the surface, whilst the chromium containing solution continues to be removed. Such behaviour is particularly prevalent at low solution concentrations, and results in formulations containing a deficiency of chromium. Chromium salts do not cover the majority of the surface silica particles

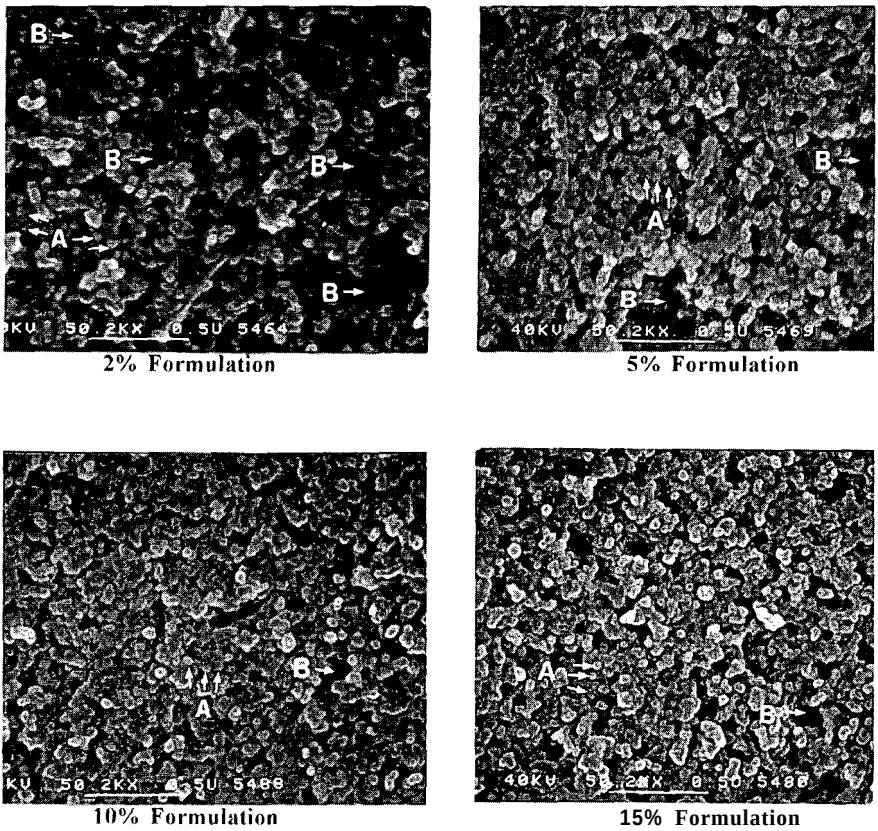


Fig. 5-28. Effect of solution concentration on agglomeration of silica particles in no-rinse, partly reduced chromate, fumed silica pretreatment[159]

The dried chromium phase remaining between the silica particles is likely to help bind the film together and as a result enhance its cohesive strength.

Application of the pretreatment

The strip to be treated is acid or alkali cleaned in the conventional way and thoroughly rinsed. Excess rinse water is removed by squeegee rolls. This is important as water carried over from the rinses will dilute the no-rinse coating of a roller-coating system. A simple two-roll arrangement operating in reverse mode can be effectively used to apply the pretreatment. The coating solution is transferred to the strip surface via an engraved metal pick-up roll and a soft rubber or plastic applicator roll. With aluminium a wet film thickness of about 12 microns and a dry coating weight of 0.16-0.32 g/m^2 is normally achieved. The coating is dried at a metal temperature of 70-100°C before application of paint or lacquer.

On continuous pretreatment lines, separate coaters are used to apply the pretreatment to the top and reverse sides of the strip. The coating can be applied successively to both sides of the strip before it is dried, or it can be applied to each side of the strip in two separate operations. In this latter case, the coating on the top side is dried before the coating is applied to the reverse side. The orientation of the strip with respect to the coater can be varied to suit the geometry of the remainder of the line.

Modified formulations

A number of pretreatment systems incorporating suspended particles in solutions of various binding or reactive agents are available. However, no commercial application of such formulations has been described.

Hydrophilic aluminium surfaces with good corrosion resistant and paint adhesion properties can be produced using formulations containing fluorides and polyacrylic acid (MW 10,000-300,000), in addition to silica and mixed hexa- and trivalent compounds. In these formulations, at least part of the trivalent chromium is introduced directly as the nitrate, sulphate, acetate or maleate salts and not via in-situ reduction of chromate compounds.[162] Such formulations can also contain phosphates, if increased water resistance is required. Addition of a nonionic surfactant comprising an ionic moiety, and a nonionic moiety composed of a polyethylene glycol or an ethylene oxide addition polymer, to solutions containing hexa and trivalent chromium gives a pretreatment formulation that has been claimed to produce metal surfaces with excellent paint adhesion and alkali or water resistance.[163] Coatings of between 5-150 mg/m^2 total chromium can be deposited.

Partly reduced chromate compounds can be replaced by a range of alternative compounds, including phosphoric and hydrofluoric acids, and one or more divalent metal ions (eg calcium or boron),[164] or acidic solutions of a trivalent metal (aluminium, nickel or iron) fluoride and/or nickel ions.[165] In the latter case, the

preferred metal ion is aluminium and the acid anion is phosphate. It is possible that such formulations react with the metal substrate in a similar manner to the fluorides in chromate pretreatments, but no detailed description of the chemistry involved has been published. Partly hydrolysed tetraalkoxysilanes[166] can also be used to replace the chromium component. The preferred series of compounds are the partly hydrolysed tretraethoxysilanes. In this case, improved film properties are obtained if at least 90% of the film has a molecular weight of below 1700. It is also beneficial to add catalysts and corrosion inhibitors to such formulations. The formulations also normally contain 1-30% (preferably 1-10%) by volume of a polar organic co-solvent to aid surface wetting and stabilise aqueous dispersion. Suitable solvents are polar organic compounds that are at least partially water soluble and volatile (eg polyhydric alcohols and ethers). Primarily developed as pretreatments for adhesive bonding, such formulations can give comparable coating performance to partly reduced chromate pretreatments in paint and lacquer tests. In formulations of this kind it is also possible to replace fumed silica with fumed alumina of similar particle size. Acid stabilised zirconium oxide sols have also been used as the basis of a series of paint and lacquer pretreatment formulations. Such materials are normally used in conjunction with fumed silica and/or a chemical coupling agent.[167]

Protective coatings formed using solutions comprising a range of combinations of mixtures of corrosion inhibiting rare earth esters or chlorides, vanadates and alkaline earth metal borates dispersed in a single phase comprising sol gels or organic polymer, are claimed to provide protection for the underlying metal surface for up to 3000 hours of salt spray testing. A range of other corrosion inhibitors have also been incorporated.

No-rinse chromium phosphate

The no-rinse chromate phosphate pretreatment (NR6207) solution is comprised of chromium trifluoride, phosphoric acid and polyacrylic acid. Film formation occurs via a similar series of reactions to normal chromate phosphate pretreatment. However, precipitation of trivalent chromium oxide occurs directly as a result of neutralisation of the acidic pretreatment solution by the metal substrate or the surface oxide film.:-

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$$
$$2Al(metal) + 6H^+ \rightarrow 2Al^{3+} + 3H_2$$
$$Cr^{3+} + 3OH^- \rightarrow Cr_2O_3 \cdot H_2O\downarrow$$

Fluoride ions in solution promote the oxide film removal and reaction with the metal substrate. Phosphoric acid reacts with the particles of precipitated hydrous chromium oxide to form a phosphate rich surface layer. Because it is a no-rinse pretreatment, aluminium fluorides or oxyfluorides formed during the reaction are also precipitated in the surface film. Polyacrylic acid in the formulation is

concentrated on the surface of the film. The surface concentration of polyacrylic acid is dependent on the concentration in the solution formulations.[36] By absorbing on the surface of several particles, polyacrylic acid may also act as a binding agent and provide cohesive strength to the pretreatment film.

Variation of the drying temperature can affect the degree of fluoride reaction. Increase in drying temperature results in decreases in the concentration of fluorides and increases in oxide level beneath the surface polyacrylic acid layer (Fig. 5-29), suggesting that fluorides penetrate deeper into the metal substrate at higher temperatures.[36] Surface chromium and phosphorus levels are unaffected by drying temperature (Fig. 5-29).

A typical XPS depth profile (Fig. 5-30) shows the concentration of carbon from polyacrylic acid in the surface of the film, and chromium and phosphorus distributions very similar to that in chromate-phosphate films. SEM micrographs of a pretreated surface show the presence of particles over part of the pretreated surface (Fig. 5-31), but not the filamented structures in the surface of chromate phosphate films.

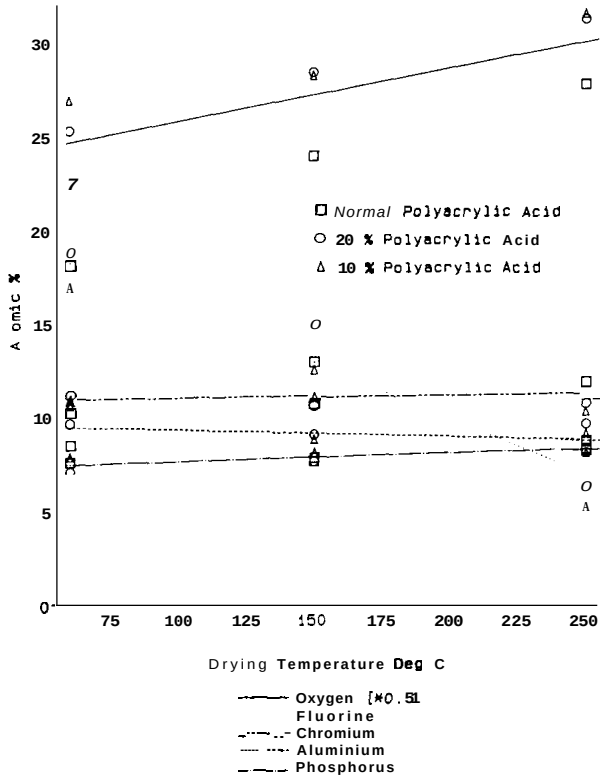


Fig. 5-29. Effect of drying temperature on surface element levels in no-rinse chromate-phosphate film after removal of polyacrylic acids[36]

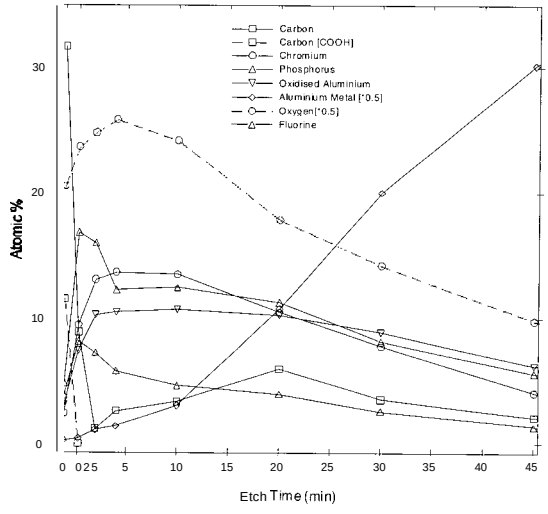
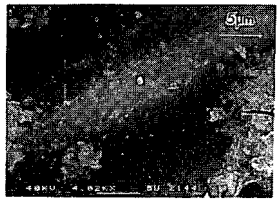
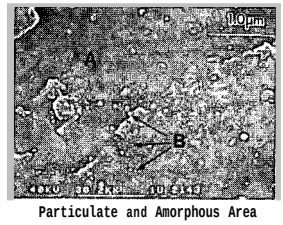


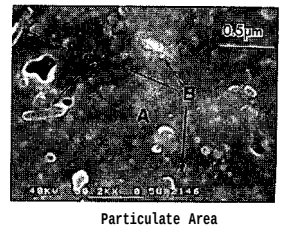
Fig. 5-30. Depth pofile of no-rinse chromate-phosphate film[36]



General Particulate Area



Particulate and Amorphous Area



Particulate Area

A . Amorphous Area of the Surface
B . Spherical Particles on the Pretreated Surface
C . Rod-like Particles

Fig. 5-31. Partially particulate structure of the surface of no-rinse chromium-phosphaie pretreatment[36]

A range of similar formulations is available containing film forming materials such as polyesters, acrylates or polyvinyl fluorides.[168] These acidic, aqueous solutions are applied to the cleaned strip surface by means of rollers. **A** wet coating thickness of about 3-5 microns produces a dry coating weight of 0.1-0.2 g/m^2. The strip is usually heated to a temperature of *35-55°C* before application of the coating, so that evaporation of the water from the pretreatment formulation is rapid. Final drying is carried out at an air temperature of 60-150°C, depending on the speed of the strip through the coating line. Many systems of this type have been described.[169,170,171,172] Related systems[173,174] are based on acid solutions, which will etch the metal surface to generate metal ions, but also contain a primer coating resin dispersion. The metal ions generated destabilise the resin dispersion adjacent to the metal surface, so that it deposits a uniform organic-inorganic coating on the metal surface. In this case the time of contact with the solution will control the thickness of coating achieved, and this coating can then be dried and further coated with suitable paint or lacquer systems.

No-rinse processes for extrusions[29,30] are claimed to give equivalent paint performance to chromium phosphate pretreatments in laboratory and field trials.[30] Surface analyses of the pretreatment demonstrated that an interaction occurs with the substrate and that the bulk of the coating consists of chromium and aluminum oxides. The polymer portion of the coating segregates to the surface in a similar manner to that found for the no-rinse chromium phosphate containing polyacrylic acid.

It is also possible to incorporate chromates into no-rinse formulations containing an organic polymer system to give a pretreatment[34] (Gardobond 4918/2) claimed to be suitable for most forms of organic finishes including powder coating. The pretreatment can also be applied by immersion.[34] Following immersion, treated components are allowed to drain before being dried in an oven at 150°C to drive off excess liquid. The treatment is claimed to be effective for all substrates.

7. NON-CHROMIUM PROCESSES

Zirconium based pretreatments

Although zirconium based pretreatments were devised originally for canstock, they also improve corrosion protection and paint adhesion of a wide variety of architectural and high strength aluminium alloys. Developments in control and formulation have resulted in the performance levels of one zirconium based pretreatment reaching a level sufficient to warrant Qualicoat approval.[175] (Qualicoat is a European quality label for painted architectural aluminium founded in 1986 by European coaters associations). However, they have not been tested over the wide range of environments in which chromate conversion coatings have proved effective.[176]

With few exceptions, the zirconium pretreatments are based on the fluozirconates. A small amount of HF may also be added to the formulation. Phosphates[177,178] or a combination of phosphates, condensed phosphates, phosphorous or hypophosphorous acids or salts[179] or phosphates and oxidising agents[180,181] have also been added. Other zirconium salts can be used in the formulations, but fluozirconates are preferred, as they simultaneously introduce fluorine and zirconium into the pretreatment system.[182] Sequestering agents (eg EDTA) can also be added to rinse formulations to prevent precipitation of aluminium dissolved during the pretreatment process.[182]

Considerable improvement in the performance of the very thin films formed by immersion processes has been achieved by incorporating the organic material into the pretreatment formulation and/or post rinsing with a solution of an organic resin. For example, early versions of the pretreatment gave adequate corrosion resistance on lacquered can-end stock, but post-rinsed versions improved the corrosion inhibition to a level where the process could also be used for pretreating sterilizable deep drawable material.[183] Some of the earliest formulations incorporating organic material[184,185,186] comprised an acidic solution of zirconium, fluoride or fluozirconic acids together with tannin or tannic acid. Other water soluble or emulsifiable polymers such as polyacrylic acid, carboxy vinyl polymer, ammonium polyacrylate, and polyvinyl alcohol or acrylate have been used. Similar compounds can also be applied in post rinsing processes. Polyphenolic compounds or their acid salts may also be used in post-rinse treatments.[182] The polymers provide a resinous glaze on the pretreated metal substrate.[176]

Formulations can be applied by conventional techniques (rinse, immersion or spray) or by no-rinse processes. An important criterion for no-rinse formulations is that they do not leave water soluble salts in the pretreatment film following reaction with the metal surface.[178] **As** a result some formulations developed for rinse application are not suitable as no-rinse pretreatments.

Titanium or hafnium can replace zirconium in many of the formulations that have been described. Titanium containing formulations will be discussed in detail later. Corrosion resistant films can be formed on aluminium and aluminium alloys using formulations comprising one of the metals selected from zirconium, titanium, hafnium, aluminium, silicon, germanium, tin and boron and aromatic sulphonic acid polymers and copolymers.[187] Complex fluorides of boron, silicon, titanium, zirconium or hafnium have been used in pretreatments designed to be carried out prior to chromate, zinc phosphate or chrome-free pretreatments.[179] Cobalt, nickel and magnesium, manganese, zinc, nickel, tin, zirconium, iron, aluminium and copper have also been included in fluo-zirconate, -titanate, - hafnate, -silicate and borate pretreatment formulations developed primarily as no-rinse pretreatments for zinc and steel, but also useful for aluminium.[189] Such formulations can incorporate film forming organic materials.

Film compositions and structures

Rinse or Immersion Systems

XPS depth profiling[190] has shown that the film formed by fluozirconate pretreatments is comprised of an outer mixed layer of zirconium, oxygen and fluorine compounds, above a layer of zirconium oxide. **A** layer of aluminium oxide separates the film from the metal substrate (Fig. 5-32).

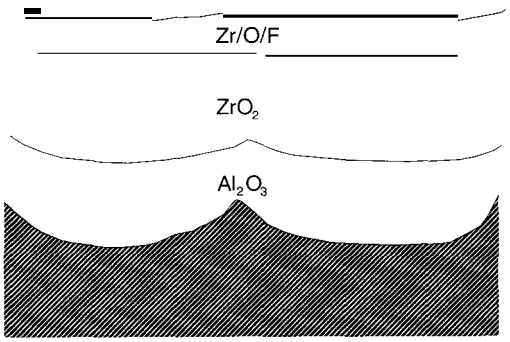
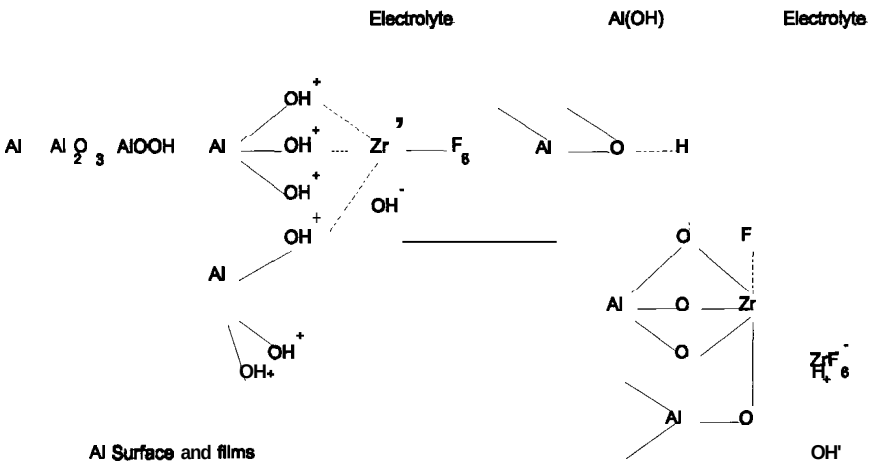


Fig. 5-32. Composition of zirconium fluoride pretreatment

Film formation occurs via interaction of the fluozirconate ion with hydroxides in the surface of the metal substrate:



Zirconium, aluminium, oxygen and fluorine are the main constituents of the film, with the zirconium accounting for about 36% of the total film weight.

Auger and SIMS depth profiling, coupled with SEM studies, have shown that addition of organic polymers to fluozirconate formulations has little effect on the

general film structure, apart from an accumulation of the organic polymer in the surface of the film (Fig. 5-33)[111]

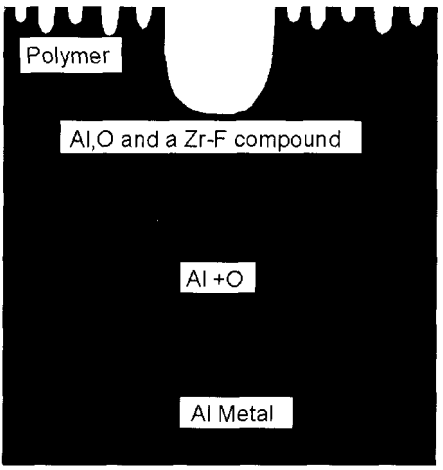


Fig. 5-33. Structure of zirconium fluoride/ polymer pretreatment[111]

However, the percentage of zirconium was much less than was found in films formed in the absence of a polymer. The film had also deposited in a series of pits which penetrated into the subsurface oxide layer. **A** series of smaller pits were also identified in the surface. The thickness of the film formed varies between 7-9nm and is almost independent of pretreatment time.[111]

TABLE 5-5

Effect of Film Thickness on Surface Composition of a No-Rinse Fluozirconic Acid-Polymer Pretreatment Film

Thickness mg/m^2	*Atomic Percentage*					
	Fluorine	*Oxygeri*	*Carbon*	*Nitrogen*	*Zirconium*	*Aluminium*
26.4	17.9	29.3	33.9	0.2	6.8	10.7
35.7	18.2	28.2	35.7	0.4	7.1	10.5
40.9	16.1	30.7	35.4	0.2	6.8	11.1
55.7	20.7	29.3	31.8	0.4	7.1	10.7
67.6	21.1	30.7	30.4	0.7	7.5	10.4
87.6	20.7	30.7	31.1	0.7	7.9	10.0
88.8	21.1	30.0	31.1	0.4	7.5	12.1
97.1	18.2	31.1	32.5	0.4	7.5	9.6
111.7	20.7	28.9	31.8	0.5	7.3	10.7

No-rinse systems

No-rinse versions of the zirconium-based pretreatment are similar to the rinse formulations, but often result in the deposition of thicker films on the metal surface. Pretreatment with a formulation comprised of fluozirconic and polyacrylic acid and free fluorides, Alodine NR6217/8, produced a compact, particulate surface film which completely covered the metal substrate,[192] and had a thickness between 10 and 40 nm (30-100mg/m^2 or 10-35mg Zr/m^2) depending on the concentration of Alodine NR6217/8 used in a subsequent dipping process. Little variation in surface composition occurred with changes in film thickness (Table 5-5). A second formulation incorporating a different polymer also had a thickness of approximately 40nm (Fig. 5-34).[193] However, this is coincidental and, like all no-rinse processes, the thickness of the deposited film can be controlled by the formulation concentration or thickness of solution applied to the surface.

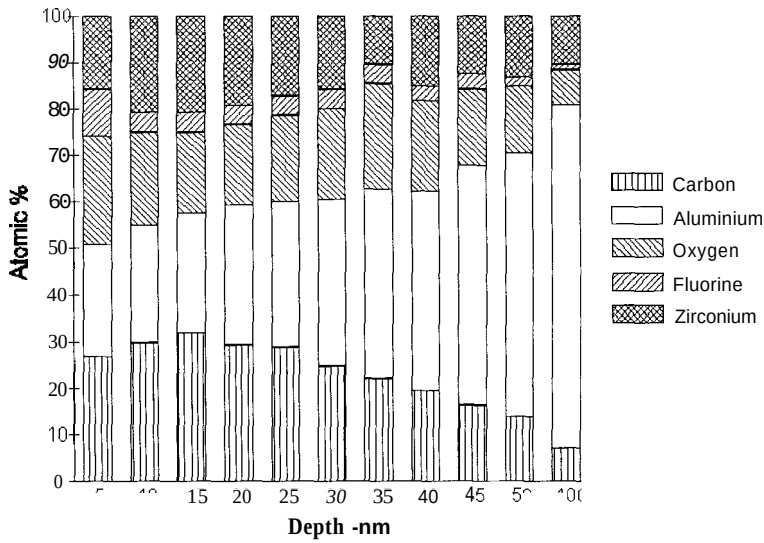


Fig. 5-34. Depth profile of a fluozirconic acid-polymer pretreatment film[193]

No-rinse processes give films of a generally uniform composition throughout the full film thickness (Fig. 5-34) apart from some concentration of the polymeric species in the surface regions of the film.[193] Some replacement of oxides with fluorides in surface regions of the film also occurs, but the majority of the film analyses as a mixture of zirconium and aluminium oxyfluorides. Double layered films, similar to those formed by immersion pretreatments, have not been found in films deposited by no-rinse processes.

Formulations and performance

One of the first fluozirconate pretreatments[194] contains boric acid, a source of fluoride, a source of zirconium, and nitric acid for pH adjustment. A typical example contains:

K_2ZrF_6 0.4 g/l
H_3BO_3 5.0 g/l
KNO_3 10.0 g/l
HNO_3 (4N) 0.4 ml/l

The solution is used at a pH of 3-5 and at a temperature of 50-65°C. Pretreatment results in a clear coating with a coating weight normally less than 0.1 g/m² (10 mg/ft²).

Good corrosion resistance, deformability and paint and lacquer performance can be obtained by treatment in a solution containing:[195]

1.5 g/l $(NH_4)_2[ZrF_6]$
26 g/l $NaNO_3$
0.5 g/l $Co(NO_3)_2 . 6H_2O$
1.0 g/l Sodium-meta-nitrobenzenesulphonate

at a pH of 5.2 and a temperature of 55-70°C. However the films formed must be passivated in a dilute solution of partly reduced chromic acid. This formulation is part of a more general series of pretreatments containing 0.1-15 g/l of complex fluorides of boron, titanium, zirconium or iron, and 0.5-30 g/l of an oxidising agent (calculated as sodium-meta-nitrobenzenesulphonate). Layer formation is accelerated by the addition of metal salts which form insoluble oxides in the coating (Zn, Ni, Co, Cr). Passivation of the pretreatment film in a dilute solution of partly reduced chromic acid is also preferred. The same solutions can be used for iron, steel, zinc and zinc-plated surfaces, so have been recommended for mixed metal pretreatment lines.

It is claimed that particularly effective coating clarity and resistance to blackening on exposure to boiling water can be obtained using a range of formulations containing fluorides, and zirconium, titanium, or hafnium compounds.[196,197] Prevention of blackening is necessary in situations where filled containers are pasteurised.

Formulations containing:[198]

1.5-10 g/l of phosphate ions (as phosphoric acid)
1-10 g/l of zirconium ions (as fluozirconic acid)

can give lacquer performance in a range of T-bend, corrosion and heat seal tests, equivalent to that achievable with a chromium based system, and far superior to that obtained by degreasing (Table 5-6).[198] In such formulations molar ratios of phosphate to zirconium and fluoride to zirconium are kept between 0.5 and 5 and 5 and 10 respectively and the pH between 1-3.5. Coating weights can vary between 20 and 200 mg/m² and the drying temperature between 50 and 120°C.[198]

TABLE 5-6

Lacquer Performance on Zirconium-Phosphate-Fluoride Pretreatments

Solution Composition			Deposition		Lacquers and Tests			
					Epoxide*	Gold lacquer		PVC**
H_2ZrF_6 g/l	PO_4 g/l	NH_4F g/l	Solu- ml/m² ml/m²	Film weight mg/m²	% detachment T2-bends†	3hr boil in saltfree water		3 day immersion in water
						% area of bubbles	% detuch-ment T1-bends†	% loss of peel strength
6.03	3.68	3.23	3	39	0	0	<5	15
8.46	2.72	1.51	6	76	0	0	0	20
6.66	2.14	1.98	3	32	<5	0	<5	21
Chromium pretreatment			6	60	0	0	<5	17
Degreasing and rinsing			–		80	100	100	100

† coated sheet bent through 180° round one (TI) *or* two (T2) intervening sheets of the same thickness

* Mobile SHX 2636 epoxide lacquer

** Heat pressed for 4 seconds at temperature of 180°C and pressure of 300N/cm²

As mentioned earlier, such formulations may also contain organic compounds or require the use of post rinsing with solutions of organic compounds. For example, 30 seconds spraying of an extruded aluminium surface with aqueous solution comprising:[182]

0.0095 g/l	Propasol-P solvent (Union Carbide)
0.0053 g/l	poly-4-vinylphenol
0.0033 g/l	N-methylethanolamine
0.0036 g/l	37% formaldyhyde solution
0.0042 g/l	phosphoric acid

at a temperature of 125°F that has been pretreated for 30 sec in a solution of

0.16 g/l	K_2ZrF_6
0.02 g/l	NH_4HF_2
0.25 g/l	49% HBF_4
0.19 g/l	HNO_3
0.056 g/l	$NH_4H_2PO_4$
0.02 g/l	Verasene (EDTA)
0.07 g/l	dried chestnut extract (vegetable tannin)

at 125°F is claimed to give a surface with excellent paint adhesion and corrosion resistance.[182]

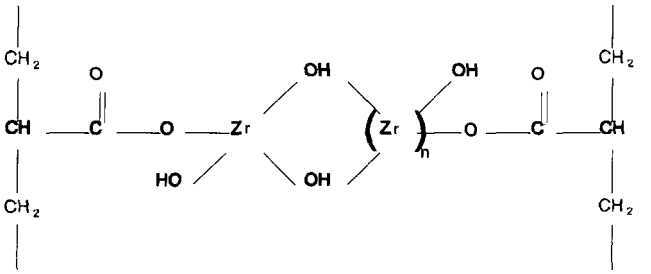
It is claimed that an exceptionally effective no-rinse, corrosion protective, surface pretreatment for aluminium and its alloys is made up of an aqueous acidic solution of approximately:–

0.8-1.2 wt% H_2ZrF_6
0.08-0.12 wt% dispersed silica
0.08-0.12 wt% of a water soluble or dispersible polymer of
3-(N-methyl-N-2-hydroxyethylaminomethyl)-4-hydroxystyrene
0.10-0.15 wt% of 1-propoxy-2-propanol.

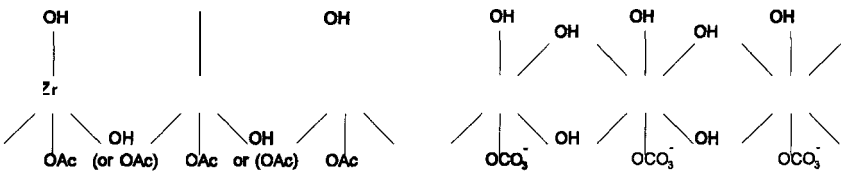
The pretreatment can also provide an effective base for organic coatings.[198] Formulations of this kind are very similar to a range of titanium based formulations described later.

Ammonium Zirconium Carbonate and Related Pretreatments

Zirconium based pretreatments based on ammonium zirconium carbonate can give effective coating performance on aluminium.[199,200] Such formulations also contain polyacrylic acid esters or salts, and can be applied by any contacting methods (spray, immersion or flow coating). The coating can also be used to enhance the corrosion performance of conventional chromate and phosphate pretreatment processes. Ammonium zirconium carbonate forms strong covalent bonds to organic acid groups which lead to the formation of a cross-linked polymeric structure on drying:-[201]



Zirconium acetate or ammonium zirconium carbonate pretreatment prevents staining of tin plate.[202] These compounds also form polymeric species during concentration and drying of aqueous solutions:–



Zirconium Acetate

Ammonium Zirconium Carbonate

but do not crosslink on drying,[201] and are less effective as pretreatments for aluminium (Table 5-7).[199] As mentioned earlier, acid stabilised zirconium oxide sols have also been used as the basis of a series of paint and lacquer pretreatment formulations.[167]

TABLE 5-7

Effect of Zirconium Pretreatment Formulation on Performance of Organic Coatings on Aluminium Can Stock

ZrO_2 Concentration	Coating and Test								
	White Acrylic Paint: 30 min Immersion in 1% Detergent Solution ut 180°F			White Acrylic Paint: 30 min Immersion in Water ut 180°F			Vinyl Interior Lacquer: 30 min Immersion in 1% Detergent Solution at 180°F		
	Reverse Impact †	Cross Hatch ††	Field Test †††	Reverse Impact †	Cross Hatch ††	Field Test †††	Reverse Impact †	Cross Hatch ††	Field Test ††
Treating Bath: Zirconium Acetate Solution									
0.5 g/l	0	0	0	7	8	8	10	6	10
1.0g/l	0	2	0	3	0	0	10	1	10
1.5 g/l	0	0	0	5	1	0	10	1	7
2.0g/l	0	0	0	5	0	0	10	0	0
Ammonium Zirconium Carbonate Solution									
0.5 g/l	2	1	0	9.5	9.9	10	10	8	10
1.0g/l	5	0	0	9.0	8.0	8	10	4	10
1.5 g/l	5	4	10	7.0	10	10	10	4	10
2.0g/l	5	6	10	6.0	10	10	10	4	10
Ammonium Zirconium Carbonate + Polyacrylic Acid									
ZrO_2 Conc	Polyacrylic Acid Conc								
.5 g/l	0.7g/l	7	9.5	10	9.9	10	10	10	2	10
.0g/l	1.4g/l	8	9.5	10	9.9	10	10	10	6	10
.5 g/l	2.1g/l	9	9.0	10	8.5	10	10	10	9.8	10
2.0g/l	2.8g/l	7	10	10	8.5	10	10	10	10	10

Scores represent the amount of paint remaining on the metal surface. Total loss gives a score of 0. No loss gives a score of 10

† Reverse Impact: Deformation from the impact of a 1/2 inch metal ball falling with a force of **24** inch pounds on to the reverse of the painted side. Impacted area subjected to tape adhesion test

†† Cross Hatch: Cross hatch area scribed to give matrix of 100 1mm × 1mm squares Sample Taped

††† Field Test: Results of taping non-scribed area

Performance of ammonium zirconium carbonate formulations

Solutions are used at a pH range of 6 to 8 and at a temperature of between 18-27°C (60-80°F), but the preferred range is between 18-38°C (60-100°F).[199] Following application, the pretreatment is dried at temperatures of between 18 and 38°C (60-100°F).[199] Contact time between the pretreatment solution and the metal surface can be from as little as 1 second up to 30 mins.[199] The preferred range of times is between 1 sec and 1 min and the preferred method of application is by spray coating. Solutions contain:–[199]

0.1-3.5 g/l ammonium zirconium carbonate (measured as ZrO_2)
0.1-5 g/l polyacrylic acid, ester or salt

Paint and lacquer performance on the pretreated aluminium canstock surfaces are superior to that achieved in control experiments using ammonium zirconium carbonate or zirconium acetate (Table 5-7).

For optimum lacquer performance a solution containing a 1:1 ratio (wt%) has been recommended:[200]

1.3 g/l ammonium zirconium carbonate (measured as ZrO_2)
1.3 g/l polyacrylic acid

Because of their high formability, films formed using this formulation can show good coating adhesion even after drawing. Overall performance of the optimum pretreatment can also be equivalent or superior to that obtained using chromate phosphate pretreatment[200] (Table 5-8).

Zirconium oxide no-rinse pretreatment also resulted in paint performance claimed to be comparable to that achieved by chromated material in salt spray and water immersion tests.[203] Performance was also comparable for all the alloys tested.

Titanium based processes

Titanium based pretreatments are gaining increased acceptance as viable alternatives to chromate processes on commercial sheet painting lines. Corrosion protection and paint performance on aluminium pretreated with titanium based formulations can be comparable to chromate pretreated metal.[204] The no-rinse titanium based pretreatment process, Alodine NR 1453, is in use on Barmet's Bedford Ohio paint pretreatment line,[39] and Permatreat 1011 from Betz is used on the coil painting line of Gentek Building Products in Woodbridge.[40] Apart from the elimination of environmental and health problems associated with chromium, the main effect of the change is an improvement in product consistency and corresponding reduction in reject rates.[39]

TABLE 5-a

Comparative Performance of Optimised Ammonium Zirconium Carbonate Polyacrylic Acid and Chromate Phosphate Pretreatments

Pretreatment	*Film Weight (mg/m^2)*	*Organic Coating Adhesion*				*Discolouration and Corrosion Resistance*					
		Side Wall		*Trimming Edge*		*Without Organic Coating*			*Ajier Organic Coating*		
		No Boiling	*30 min boiling water*	*No heat treatment*	*180 ℃ for 10 min*	*Discolouration*		*Corrosion*	*Corrosion*	*Blisters after retort test*	
						boiling service water	*Retort 125 °C*	*spray*	*spray*	*drawing no per $50cm^2$*	*drawing no per $36.6cm^2$*
Optimum AZC /PAA	32	N	N	N	N	5	5	3	5	0	0
Chromate Phosphate	40										
No Treatment		D	D	N	—	1	1	1	1	0	32

Organic Coating Adhesion: D: Delamination N: No delamination

Discolouration after Boiling: None: 5 4 3 2 1 Blackened Surface

Discolouration after Retort: None: 5 4 3 2 1 Whitened Surface

Salt Spray Test: None: 5 4 3 2 1 Corroded Surface

Acidic and alkaline titanium based formulations have been developed for immersion or solution pretreatment. Alkaline solutions (pH 11.5-13.5) contain titanium ions and a complexing agent. After rinsing, the film formed is treated in an acid solution containing tannin or tannic acid.[205] Most acidic formulations are based on fluotitanic acid and may also contain tannin or tannic acid,[184,185] other organic acids, polymers and other metal oxides.[204] Film growth of phosphate, titanium, fluoride based pretreatments can be accelerated by the use of a number of materials individually or in combination. These include nitrous, nitric, tungstic, molybdic or permanganic acids, their water soluble salts, or water soluble organo-peroxides.[206] Apart from the replacement of fluozirconate, ZrF_6^{2-}, by fluotitanates, TiF_6^{2-}, many titanium-based formulations are similar to the zirconium formulations described earlier. Fluo compounds of Hf, Si, Ge, and Sn can also be used in analogous pretreatment formulations, but fluotitanic acid is preferred. Formulations can be applied by spraying or immersion or they may be used as no-rinse pretreatments.[?"'] Incorporation of various divalent or tetravalent metals and a number of other compounds results in formulations suitable for pretreating steel, galvanised steel or zinc surfaces, but which can also be used for aluminium.

High resolution XPS studies of films formed by fluotitanate pretreatments suggest that the overall film forming reaction is:–

$$H_2TiF_6 + 2Al_2O_3 \rightarrow 4AlOF + TiOF_2 + H_2O$$

Fluotitanic acid may catalyse aluminium oxidation–

$$2Al + 3H_2TiF_6 \rightarrow 3H_2 + 2Al^{3+} + 3TiF_6^{2}$$

$$2Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^{+}$$

$$\text{net: } 2Al + 3H_2O \rightarrow 3H_2 + Al_2O_3$$

An auger depth profile (Fig. 5-35) shows that no-rinse versions of fluotitanate pretreatments can result in films of uniform composition with a broad interfacial region of mixed metal oxyfluorides.[193] Angular resolved XPS[193] shows that the concentration of fluorides is higher in the top 9 nm of the film than elsewhere, and that the organic polymer may also be concentrated in the surface of the film. Structures of this lund may be typical of fluotitanate pretreatment films. An XPS depth profile of a second formulation (Fig. 5-36) shows the presence of higher fluorine levels in surface regions of the film, and the rapid initial decrease in carbon, associated with a surface excess of organic material. Although concentrated on the surface of the film, organic material is also present throughout the full thickness of the film.

A combination of XPS, Auger depth profiles and chemical analysis suggests that the surface region of the film is comprised of :–

$$4AlOF \cdot TiOF_2 \cdot H_2O$$

but the composition of the majority of the film is given by the formula:–

$$Al_2O_3 \cdot 4AlOF \cdot TiOF_2 \cdot H_2O$$

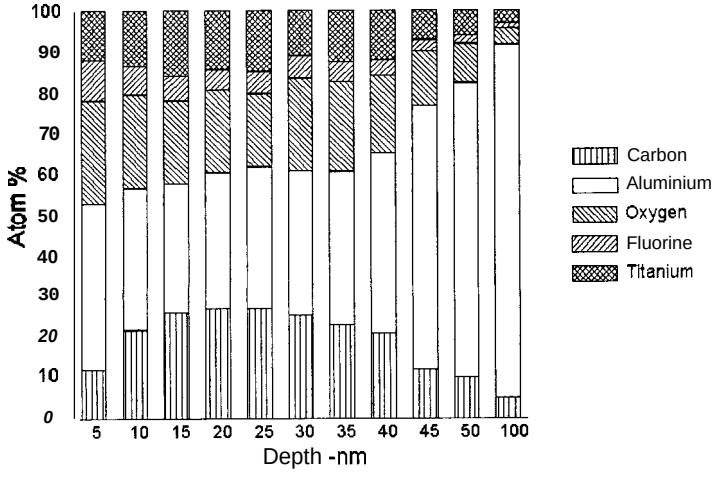


Fig. 5-35. Depth profile of a fluotitanic acid-polymer pretreatment film[193]

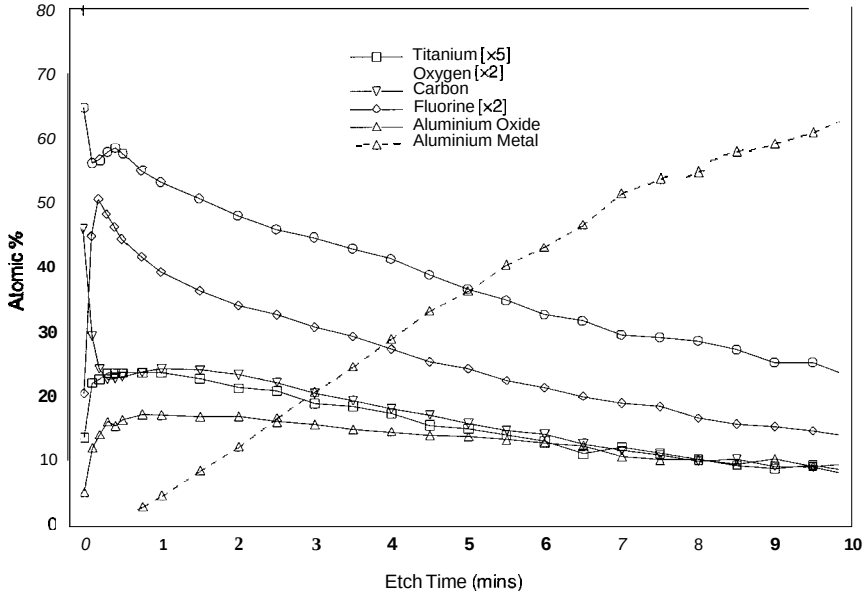


Fig. 5-36. XPS depth profile of fluotitanic acid- polymer pretreatment film on acid cleaned AA5754 alloy

Formulations and performance

Most titanium based pretreatments contain fluotitanic acid, but usually also contain a variety of other materials. Typical examples of one series of formulations contain:[204]

i) H_2TiF_6 or H_2ZrF_6, H_2HfF_6, H_2SiF_6, H_2AlF_6, H_2GeF_6, H_2SnF_6 or H_2BF_6 but H_2TiF_6 is preferred. (Mixtures can also be used)
ii) Gluconic acid or hydroxy carboxylic acids containing two hydroxy groups : $CH_2OH(CHOH)_{2\rightarrow11}COOH$.
and optionally:
iii) Oxides, hydroxides or carbonates of Ti,Zr,Hf,Si,Al,Ge,Sn,B.
iv) Tannic acids and water soluble polymers or copolymers of x-(N-R_1-N-R_2-aminomethyl)-4-hydroxy-styrene (x = 2,4,5 or **6,** R, is an alkyl group containing 1 to 4 carbon atoms and R, has the general formula: $H(CHOH)_{1\rightarrow7}CH_2$).
v) Fluorine free inorganic acids or alkalis. (To adjust pH)
vi) Antifoaming agents

Such formulations can be deposited by spraying or immersion. Gluconic acid or other hydroxy carboxylic acids are required in the formulation in order to prevent precipitation of titanium from solution during aluminium pretreatment. If tannic acids or water soluble polymers or copolymers have not been included in the formulation, it is advantageous to contact the pretreated surface with the water soluble polymer, x-(N-R_1-N-R_2-aminomethyl)-4-hydroxy-styrene, following rinsing and before drying.[204]

Solution concentrations can vary widely but the preferred formulation contains:

H_2TiF_6 (and H_2ZrF_6 and/or H_2SiF_6)	6.5 to 6.6 mM/l : fluorine content 39 to 40 mM/l
Gluconic acid	0.35 to 0.36 × conc. of H_2TiF_6 or fluoracid
Preferred hydroxy-styrene[204]	530 to 800 mg/l
Fluorine free acids	added to give solution pH of 2.9 to 4.5

To compensate for loss of available fluorides due to complexing with aluminium, fluorides should be added to maintain the original solution concentration. Because of preferential loss of titanium during the pretreatment process, make-up solutions contain higher proportions of H_2TiF_6

Pretreatment can be carried out over a range of times and temperatures but a temperature range of 43 to 44°C and a time of between 4.9 and 6 seconds are preferred. The pretreatment can be dried at ambient or elevated temperature, but the maximum temperature reached by the metal should be kept below 35°C. The ideal coating deposited should contain 1.5 to 4.8 mg/m^2 of titanium.,''

A range of formulations is capable of giving good corrosion protection (e.g. Table 5-9). Exposure to a variety of corrosive environments did not result in loss of paint or blistering on scribed areas produced using perpendicular cuts from a

Gardener cross hatch tool with eleven knife edges 1.5 mm apart. However, in feathering tests, performed by pulling a sample apart along a scored, folded edge and measuring the maximum width of the feathered edge of the paint,[204] the best results were obtained with samples containing the aminomethyl-4-hydroxy-styrene polymer (Table 5-9). They were also the only samples where paint could not be removed by repeated adhesive taping of O-T bend (ASTM Method D4145-83).

TABLE 5-9

Performance of Paint on Fluorotitanate/Aminomethyl-4-hydroxy-styrene Polymer Pretreated of MD 301 Alloy Substrates

Formulation: (parts per 1000 by weight) 7.5 pts 60%' H_6TiF_6) pts 50% gluconic acid 55.2 pts HNO_3 50.0 pts NH_4OH (29.9'3 NH_3). 500ml diluted to 6L anc ncluding:			pH	weight of Ti leposited mg/m^2	Valspar™ Paint					
					9835-001				92X205B	
					15 mins Exposure {oilingDowfax™ 2A1 Sln‡		30 mins Exposure Deionised Water at 68.3°C		90 mins Exposur Steam (120°C Under Pressure)†	
3.5% HNO_3	10% NH_4CO_3	32% polymer sln			Cross-Hatch Paint Left)	Feathering (mm) Largest Distance	Cross-Hatch (Paint Left)	Feathering (nun) Largest Distance	Cross-Hatch (Paint Left)	Number of Blisters
--	11ml	0ml	2.9	4.8	100%	0.40	100%	0.15	100%*	0*
--	11ml	5ml	3.0	5.6	100%	0.35	100%	0.25	100%	0
8ml	11ml	10ml	3.0	5.2	100%	0.40	100%	0.15	100%	0
16ml	11ml	15ml	3.1	5.6	100%	0.25	100%	0.15	100%	0
25ml	11ml	20ml	3.1	4.9	100%	0.20	100%	0.05	100%	0
25ml	11ml	50ml		7.0	100%	0.20	100%	0.20	100%	0

* mean of two tests
† all % values are weight percentages
‡ 45% active sodium dodecyl diphenyloxide disulphonate (Manufactured by Dow Chemicals)
†† Identical results also obtained using Valspar 9009-139 painted 5353 alloy

Samples of 5050 alloy pretreated with a mixed titanium/ zirconium formulation derived from a basis solution containing:

4.19% (w/w) 60% H_6TiF_6 (w/w)
3.07% (w/w) 20% H_6ZrF_6 (w/w)
2.15% (w/w) gluconic acid in 240 ml

diluted from 240 ml to 6 litres with:

31.9g (70.8% w/w) HNO_3
43ml NH_4OH (29.9% NH_3) 10g
32% of the aminomethyl-4-hydroxy-styrene polymer sln

and coated with Valspar 9009-139 paint, consistently gave the highest possible ratings in cross hatch and 90 minute steam exposure tests, and minimal or zero loss of paint in the O-T bend tests. Replacement of the aminomethyl-4-hydroxy-styrene polymer with 60 g of 5% tannic acid and removal of the nitric acid in the formulation had no effect on cross hatch and blister performance but did result in some loss of performance in O-T bend tests.

No-rinse formulations

Similar formulations based on H_6ZrF_6 and H_6TiF_6 and containing:

2.2 to 22.0 g/l Zr(IV) and/or
1.4 to 14.0 g/l Ti(IV)
2.4 to 24 g/l orthophosphoric acid
3.0 to 30 g/l fluoride
0.1 to 1.5 g/l of a soluble or dispersable organic film forming agent eg polyacrylic acid

can be contacted to a metal surface and allowed to dry without rinsing.[207] Contact times can be varied between 1 and 40 seconds and the drying temperature between 50 and 125°C. The pH of the formulations can vary between 1 and 3.5.

Permanganate Conversion Coatings

Like chromates, permanganates can reduce at the metal surface. Reduction can result in the formation of manganese(IV) oxide[208] or a mixture of manganese(IV) oxide and manganese(II) hydroxide:-[209]

Anodic reaction

$$Al + 4OH^- = Al(OH)_4^- + 3e^-$$

Cathodic Reaction

$$MnO_4^- + 3e^- + 2H_2O = MnO_2 + 4OH^-$$

$$MnO_2 + 2e^- + 2H_2O = Mn(OH)_2 + 2OH^-$$

The primary component of most pretreatment formulations is potassium or sodium permanganate. Because of their non-toxicity, such formulations do not present the effluent disposal and handling problems associated with chromate treatments. Non-toxicity of permaganates also means that waste disposal and

handling present fewer problems than many of the non-chromium conversion processes.

Immersion of an aluminium alloy in an alkaline permanganate solution can give films with a marked decrease in corrosion current, and a more negative corrosion potential than the untreated surface (Table 5-10).

TABLE 5-10

Corrosion Behaviour of AA 7020 Alloy Following Treatment in Alkaline Permanganate

Treatment Time (mins)	*Corrosion Potential* E_{corr} *mv/SCE*	*Corrosion Current Density* i_{corr} *A/cm²*	*Pitting Potential* E_{pit} *mv/SCE*	*Repassivation Potential mv/SCE*
0	-900	12.00	-900	–
0.5	-1180	0.22	-900	-920
1	-1220	0.34	-890	-940
1.5	-1250	0.41	-880	-925
2	-1260	0.44	-880	-920
3	-1260	0.49	-880	-930

Pitting potentials of -890 ± 10mV vs SCE and repassivation potentials of -920 ± 20mV vs SCE, coupled with more clearly defined passivation ranges, suggest that films with optimum general and pitting corrosion resistance are formed within 1.5 minutes treatment time.

The most widely known permanganate pretreatments are the Sanchem processes.[210,211,212,213] Pretreatment results in the formation of a surface film with the same characteristic yellow colouration as that of chromium chromate pretreatments. Coatings are very uniform in colour and texture. The process is used to pretreat the rear nests of US Postal Services lock boxes[213] and has outperformed a number of other chrome-free pretreatments in a series of corrosion and paint performance tests.[214] Unlike chromate conversion coatings, films do not lose their corrosion resistance when heated above 65°C (150°F) or when stored for long periods.[215]

The original version of the Sanchem process[210] involves successive immersion in solutions of sodium bromate, distilled water, aluminium nitrate/lithium nitrate, and potassium permanganate. The thickened porous oxide film formed on the metal surface is sealed by immersion in a solution of potassium silicate. The coating gives effective, but inferior, corrosion resistance to that achieved by a

chromate conversion coating in a standard salt spray test, ASTM-B-I 17, (Fig. 5-37). Disadvantages of the process are the large number of treatment steps, the long immersion times (up to 7 minutes) and the different temperatures required for each stage of the process.[176] The pretreatment also has to be applied by an immersion process, so cannot be used to pretreat components with large surface areas.[214]

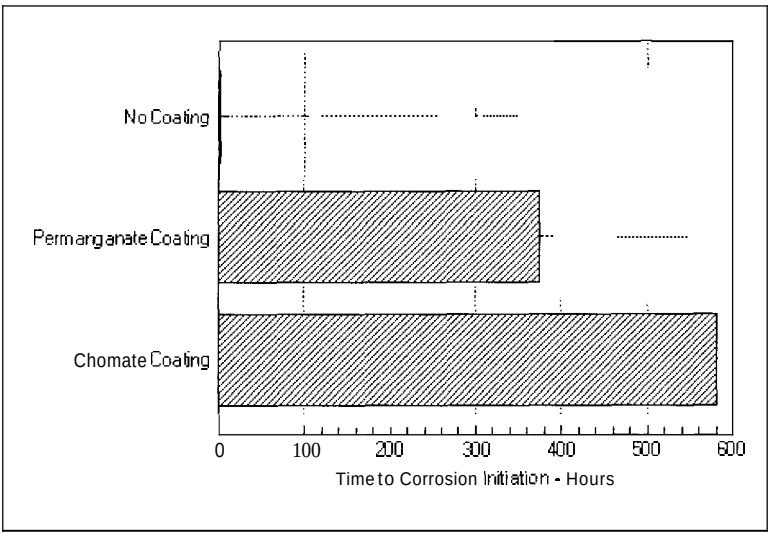


Fig. 5-37. The Effect of chromate and permanganate conversion coatings on the time for corrosion on 2024 alloy in a salt spray[176]

Many of the practical disadvantages of the original process are overcome by combining alkali metal chlorides, permanganates and nitrates into a single pretreatment solution."' The formulations can be buffered using alkali metal borates, benzoates or carbonates, boric or benzoic acid. The minimum manganese content of the solution must be above 700 ppm. For pure aluminium, and alloys that do not contain excessive amounts of copper, zinc or iron, 0.5-2 minutes of treatment at temperatures between 57-68°C (135-155°F) (Fig. 5-38) give films with the characteristic yellow colour[213] that do not pit for at least 336 hours in salt spray testing (ASTM-B- 117). For example immersion of an aluminium panel in a solution containing:

1% borax ($Na_2B_4O_7H_2O$)
2% potassium permanganate($KMnO_4$)
97% water

at 68°C (155°F) gave a surface that did not pit on exposure to a salt fog for 336 hours.

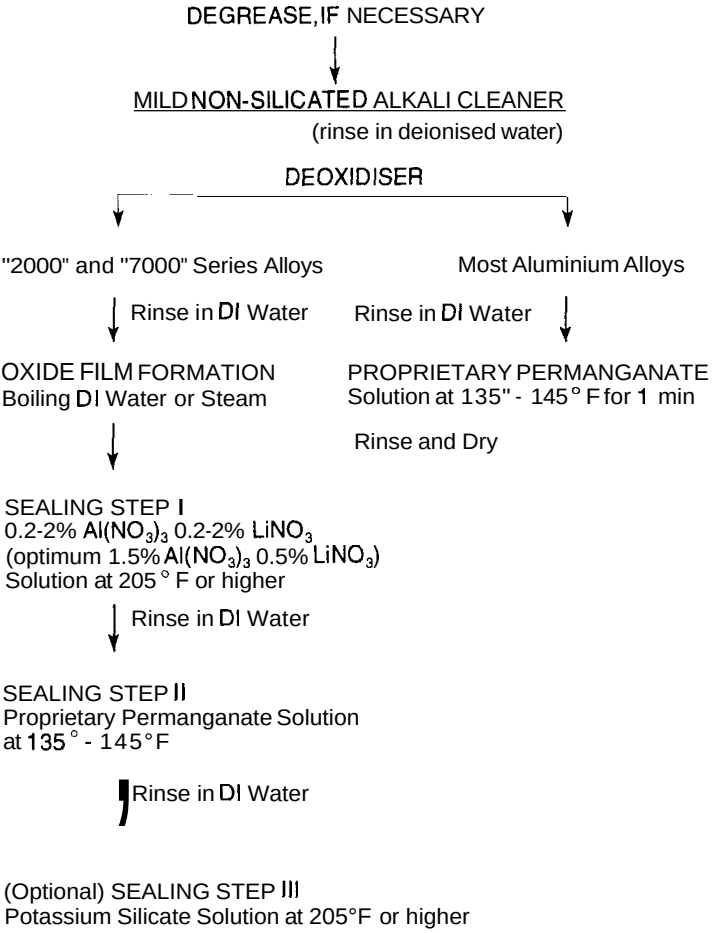


Fig. **5-38.** The Sanchem process[213]

More corrosion susceptible alloys such as the 2000 or 7000 series require an initial thickening of the oxide film on the metal surface. (Fig. 5-38). Oxide films are thickened by treatment with boiling deionised water or steam, and partially dehydrated in an aluminium nitrate/lithium nitrate solution. Following film thickening, the metal is treated in the permanganate solution using the same conditions as those employed for most other alloys (Fig. 5-38). During this stage various oxides of manganese are trapped within the thickened oxide film. For maximum corrosion protection the film can be sealed in a potassium silicate solution. This converts the aluminium oxide film to potassium aluminium silicate. The sealed film continues to provide good adhesion to organic coatings.[213]

The coatings are compatible with epoxy polyamide coatings and are effective in reducing filiform corrosion underneath painted systems (Table 5-11).

TABLE 5-11

Typical filiform corrosion test results of painted 2024-T3 aluminium alloy

Coating	*Length and density of filiform corrosion on scribe mark*		
	Deoxidised	*Chrome Chromate 60 mg/ft²*	*Sanchem process*
One-coat urethane	Dense, 5-8 mm	Moderate, 2 mm	Moderate, 2 mm
One-coat urethane gloss	Dense, 8 mm	Moderate, 4 mm	Moderate, 2 mm
MIL-P-85582[a]	None	None	None
MIL-P-23377[a]	Few, 5-8 mm	Few, 2-5 mm	Few, 2-4 mm
MIL-P-23377[b]	Few, moderate, 3-8 mm	Few, 2-3 mm	Few, 2 mm
Non chromated"	Dense, 10 mm	Dense, 2 mm	Dense, 2 mm
Epoxy[b]	Dense, 10 mm	Dense, 2 mm	Dense, 2 mm

[a] primer only

[b] Top coat of MIL-C gloss white over primer

Nitrates in the formulations can be replaced by phosphates.[215] For example treatment of 3003 alloy in a phosphate containing formulation:

3% potassium permanganate ($KMnO_4$)
1% phosphoric acid (H_3PO_4-85%)
0.4% sodium hydroxide (NaOH)
1.0 % lithium chloride (LiCl)
94.6% water
pH = 7

at a temperature of 68°C (155°F) for 30 seconds gave a surface with a bright silver appearance that did not darken during exposure to a salt fog for 24 hours at 35°C (95°F). (ASTM-B-117). However, the behaviour following more prolonged exposure has not been recorded.

The main disadvantages of the Sanchem process are the high temperatures and the highly alkalinity of the solutions required.[216] The coatings produced also have limited corrosion performance in severe aqueous saline environments.

Other permanganate based pretreatments

Formulations containing potassium permanganate and a range of other elements have also been described. Corrosion resistant coatings can be formed by reacting

aluminium surfaces with solutions containing potassium permanganate and cerous chloride.[216] Strontium chloride may also be added to the formulation. Corrosion resistance can be improved by post treatment in alkaline molybdate, nitrate or metasilicate solution. Treatment of the coated surface with an alcoholic solution of glycidoxy-polyfunctional-methoxy silane, with or without phenyl trimethyl silane, improves corrosion resistance further.[216]

Ceria based pretreatments

Rare earth metal salts are effective corrosion inhibitors for a variety of metals and alloys.[176] However, only the potential of cerium salts for increasing the corrosion protection of aluminium and aluminium alloys has been investigated in detail.[217,218,219,220] Corrosion protective films can be formed simply by immersion of an aluminium alloy in a solution containing 100-1000 ppm cerium chloride. Precipitation of a hydrated cerium oxidelhydroxide, or cerium oxidelhydroxide and aluminium oxide, occurs on cathodic sites as a result of the increase in pH associated with oxygen reduction. Cerium in the film occurs in both the Ce(III) and Ce(IV) forms. Following treatment, the pitting potential of the surface is increased and corrosion current reduced by an order of magnitude. Corrosion protection is believed to be due to cathodic inhibition affecting the rate of oxygen reduction.'" [222] The degree of protection strongly depends on the time of immersion. Optimum protection requires an immersion time of 20 hours. Film formation can be accelerated by cathodic treatment in cerium chloride or in cerous nitrate dissolved in butoxyethanol but the films formed have lower corrosion inhibition."'

Cerium chloride is also used in high temperature processes (90-100°C). In some of these processes, treatment is preceded by a 24 hour exposure of a clean deoxidised surface to saturated water vapour at 100°C and a 2 hour treatment in cerium nitrate solution at 90-100°C. An optional third stage of the process requires positively charging the metal surface while in contact with an aqueous molybdenum solution.[220] The films formed are predominantly hydrated aluminium oxide.[223,224] A small amount of cerium is incorporated within the film during the cerium nitrate treatment, and ceria rich submicron particles are deposited on the surfaces of the film during cerium chloride treatment. Many of the deposition sites are associated with large intermetallic particles in the metal substrate.[223] During anodic polarisation molybdenum is incorporated within the film and deposited particles. Variation of cerium/molybdenum ratio within films formed on different alloys may be related to variations in corrosion performance.[224]

For the copper containing alloys, 2024-T3 and 7075-T6, improved corrosion performance is achieved by electrochemically removing surface copper containing intermetallics prior to processing.[225] In addition, anodic polarisation in molybdate solution is carried out prior to treatment in boiling cerium chloride, and preconditioning by exposure to water vapour at 100°C is not used. On 7075-T6 alloy it is possible to produce surfaces where corrosion cannot be detected

visually or by electrochemical impedance spectroscopy during 30 days exposure to 0.5M NaCl.[225] Significant improvement in localised corrosion of 2024-T3 alloy is also obtained, but with this alloy, optimum performance is obtained using a process involving immersion in hot cerium acetate followed by anodic polarisation in sodium molybdate and immersion in hot cerium nitrate.[225]

Ceria based coatings can be produced much more rapidly by immersion of aluminium in an aqueous solution containing a cerium salt, an oxidising agent and various organic additives.[176] **A** uniform corrosion resistant coating can be formed on 7075 alloy by a minimum of 3 minutes treatment in acidic cerium chloride, hydrogen peroxide solutions.[226] The basis of the method is oxidation of the cerium cations to the ceric (IV) state by hydrogen peroxide and the precipitation of ceric compounds on the metal surface as a result of the pH changes in the vicinity of the surface caused by acid attack of the metal substrate. It has been claimed that films formed by the process can give corrosion performance and paint adhesion comparable to that resulting from chromate conversion.[176] Following immersion of a coated 7075 alloy for 40 days in salt solution, the corrosion rate is similar to that of metal protected by a chromate conversion coating (Table 5-12).

TABLE 5-12

Corrosion Performance of Cerium Based Pretreatment[176]

Pretreatment	*Corrosion Rate* $\mu g/m^2/s$
No coating	*3.0*
Cerate coating	0.4
Chromate coating	0.1

The coating can also be used a basis for epoxy polyaniide paint films. Adhesion is comparable to that achieved with a chromate conversion coating.

Cobalt based pretreatments

Cobalt based pretreaments have been developed primarily for the aircraft industry as possible replacements for chromate based formulations. **A** range of processes is available, where paint adhesion and corrosion performance of the films formed are at least comparable with that resulting from chromate pretreatment. However, in a number of instances the performance of the coating is critically dependent upon processing parameters. For example, well defined, iridescent coatings can be formed on aluminium by treatment with a solution of a hexacoordinated ammoniated $Co[(NH_3)_6]X_3$ complex (where X is

NO, Cl, Br, CN, SCN, $1/3PO_3$, $1/2SO_4$, $C_2H_3O_2$, and CO_3),[227,228] but paint adhesion is critically dependent on the ammonia content of the pretreatment solution, and this is difficult to control.[227] Almost colourless films are formed by pretreatment in solutions of $Me_3[Co(NO_2)_6]$ where Me = Na, Li or K, but here applications are limited by the maximum thickness of film (90 mg/m^2) that can be deposited. Such limitations can be overcome by use of cobalt (III) hexavalent complexes, $[CoR_6]^{3-}$ of a variety of metals (Na, Li, K, Ca Zn, Mg, Mn), where R is a carboxylic acid containing 1 to 6 carbon atoms. The surfaces of the films are highly porous and this is thought to improve paint adhesion.

Pretreatment formulations are prepared by dissolution of Co(II) salts and a metal acetate (eg Na, Mg or Ca acetate) *to* form **a** solution of the cobalt (III) hexacarboxylate complex. Solutions can contain between 0.01M and the saturation limit of the complex, but optimum performance is obtained using solutions containing between 0.04 and 0.15 moles of the Co(II) salt. Pretreatments based on cobalt acetate give the best overall performance, but the best paint performance is obtained using cobalt nitrate. The preferred metal acetate is sodium acetate. Addition of wetting agents (alkyl fluorides, fluocarbons or metal fluorides) eliminates the need for sealing of the films following pretreatment. Pretreatments can be applied by immersion, hand or spray processes.

TABLE 5-13

Preferred Compositions and Pretreatment Conditions for Cobalt Based Formulations

Formulation	*Make-up per litre*	*Control Range*	*Pretreatment Time at 60°C (140°F)*
$Co(C_2H_3COO)_6 . 4H_2O$ and	33g	30-35g	
$Mg(C_2H_3COO)_2 \cdot 4H_2O$ or	85g	80-90g	5-8min
$Ca(C_2H_3COO)_2 \cdot H_2O$ or	70g	65-75g	15-20min
$Na(C_2H_3COO) . H_2O$	125g	120-130g	12-15min
In addition formulations contain:.			
Alkyl-Fluoride (MSP-ST)	4-5ml		
MgF_2 or	2g	1-3g	
CaF_2	2g	1-3g	

Materials pretreated using optimised formulations and conditions (Table 5-13) can withstand 168 hours salt spray exposure (ASTM-B117), and

give good wet and dry adhesion for high performance aircraft chromated epoxy primers and non-chromated epoxy enamel top coats.[227]

Other variations to cobalt based processes claimed to be commercially practicable for the aircraft industry[229] involve contacting the metal surface with an aqueous solution prepared by reacting:

(i) a cobalt (II) salt
(ii) an ammonium salt
(iii) one or more complexing agents selected from a soluble metal carboxylate, a soluble metal nitrite or ammonia.
(iv) a water soluble amine
(v) an oxidising agent.

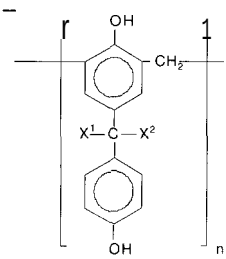
Pretreatment is continued until the surface of the substrate is oxidised and the cobalt conversion coating is formed. Similar formulations also form the basis of commercially practicable pretreatments for non-aerospace applications. In such formulations the ammonium salts used in the aerospace system are omitted.[229]

The main component of the coating formed in all cases is aluminium oxide, but they also contain a mixture of cobalt oxides: CoO, Co_2O_3 and Co_3O_4. Aluminium oxide is the main component at the interface between the film and metal substrate, while Co_2O_3 and Co_3O_4 are concentrated at the surface of the film, and the centre regions contain a mixture of all four oxides.[227]

8. PHOSPHATE PROCESSES

Phosphoric acid based processes

A very thin passive film, similar to films formed by chromate processes, can be prepared by treatment of aluminium with dilute solutions of phosphoric acid . The film gives improved paint adhesion. The process is usually preceded by an alkaline cleaning operation. Certain phosphoric acid mixtures with organic acids and emulsifiers, as well as some proprietary solutions (notably Deoxidine), can be used to clean the metal and form a film suitable as a paint base. Addition of soluble organic polymers of the type :–



to a solution containing an oxidising agent, phosphoric acid ions and condensed phosphates **at** a pH of less than 6.5 gives a solution which rapidly forms a

corrosion resistant coating on aluminium, with good paint adhesion properties that is claimed to be more resistant to mechanical stress than many other pretreatments.[230] Conversion coating films can also be formed on aluminium using formulations containing an organic film forming agent, aluminium ions chelated with caboxylic acids and phosphoric acid.[231]

Films can also be formed on aluminium by hot ac anodizing in phosphoric acid.[43] A short treatment time (1-5 seconds) in dilute phosphoric acid at elevated temperatures (45-70°C) is sufficient to give a highly filamented surface film[232] with a similar topography to the dc phosphoric acid anodic films used by the aircraft industry as the basis for adhesive bonding[233] (Fig. 5-39). These processes have been described in Chapter 4.

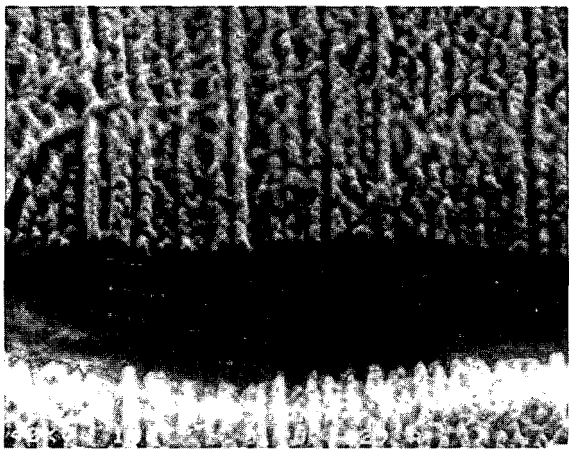


Fig. 5-39. Filamented structure of ac phosphoric acid anodic film[232]

Metal phosphate processes

Most phosphate pretreatments involve heavy metal phosphates and are modifications of formulations used to pretreat steels and zinc.[11,12] They were developed by the Parker company who referred to the processes as Bonderizing. The main advantage of the processes over other chemical and anodic pretreatments is their effectiveness as pretreatments for other metal surfaces, so they are preferred as pretreatments for mixed metal surfaces, containing large areas of iron, steel or zinc in addition to aluminium. As a result, the pretreatments are of considerable importance in motor vehicle manufacture, where use of aluminium components in conjunction with steel and zinc is increasing.[234] Vehicle bodies may include

several types of uncoated steel, one or more types of zinc-coated steel, and one or more aluminium alloys all of which must be cleaned, pretreated and coated on a continuous finishing line.[203] Such systems require fine tuning in order to achieve the required corrosion protection of all metals. Table 5-14 summarises the use of phosphate pretreated aluminium in car manufacture in Europe, Japan and the United States in 1993.

TABLE 5-14

Use of Phosphate Pretreated Aluminium in Vehicle Manufacture[14]

Country	*Company*	*Part*
United States	Ford	Hood
	Navistar	Truck cabins
Japan	Mazda	Hood, Fender, Sunroof
	Mitsubishi	
	Nissan	
	Suzuki	
	Toyota	
England	Rover	Hood,door,trunk lid
Germany	Audi	All Aluminium Car
	Mercedes-Benz	Roof of Road Star
	Porsche	Hood, Door, Fender
Sweden	Volvo	Trunk lid
Italy	Masarati[235]	All Aluminium Car

The phosphating process has also found application in the manufacture of refrigerators, typewriters, furniture and many other types of work. Some processes have been used in the deep drawing of aluminium because they permit deeper draws and reduce breakages. Chromate pretreated aluminium can be treated in phosphate conversion solutions. Some leaching of Cr(VI) does occur but this is rapily reduced to Cr(III), which only inhibits the phosphating reactions in high concentrations.[14]

Phosphating solutions contain a metal acid phosphate, an oxidizing agent, and a complex fluoride which accelerates the coating action. They also contain other unpublished addition agents. Films are formed as a result of reaction of aluminium with the phosphoric acid in the pretreatment formulation, and the main requirement of the metal in solution (e.g. iron, manganese, zinc or cadmium) is that it forms an insoluble phosphate during reaction. Nitrate and fluosilicate or fluoborate ions in solution activate the reaction. Saturation of the solution at the interface leads to the deposition of the phosphate coating on the metal surface.[12]

Of the three main types of phosphate processing in general use, zinc and iron phosphating are used to prepare corrosion resistant coatings and paint bases on aluminium.[236] Manganese phosphate pretreatment is used primarily to prepare wear resistant surfaces on bearing surfaces. The primary component of zinc phosphate pretreatment films on aluminium (and galvanised steel) is essentially hopeite ($Zn_2Fe(PO_4)_24H_2O$). Hopeite and/or phosphophyllite ($Zn_2Fe(PO_4)_24H_2O$) are deposited in the films formed on steel surfaces, so there can be composition differences between coatings deposited on steel and aluminium.. Iron phosphate coatings are amorphous and typically comprised of vivanite ($Fe_3(PO_4)_28H_2O$)) and magnetite (Fe_3O_4).[236]

Nickel or cobalt containing phosphating pretreatments have also been described. Such solutions also contain perchlorates and fluoride ions and were again developed for mixed metal pretreatment lines.?"

Under some circumstances, phosphate coatings on aluminium do not provide such good corrosion resistance as the chromate coatings in marine environments. Increased depths of pitting occur on phosphate pretreated surfaces.[238] In addition, zinc and iron phosphate pretreatments, used without a final chromate rinse, were consistently outperformed by chromate, zirconium, and titanium based pretreatments in corrosion testing of painted samples. Poorer performance occurred on a range of alloys.[203]

Zinc phosphating

Zinc phosphate coatings may be produced by immersion, spray or spray-immersion techniques and require a minimum of 5 stages in order to produce a satisfactory coating.[236]

i) Cleaning
ii) Water rinse
iii) Phosphate formation
iv) Water rinse
v) Acid rinse

The cleaning operation varies depending on the end use of the product. For paint pretreatment the metal can be cleaned using a titanated cleaner. This removes oils and other contaminants and activates the surface so that it gives crystal refinement in the coating formed. In automobile manufacture, an alkaline etching cleaner has been recommended, as it removes oxides and surface heterogeneities in addition to corrosion protective oils and lubricants.[14] Again, surface activation is required, and specially developed liquid conditioners are available for this purpose, eg an aqueous solution and/or dispersion of:[239]

titanium phosphate, pH 7-10, contains 0.001-0.2 g/l Ti,
0.1-4 g/l phosphates
0.05-20 g/l one or more fine particle layered silicate with cation exchange

capabilities. eg magnesium silicate and/or alkali silicate
optionally other usual components found in activating solutions.

For corrosion protection where crystal refinement is not required, acid or alkaline cleaning can be used. Hot water is used for the water rinses.

The final acid rinse gives additional paint bonding and corrosion protection to the film. Such rinses can be mixtures of hexa and/or trivalent chromium compounds, but like chromate pretreatments it is preferable to replace them by trivalent or chrome-free formulations.[236] A number of other formulations are available, including a fluoride-free polymer that seals the film via complex formation, and an inorganic fluoride where reaction with the film blocks the pores in the phosphate layer."

If electrophoretic paint is to be applied, it is necessary to rinse in deionised water to prevent carry-over of species such as phosphate or chromate into the electrophoretic paint. The water resisting, secondary adhesion of paint films to zinc phosphate coatings can been improved by spraying the pretreated surface with an additional zinc phosphating solution.[240]

An early version of a zinc phosphate pretreatment solution[241] contained

acid zinc phosphate	28 g/l
phosphoric acid (75%)	25 g/l
chromic acid	10 g/l
wetting agent	0.5 g/l

More generally, zinc phosphating and other Bonderizing processes" require a solution of metal ions, phosphoric acid, an oxidizing agent and a double fluoride. The oxidising agent can be 0.1-1.0% sodium nitrate (concentration is not critical) sodium iodate (0.5-1.0%), potassium periodate (0.5-1.0%), potassium bromate (0.4-1.0%), quinone (1.0-2.0%), hydrogen peroxide (0.3-0.5%), potassium perchlorate (5.0-6.0%), sodium persulphate (0.2-0.4%) or potassium permanganate (0.012%). The double fluoride is normally a fluosilicate but can be replaced by fluoborate, fluotitanate, fluostannate, fluozirconate, or fluovanadate. The pH range of a zinc phosphate pretreatment is normally between 2.8 and 3.5.

An example of a solution of this type contains:

zinc (Zn^{2+})	0.7% (wt)
phosphate (PO_4^{3-})	1.0% (wt)
nitrate (NO_3^-)	2.0% (wt)
fluoborate (BF_4^-)	1.0% (wt)

For paint pretreatment, a coating thickness of 0.54-1.94g/m^2 (50-180mg/ft^2) has been recommended[236] and this is produced by the conditions included in Table 5-15.

TABLE 5-15

Summary of Zinc Phosphating Paint Pretreatment Conditions[14]

Pretreatment Method	*Temperature (°C)*	*Time (seconds)*
Immersion	50-60	45-180
Spray	50-72	60-120
Spray (Coil Pretreatment)	60-72	15-30'

† Produces a film of between 0.65-1.3g/m²

Low temperature formulations can be operated at 20-38°C and applied using spray immersion or brushing techniques[236]. Coatings used as a basis for cold forming or for corrosion protection are normally approximately 10 times thicker than those used as paint bases.

Zinc phosphate, the oxidizing agent (sodium nitrate), and fluoride are used up during processing, so replenishing salts are added to maintain a constant solution composition. Some compositions of phosphate coatings found by chemical analysis are given in Table 5-16.

TABLE 5-16

Composition of Bonderite coatings[242]

	Immersion			*Spray Bonderizing*		
Basis metal	*1100*	*2024-T*	*Steel*	*1100*	*2024-T*	*Steel*
Constituents %*						
Zinc (Zn^{2+})	31.0	32.5	31.4	38.1	32.9	39.8
Phosphate (PO_4^{3-})	37.2	39.8	42.1	41.8	35.1	41.0
Fluoride (F-)	2.7	4.1	1.4	1.9	3.3	1.9
Aluminium (Al^{3+})	1.2	3.2	–	1.0	3.0	–
Iron (Fe^{2+})	0.4	0.4	8.2	1.8	1.5	4.2
Copper (Cu^{2+})	–	3.1	–	–	4.6	–
Magnesium (Mg^{2+})	0.1	0.4	–	0.3	1.0	–
Chromium' (Cr^{6+})	0.04	0.03	0.1	0.4	0.8	0.7

* The remainder (up to 100%) is water, part of which is hydrated to the zinc phosphate

† The presence of chromium is due to the chromic acid rinse.

In mixed metal phosphate processing (eg together with iron, steel and zinc) dissolved aluminium can inhibit or prevent the formation of the coating on other metal surfaces. eg. 0.3 g/l, aluminium ions in solution can completely prevent the formation of a zinc phosphate coating on steel. To prevent this, aluminium ions must be precipitated from the pretreatment solutions. Fluorides are normally added to remove aluminium because they form the anion AlF_6^{3-}, which can be precipitated as cryolite, Na_3AlF_6.[243] Baths of this type work satisfactorily with low proportions of aluminium present in the components being processed. However, they are less satisfactory, if a high proportion of aluminium is being treated, because cryolite precipitates only slowly from solution. The rate of precipitation can be increased by using a mixture of sodium and potassium fluorides (eg Amchem Granodine 38[244]). This results in the formation of NaK_2AlF_6, which is less soluble than cryolite so precipitates more rapidly.[245] Increase in the fluoride level of the baths can also help to overcome problems of aluminium build-up.[244] A typical bath of this type[245] contains the following:

zinc oxide	10.2 (% wt)
nickel oxide	1.85
phosphoric acid *(75%)*	44.3
nitric acid	4.5
hydrofluoric acid (70%)	0.97
fluosilicic acid (35%)	4.2
water	33
sodium and potassium nitrites (as required)	1:2 ratio

The use of borofluorides rather than silicofluorides in phosphating solutions for aluminium has been claimed to give benefits,[246] as have accelerators such as sodium nitrobenzene sulphonate[247,248] and chlorates.[247,249]

For treatment of surfaces with a high aluminium content, a fluoride based formulation has been designed[250] that results in the formation of a dense phosphate layer on the metal surface. The fluoride content of the solution is critical, particularly with respect to coating formation on aluminium. If the fluoride levels are too low, a poor coating is formed on the aluminium surface, but steel areas are coated normally.[14] Treatment with a formulation containing both zinc (0.4-2.5 g/l) and iron (II) (4-400 mg/l), together with phosphates (5-26 g/l), fluorides (0.4-1.5 g/l) and ammonia (0.01-2 g/l), is claimed to give good coverage of the metal substrate.[251]

An alternative method of producing a zinc phosphate film on aluminium panels suitable for automobile bodies is to plate a 0.05-0.38 g/m^2 zinc layer on the surface of the panel using a displacement plating or electroplating process, and to subject the coated panel to chemical conversion treatment with zinc phosphate, using conditions that completely dissolve the zinc layer.[252] It is claimed that the resultant films can prevent filiform corrosion and blistering after painting.

Iron phosphate coatings

The primary use of iron phosphate coatings is to provide a clean uniform base for paints. They are particularly important when paint adhesion and appearance are of prime importance and corrosion protection is less critical.[236] Processing conditions for iron phosphate pretreatment require a temperature range of 30-70°C and spray times of 45-180 seconds. Iron phosphate formulations are used at a higher pH (4.0-5.5) than the corresponding zinc phosphate formulations.

No-rinse phosphating

No-rinse phosphating systems have been developed.[253,254] Phosphating solutions can contain molybdates, tungstates, vanadates, niobates or tantalates.[254] A range of metal phosphates can be used including: Ca, Mg Ba, Al, Zn, Cd, Fe, Ni, Co and/or Mn. Adhesion of such films to the metal substrate can be improved by the addition of fluotitanates, -zirconates, -stannanes, -borates or silicates. It is also an advantage to add a reducing agent selected from: aldehydes, oxycarboxylic acids, hydrazine, hydroxylamine and/or hypophosphite in sufficient quantity to reduce the molybdates, tungstates, vanadates, niobates or tantalates by one oxidation level.

Pollution control

Pollution can be reduced by recovery of all rinse waters and chemicals using a system similar to the one shown in Fig. 5-40.[255] Here a peroxide accelerated zinc phosphating process is used, and continuous treatment of the cleaning, phosphating and rinsing processes is carried out.

9. PRETREATMENTS BASED ON CHEMICAL COUPLING

Because the materials involved in fibre reinforced composites and coatings technology are similar, developments in fibre/polymer adhesion can also be applied to improving the performance of organic coatings on metal surfaces. For example, silanes used to pretreat glass fibres to improve the adhesion to phenolic resin matrices[256] also have the ability to improve paint adhesion.[257] Similarly, titanates, employed to promote glass-resin adhesion in composites and improve filler binding and the pigment dispersion in solvent-borne inks,[258] also inhibit corrosion of aluminium surfaces,[259] and increase the bond strengths of adhesives on anodized surfaces.[258] Silanes can also be used as post-rinse treatments to enhance the performance of other types of pretreatments.[260] In this case, stabilisers are added to the silane to prevent polymerisation and precipitation from aqueous solution. The main application for this type of treatment has been with iron phosphate coatings.

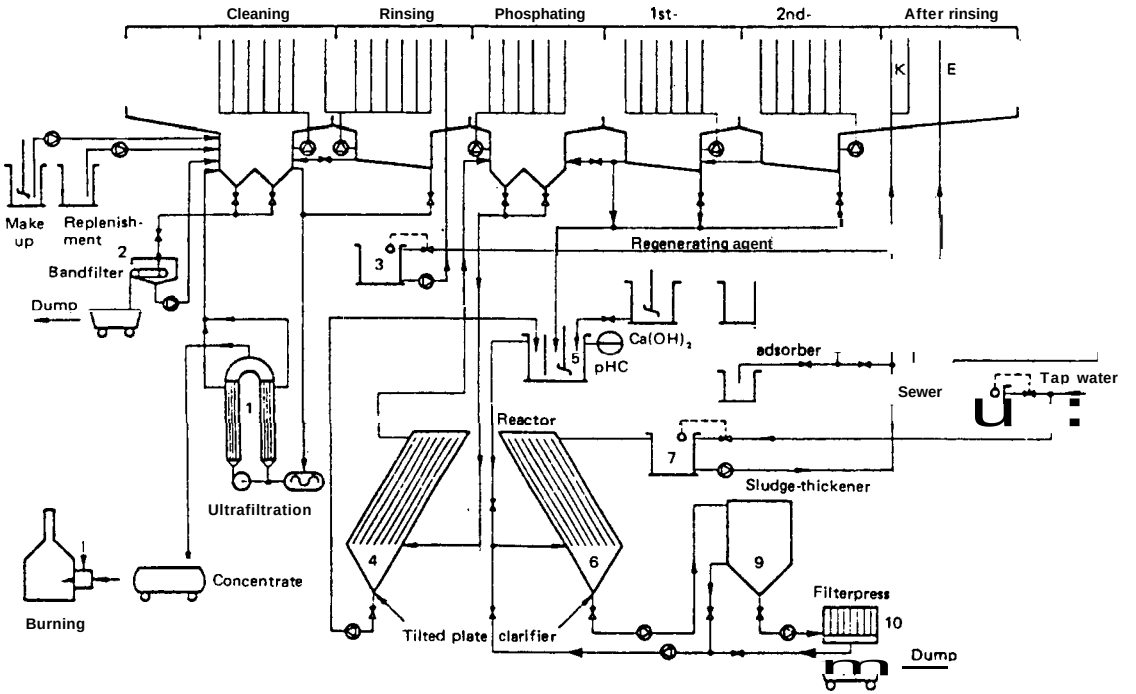


Fig. 5-40. Total recycling of peroxide-accelerated zinc phosphating processes[255]

1. Ultrafiltration unit for the cleaning baths
2. Filtration unit
3, 7. Pumps
4, 6. Lamellar clarifiers for separation of phosphate sludge
5. Neutralization chamber (pH 8.5 to 8.9 with $Ca(OH)_2$)
8. Tenside adsorber
9. Sludge thickener
10. Filter press
11. Dehydrated sludge
12. Rcvcrse osmosis plant producing deionised water for final spray rinse (E)

Silanes

Silanes are organosilicon monomers with the general formula:–

$$R\text{-}Si\text{-}(OR')_3$$

where R is terminated by an organofunctional group (eg epoxide, methacryl, vinyl or amide) and R' is usually a methyl or ethyl group. It is probable that silanes and other similar coupling agents promote the adhesion of organic coatings by chemically bonding to the metal substrate and the organic coating. Substrate bonding is believed to occur via the hydrolysis of the alkoxy (OR') group to form the silanol:[176]

$$R\text{-}Si\text{-}(OR')_3 + H_2O \rightarrow R\text{-}Si\text{-}(OH)_3$$

and this chemically bonds to hydrated oxides on the substrate surface. Self condensation of the silanol groups results in the formation of a polymeric film on the metal surface. If chosen correctly, the organofunctional group (R) reacts with the basis polymer of the paint film to complete the chemical coupling between the film and metal substrate.

The composition of silane films can vary depending upon the temperature of application and substrate composition.[261] Infrared studies have shown that absorption of y-aminopropyltriethoxysilane on 1100-series or 2024 alloy substrates treated in an aqueous solution of the silane (pH 10.4) for 1 min, and dried at room temperature for 30 min, results in films of low molecular weight siloxane polymers containing a considerable amount of absorbed carbon dioxide in the form of amine bicarbonates. Drying of the films at 110°C results in increased polymerization and dissociation of bicarbonates in films deposited on the 1100-series alloy substrates, but on films deposited on 2024 alloy, there is little significant increase in polymerization, and the amino groups are oxidised to imines. Similarly, after drying at 150°C, the amine groups in films formed on 2024 alloy are oxidized to the imines, but the oxide on 1100 alloy inhibits the free radical oxidation reaction. Dissociation of the bicarbonates, and oxidation of the amino groups, are important factors in the reaction of the primers with epoxy resins.[261]

Application and performance

Silane pretreatments can be deposited on the metal surface by immersion in a dilute 1-2% alcoholic/water or acidified methanolic solution of the compound. Improvements in paint adhesion can be comparable to that achieved by chromate conversion. Following initial reaction, adhesion appears to be relatively independent of pretreatment time.[176] Paint adhesion is also maintained in moist environments (Table 5-18).

TABLE 5-18

Effect of Silane Pretreatment and Water Exposure on the Adhesion Strength of Polyurethane and Epoxide Paints on aluminium

Paint	*Silane*	*Adhesion Strength (MPa)*		
		Before Exposure	*After Exposure*	*Dried After Exposure*
Polyurethane	None	12.5, 11.4	3.8	9.9
	MAPTS	32.3. 33.1	10.1	21.7
	BAPTS	23.2, 26.3	11.1	22.8
Epoxy Polyamide	None	21.3, 20.3	5.6	11.2
	MAPTS	30.8, 30.2	12.0	19.6
	BAPTS	29.7, 32.6	12.9	20.5

MAPTS : methylacryl propyl trimethyl siloxane
BAPTS : beta amino ethyl amino propyl trimethyl siloxane

Silane pretreatment can also increase underpaint corrosion resistance to a level similar to that obtained following chromate pretreatment.

Silanes can also be applied to surfaces during mechanical abrasion. In an effective prebond primer system, developed for adhesive bonding of aircraft alloys,[262] a partially hydrolysed aqueous solution of 3-glycidoxypropytrimethyl silane is applied to adherend surfaces during mechanical abrasion (wetsanding), prior to drying and the application of **a** corrosion resistant primer. Wedge tests have confirmed the effectiveness of such a system.[262] Tenacious, covalently bonded layers between paint films and metal substrates can also be formed by treatment with an alkaline silicate or aluminate solution (>0.005M), containing an organofunctional silane (>0.1 vol%) and a cross linking agent with two or more trialkoxysilyl groups (>0.02M vol %)[263] Formulations containing acrylamide:acrylic acid copolymer, a water soluble inorganic silicate and organofunctional silanes have also been described.[264]

Polydiorganosiloxanes

Pretreatment with polydiorganosiloxanes, such as polydimethylsiloxane, can also be used to enhance bonding between room temperature curing silicone elastomers and aluminium substrates.[265] The method finds particular application in the construction industry for the bonding of sealants to non-porous substrates such as aluminium.

Titanates

Titanates are organo-titanium compounds with the general formula:

$$R'OTi(OR),$$

Amongst other functional groups, R' can be an isopropyl group, and R may be a methacrylate, acrylic, sulphonyl or phosphate group.

Infrared evidence[259] implies that the compounds react with free protons on the metal surface[258] to produce a monomolecular surface layer:

$$R'OTi(OR)_3 + AlOH \rightarrow AlOTi(OR)_3 + R'OH$$

The alkoxy group, RO, is available for reaction with appropriate groups in the polymer coating.

Titanates can give a degree of corrosion protection to untreated metal surfaces. For example, dip coating of aluminium in a 2% solution of an amino adducted ethylene titanium pyrophosphate in xylene in water, significantly reduced corrosion during 500 hours of exposure to salt spray or 1000 hours in air at 100% relative humidity.

The effects of the pretreatments on paint performance have not been evaluated. However, work on adhesive bonding[259,266] has established that the treatment is only effective if it results in the deposition of only the monolayer initially adsorbed on the metal surface. Bonding between the initial layer and subsequent layers is weak.[258]

10. MECHANISMS OF PAINT ADHESION

One of the important mechanisms of adhesion promotion of conversion coatings is the protection of the metal substrate from corrosive attack, and the prevention of spreading of corrosion at the paint/metal interface, if the coating is damaged. For this reason, most corrosion tests on painted materials include the deliberate scratching of the paint, and assessment of the degree to which corrosion and paint loss occurs in the damaged region. The presence of free chromate or chromic oxide in many films is important in this regard, as they may act in a similar way to chromate pigments in paint primers, helping in repairing and maintaining the oxide coating without appreciably increasing the thickness of the film. Improved corrosion protection is believed to originate from the partial release of Cr(VI) compounds from the film when it is exposed to moist or corrosive environments. Released material can repair defects in the film by reaction with aluminium metal at the defect site. Released Cr(VI) compounds may also protect areas where the metal substrate has been exposed or weakened, as a result of stressing during the fabrication of painted material. If the surface Cr(VI)/Cr(III) ratios reflect the bulk Cr(VI) levels, the very high ratio found on the surface of no-rinse formulations,

such as Accomet C, means that the levels of Cr(VI) in the film are also very high. In consequence, protection from migrating Cr(VI) compounds would be expected to be more prolonged than most other forms of chromate pretreatment. However, most non-chromium forms of pretreatment do not appear capable of releasing corrosion inhibiting compounds in a similar manner.

Of the other factors that may influence the performance of organic coatings, the microstructure and chemistry of the substrate are likely to be amongst the most important. The importance of surface chemistry has been clearly shown by the influence of contaminants[267] and coupling agents[268,269] on adhesive properties. Corrosion inhibitors on surfaces can also have a significant effect on the durability of adhesive bonds.[270] With regard to surface topography, instances have been reported where improved adhesion has been correlated directly with the onset of the growth of micro-filaments on anodized[271] or boiling water treated[272] aluminium substrates. In other cases, penetration of organic coatings into microparticulate films[273] has been suggested as a cause of improved adhesion. Most pretreatment processes do not produce filamented surface structures. However, pretreatment can result in the deposition of films comprised of spherical 30-50nm particles.[36,92,99,159] With such surfaces, keying of the paint or lacquer could be enhanced by penetration of polymeric material into the spaces between such particles. The wide range of different macro-topographies, determined by process conditions and pretreatment type, means that macro-topography is unlikely to have a general effect on paint adhesion.

11. APPLICATIONS OF CHEMICAL CONVERSION COATINGS

Organic finishing

The most important application of chemical conversion coatings is as a basis for the application of organic materials, particularly paints and lacquers. In the case of aluminium sheet, the process is normally carried out in the coil form (Fig. 5-25) with continuous spray cleaning and conversion coating, followed by paint or lacquer application. Conversion coatings of the no-rinse or chrome-free type are normally used, and major end-uses include painted sheet for architectural and caravan applications, lacquered strip for canning products, and foil for conversion and laminating. Other forms of aluminium, such as extrusions or castings, are usually batch pretreated using chromate or chromate-phosphate processes.[274] In car bodies, when aluminium is present in combination with other materials such as steel, phosphate pretreatments are normally used prior to painting. Amorphous chromate and phosphate coatings have also been used as paint pretreatments for computers and business machines.[275] Chromate, and particularly

chromate-phosphate treatments, are used for electrocoated and powder coated aluminium products.[276]

Architectural applications

In architecture, chemical oxide, chromate and phosphate films have been used to give inexpensive grey, green and orange brown finishes on roofing, siding, ceiling panels, tiles and wall cladding. For exterior exposure the conversion coating is sometimes protected by a thin clear methacrylate or cellulose acetate butyrate coating, which increases weather resistance and facilitates cleaning,[277] but filiform corrosion occurring beneath the lacquer is a serious danger with this type of finish.[278]

In the **U.S.A.,** the M.B.V. process has been used to produce a slate-grey effect on aluminium shingles, and in Sweden the chromate-phosphate processes have been widely used to produce a green coating for the roofs of farm buildings. Industrial roofing and siding has also been made from conversion coated aluminium (Fig. 5-41) but the ready availability of prepainted sheet has reduced such applications.

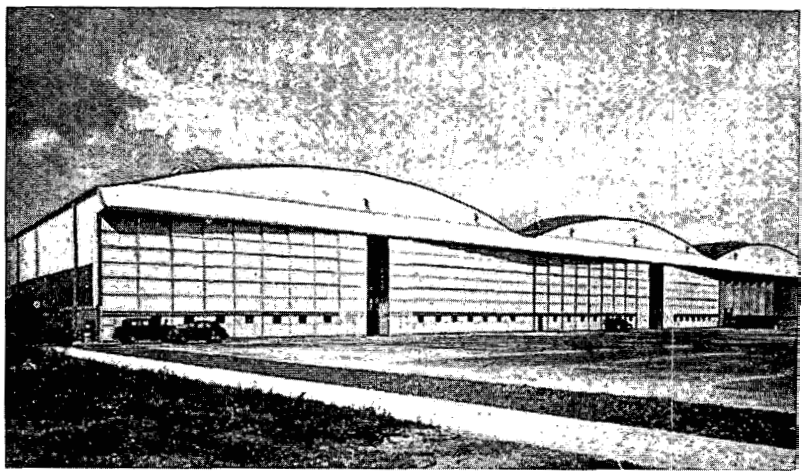


Fig. 5-41, The major part of the walls of these hangars at London Airport were constructed of corrugated aluminium sheeting treated by the Alocrom process

Adhesive bonding

Chemical pretreatments for adhesively bonded structures have been used and tested extensively in experimental structural bonding programs. Chromate-phosphate pretreatments,[279,280] and some other chromate-based pretreatments,

have been used as adhesive bonding pretreatments for aluminium sheet used to manufacture a range of experimental aluminium vehicles (Fig. 5-42). Early vehicles of this kind were replicas of standard models, normally manufactured in steel, and were formed from conventionally pressed aluminum components.[279] A small number of spot welds were used to hold the vehicle structure together prior to curing, but the main method of joining employed was adhesive bonding. Since such components were pressed from flat pretreated sheet, the pretreatment must be capable of providing an effective base for the adhesive, after it has been subjected to the stresses of the pressing operation. Such vehicles have successfully passed all the standard tests used by the automobile industry (pavé tests, corrosion cycle, crash tests, pothole break etc).[279] This technology is now being used in production vehicles.

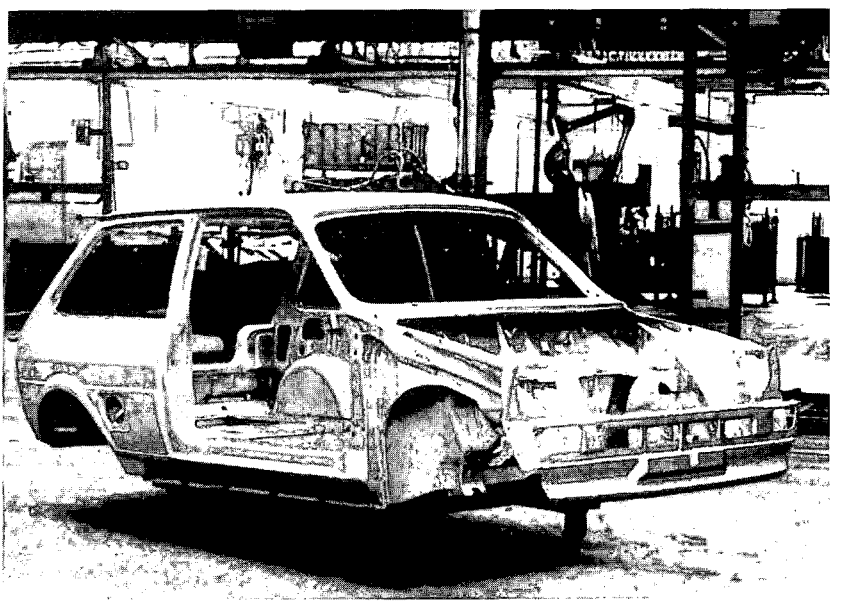


Fig. 5-42. Replica BL Metro vehicle manufactured from adhesively bonded panels pressed from pretreated aluminium sheet[279]

Chromate-phosphate pretreatment can increase the bond strength of a cured adhesive[281] to an aluminium surface, although this is not always the case, and the main effect on adhesion is the higher degree of retention of adhesive bond strength in moist or corrosive environments.[282] Retention of strength occurs in joints in stressed and unstressed environments. Chromate phosphate and some other

chromate pretreatments can also be stored for a considerable time prior to use without having a detrimental effect on adhesive bonding. Initial adhesive bond strength and strength retention on exposure to salt spray is comparable to that obtained using the Boeing 555 phosphoric anodizing process, one of the standard adhesive pretreatments used in the aircraft industry.[282] However, it should be noted that it is standard practice in the aircraft industry to prime a pretreated surface prior to the application of the adhesive, and this could have a marked effect on the properties of the adhesive bond formed.

Chromate (Alocrom 1200) pretreatments have been reported to have a more variable effect on the performance of adhesives. In some instances[283] initial bond strengths have been found to be much lower than found for untreated material, but bond strength is maintained during prolonged exposure to corrosive environments. Low bond strengths can be caused by interfacial failure between an excessively thick film and the metal substrate.[284] Such films also give poor corrosion performance. Deposition of layers of particles of differing sizes[94] could lead to such films having poor cohesive strength. However, paint tests have shown that it is possible to produce Alocrom 1200s pretreatment films with good adhesion properties.[214]

Few no-rinse or chrome-free pretreatments for adhesive bonding have been described. However, zirconium/fluorine/phosphate (Bonderite *777)* and an experimental zirconium/fluorine/phosphate (EP2472) pretreatment have both been reported to give adhesive performance in stress-humidity testing equivalent or superior to a chromate-phosphate system (Bonderite *705*).[281]

Heavy-metal inserts

Conversion coating is an alternative to anodizing for the treatment of aluminium alloy castings containing inserts of heavy metals. Such material can only be anodized if the insert metal can be effectively masked. Otherwise the anodizing current will short circuit through the inserts, and as a result, the current density at the aluminium surface will be reduced to a point where anodizing cannot occur. Pitting and dissolution of the insert also occurs. Masking is an extra operation and has to be applied to each article separately, sometimes at considerable expense. Such problems do not occur if the material is conversion coated, provided that the surface of the insert is small compared to that of the aluminium. Mixed metal surfaces, of a large heavy-metal:aluminium surface area ratio, are probably most effectively protected by a phosphate treatment.

Aluminium alloys coupled with carbon-steel bolts, nuts and washers, which may be cadmium or zinc plated can be pretreated with the Alrok process.[285] The treated aluminium is only lightly corroded after salt-spray testing.

Other applications

Chromate-phosphate pretreatment provides a surface with sufficient corrosion resistance to protect aluminium data storage media.[286] Zinc phosphate coatings can be reacted with sodium stearate to form a lubricant suitable for cold extrusion of relatively large aluminium alloy components.[287] Automatic barrel chromating plant has been used for aluminium brake cylinders. The barrels are of stainless steel and are transferred mechanically through the tanks.[79]

Future applications may include space structures.[288] Statistical analysis of slip coefficients for shear joints to provide data for the initial design of shear loaded threaded bolted joints typical of those used in space structures has shown that chromated and anodized aluminium have better slip resistance than untreated metal.

12. COLOURING PROCESSES

Many of the chemical conversion processes described produce coloured coatings on the metal surface. Natural colours include shades of grey, green, yellow, or brown, but suitable conversion coatings can be further coloured by the absorption of dyes or pigments. In general, however, such finishes are not particularly pleasing from the decorative point of view, having rather a muddy appearance. For production of **a** coloured finish on aluminium, other than paint, first consideration would normally be given to a dyed anodic oxide coating (see Chapter 10).

Black, and certain other decorative finishes, can be produced directly on aluminium by chemical processes. Black colours can be obtained by immersing the metal in a solution containing:[289]

potassium permanganate	5-10 g/l
copper nitrate	20-25 g/l
nitric acid	2-4 ml per litre

at 80°C or above for about 20-30 minutes. Scratch brushing of the metal surface during processing may also be necessary. By lowering the copper nitrate content to 5 g/l, a dull brown colour is obtained in a treatment time of 10-15 minutes.

Treatment in molybdenum containing solutions can also be used to produce a black colour on aluminium. A boiling solution containing 10-20 g/l ammonium molybdate and 15 g/l ammonium chloride gives a deep black colour in 1-2 minutes.[290] Similar blackening processes, but also including a sulphur compound and an organic reducing agent, have been patented.[291] A process of this type was developed by Alusuisse[292] under the name of Chemalor-S. This required an initial etching process in a 2-15% (wt) iron chloride solution at 70-95°C, followed by

blackening in a 40-60 g/l ammonium hepta-molybdate, 40-80 g/l aluminium trichloride solution at pH 2-3; 2-8 min. treatment at 90°C was required. The blackened aluminium was finally treated in an alkaline chromate solution, containing 13-17 g/l sodium chromate and 40-50 g/l sodium carbonate for 1/2-3 min. at 85-92°C. A coating 2-4 microns in thickness with good abrasion resistance, corrosion resistance, light fastness and chemical resistance was produced.[293] It was used on components such as heat sinks and camera parts.

Other black finishes have been produced in solutions containing sodium carbonate, sodium chromate, potassium ferricyanide and a lead salt,[294] or sodium nitrite, sodium silicate, zinc sulphate and calcium or magnesium chloride,[295] or chlorides, sulphates and bicarbonates of sodium salts and a catalyst and a compound for maintaining the solution pH sufficient to promote reaction.[296]

A recent application of black chemical conversion coatings has been in the field of solar energy and many companies have developed systems for this application. Alcoa[297] claim the use of a silicate-borate solution at 66-100°C and a pH of 8-10. This is said to provide an economical aluminium solar collector surface with high solar absorptivity and low emissivity.[298] The corrosion resistance of the finish is good, but a slight loss of absorptivity and decrease in emissivity occurs during exposure, the effects of which are not yet fully evaluated. Reynolds suggests the use of a chromium oxide coating containing permanganate-modified copper oxide,[299] whilst Sumitomo claim the use of chromate-phosphate coatings which are subsequently oxidized at 400-600°C to give an oxide coating on the surface.[300]

A whole spectrum of colours, from ochre to violet via brown-red, can be produced by treating a chemical conversion coating with a.c. in an aqueous electrolyte containing elements such as selenium and tellurium."" A blue bronzing solution containing 5 g/l each of potassium ferricyanide and ferrous chloride has also been produced.[290]

A grey iron-like colour is formed on aluminium by treatment with a solution containing 25 g/l potassium sulphide and 1 g/l vanadium sulphate at 80-90°C; the colour can be modified by adding certain organic and inorganic colouring materials to the treatment solution to produce brown, golden yellow and even red.[302]

A reddish brown colour is obtained in the following solution:

potassium permanganate	320 g/l
cadmium nitrate	100 g/l
ferrous chloride	20 g/l
nitric acid	20 g/l

In general, chemical colouring processes give poorer and less durable finishes to those produced by the dyeing of anodic oxide films. However, chemical colouring can be superior to anodizing and dyeing if the article to be coated contains heavy metal inserts, which are difficult to mask for anodizing. Also, self-coloured coatings resulting from the production of a coloured inorganic substance are often more light fast than dyed finishes.

A combination of conversion coating and organic dyeing has been used in the development by Lea Mfg. Co. of the Decoral process. This process produced a coating which was readily dyed to give bright clear colours. In this process, the cleaned aluminium component was placed in an alkaline solution of a ferricyanide compound[303] containing 0.1-0.5 moles/l potassium ferricyanide, 0.1-0.5 moles/l potassium carbonate and 0.1-0.5 moles/l trisodium phosphate at pH 11-12. Treatment for 5-20 min. at 25-35°C was usually required. The coating produced could be dyed in a range of organic dyestuffs, similar to those used for dyeing anodized aluminium, and the dyed surface was usually sealed with a suitable lacquer, wax or resin coating. An alternative conversion coating solution replaced the potassium ferricyanide with ferric nitrate.[304] The coating produced could be up to 2.5 microns in thickness, had good heat and corrosion resistance,[305] and was an alternative to thin, decorative anodic coatings. Its major benefit was with small components as they could be barrel processed, a technique which is very limited with anodizing processes. **As** a result components such as pencil ferrules or shoe eyelets were often processed in this way.

13. RELATED PROCESSES

Whilst they are not conversion coatings, several related processes employ phosphate or silicate coatings to give surface protection or decoration.

I.C.I. developed a range of clear organo-metallic phosphate coatings for application to a variety of substrates including organic polymers, glass and metals such as aluminium.[306] The application of iron and/or chromium phosphates to aluminium surfaces, particularly anodized aluminium surfaces, results in the deposition of glassy Fe/Cr phosphates on the surface.[307] This reduced the tendency for smut formation on exposure and reduced dirt retention, and, with dyed coatings, the U.V. light fastness of the finishes could be improved. However, problems were experienced in application of the coatings to complex extruded shapes. **A** finish which has been used more widely was developed by Dow-Corning and marketed under the name of Vestar.[308] This produced a silica coating on the aluminium surface. The coating solution contained dispersed small silica particles chemically treated with a silicone matrix. The alcohol thinned coating material could be treated as a normal organic coating, and could be applied by conventional dipping or spraying methods to cleaned aluminium surfaces. The films deposited were stoved at 150-250°C and this left a largely inorganic coating (only 9% carbon) on the aluminium surface. The coating was completely clear and so was particularly suitable for protecting bright aluminium surfaces for components such as reflectors, automotive trim and road wheels. It had good abrasion resistance, heat resistance and corrosion resistance, but the coating solution itself had limited stability.[309]

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CHAPTER 6

The Fundamentals of Anodizing

1. INTRODUCTION

This chapter covers the fundamental aspects of the processes used to produce commercial porous anodic films, mainly by reviewing the current state of scientific understanding. It draws heavily on the work of the UMIST group who have dominated the development of the scientific understanding of anodizing published in the West over the last thirty years.

Initially, in order to provide context, a description is given of the position of anodizing among the range of filming and electrochemical processes to which aluminium may be subjected in aqueous solutions. Non-porous barrier films and thicker porous films can be produced by anodizing depending on conditions used.

Subsequently, there is a review of proposed mechanisms attempting to explain anodic film formation in aqueous solutions. This starts by considering the barrier layer where growth processes are taking place, then how and why pores nucleate, moving to the characteristics of steady-state porous anodizing and the morphology of the resulting film. Subsequently, work on film composition and structure is reviewed. This focusses on the nature of anodic film material, and how this may be modified by localized processes such as dielectric breakdown and the effects of aluminium alloy composition. Finally, a section covers surface chemistry. An attempt has been made to relate the more fundamental aspects of academic research to anodic film properties of commercial importance. Certain properties, eg anodic film hardness, are of considerable importance to products. The immediate significance of others is perhaps less clear, but, resulting from them, often novel applications for anodized aluminium have been suggested.

Filming processes on aluminium

Aluminium is a very base metal. However, it readily becomes covered by an oxide or hydroxide film. The behaviour and characteristics of this film in any particular environment largely determine the corrosion resistance of the metal surface. The film is generally 3-10 nm thick and thus may afford relatively little protection in aggressive environments. However, the protective properties may be enhanced by further oxidizing the surface. Chemical conversion coatings which replace or supplement the "natural" air-formed film have been described in a previous chapter. Anodizing is distinct from these processes in that the surface is **oxidized** electrolytically and a much thicker film can be formed. Film formation can also occur on aluminium when it is cathodically polarized and a thin, hydrous oxide may be produced.

Anodizing processes

When aluminium is anodically polarized in an electrolyte, the negatively charged anion in solution migrates to the anode where it is discharged with the loss of one or more electrons. In an aqueous solution the anion consists in part of oxygen which unites chemically with the aluminium. The result of the anodic oxidation depends on a number of factors, particularly the nature, concentration and temperature of the electrolyte and the electrolytic operating conditions such as current and voltage. In simple terms the following processes can occur at the anode.

(1) The reaction products may be essentially insoluble in the electrolyte, and form a strongly adherent barrier-type film on the aluminium. Film growth continues until its resistance prevents current from reaching the anode. The films are extremely thin and dielectrically compact. They may be formed in a number of generally relatively neutral pH salt solutions of which borate or tartrate solutions are common examples. Such films, formed at high voltages, find application in the production of capacitors and for the protection of very thin aluminium coatings formed by vacuum deposition techniques, which are used in the electronics industry.

(2) The reaction products may be sparingly soluble in the electrolyte. An adherent film forms as above, but is accompanied by localized field-assisted dissolution which produces a regular array of essentially parallel-sided pores in the film (Fig 6-1 gives the nomenclature used for porous anodic film morphology). These pores allow continuing current flow and thus film growth. Electrolytes used are generally acid and include sulphuric, phosphoric, chromic and oxalic acids. The films formed are used to pretreat aluminium surfaces to facilitate good adhesion of paints, lacquers or adhesives, and as they may be very hard and many microns thick, they find extensive application for protective and decorative purposes.

(3) The reaction products may be moderately soluble. Under these conditions, electropolishing may be possible if a suitable electrolyte is used (see Chapter 3).

(4) If the anode reaction products are fully soluble in the electrolyte, then the metal is dissolved until the solution is saturated. This reaction takes place in some strong inorganic acids and bases.

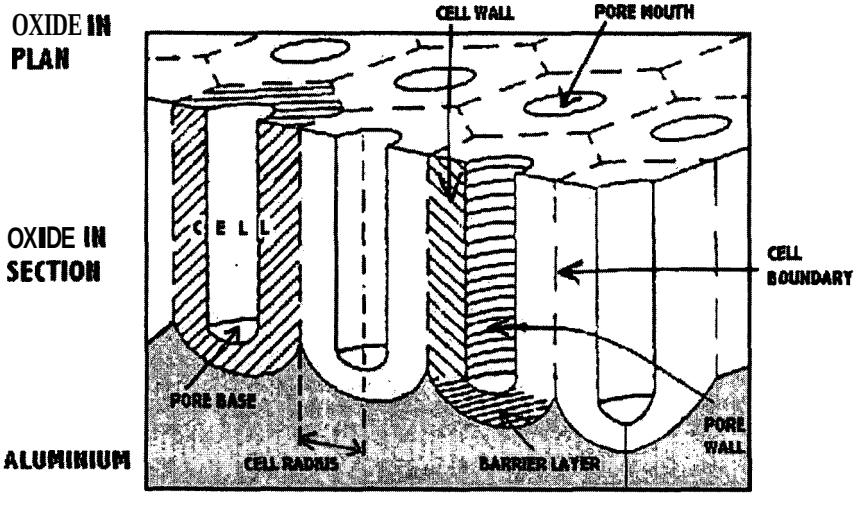


Fig. 6-1. Schematic representation of a porous anodic film showing the principal morphological features

As may be appreciated, the boundaries between these different processes are not well defined. For instance, porous anodizing under aggressive electrolyte conditions may lead to a very low limiting film thickness, which is approaching the situation during electropolishing.[1,2] Indeed, some workers have found porous oxide films present on aluminium surfaces after electropolishing. Also, as described below, the difference in conditions that determine whether a porous or barrier-type anodic film is produced can be quite slight.

Other anodic processes that can take place on aluminium are localized rather than relatively uniform over the surface, often originating from alloy microstructure or topography. These include corrosion processes (see Chapter 1) and dielectric breakdown where local current concentration may cause heating and subsequent crystallization of the adjacent film material.

2 ANODIC FILM FORMATION

This section starts by describing some key features of porous film growth which are relevant to practical anodizers. Subsequently, more scientific detail following the sequential development stages of a porous anodic film is introduced. Initially, this focuses on barrier layer formation and thickening, drawing heavily on the understanding of barrier-type anodic films. Although barrier anodizing is not the focus of this chapter, it relates closely to porous anodizing and, in some aspects, has been the subject of greater investigation. Important factors that distinguish porous from barrier-type films are detailed. Subsequently, the initiation of pores is described, followed by a review of the factors that control the porous morphology and how it may be modified. This has relevance to colouring processes, and properties such as hardness and corrosion resistance.

Porous film growth and morphology

Porous anodic films formed on aluminium in electrolytes such as sulphuric acid are characterized by a very uniform morphology. Pores are approximately cylindrical, situated in generally close-packed hexagonal cells, and separated from the aluminium by a thin layer of oxide. Many of these features are determined by the anodizing voltage as described below. Thus, the course of porous film development is revealed by monitoring the change of voltage when anodizing at constant current, or current when anodizing at constant voltage (Fig 6-2). The compact barrier layer thickens during stage I. Incipient pores develop in the barrier film during stage II, while the classical film morphology starts to arise during stage III. Steady-state propagation of the pores continues through stage IV. However, the thickness of the porous film is controlled coloumbically, that is it depends on the amount of charge passed. Consequently, when anodizing at a constant current density, the film thickness is proportional to the anodizing time. This relationship falls down for thicker films and those produced under particularly aggressive solution conditions, where the effects of chemical dissolution become significant.

The anodic reaction that leads to film growth takes place at the metal/oxide interface, and therefore the film is effectively growing from within rather than building up on its outer surface, as is the case with plating or painting processes. This means that the outer part of the film is in contact with the electrolyte for the full anodizing time, and, depending on conditions, may become considerably dissolved chemically (without field enhancement) by the end of the anodizing process. Underlying regions of the film are progressively attacked to lesser extents. Thus, the pores are tapered being wider at their mouths than near the aluminium substrate. It then follows that the maximum film thickness achievable depends on the ability of the electrolyte to chemically dissolve the film. When anodizing has been continued for sufficient time that the pore walls at the outer

surface are vanishingly thin, then although anodizing may continue to produce film material at the metal/oxide interface, no further net film thickening takes place. Understanding the factors that control this balance between the rate of film formation and the rate of film dissolution forms a vital part of practical anodizing technology.

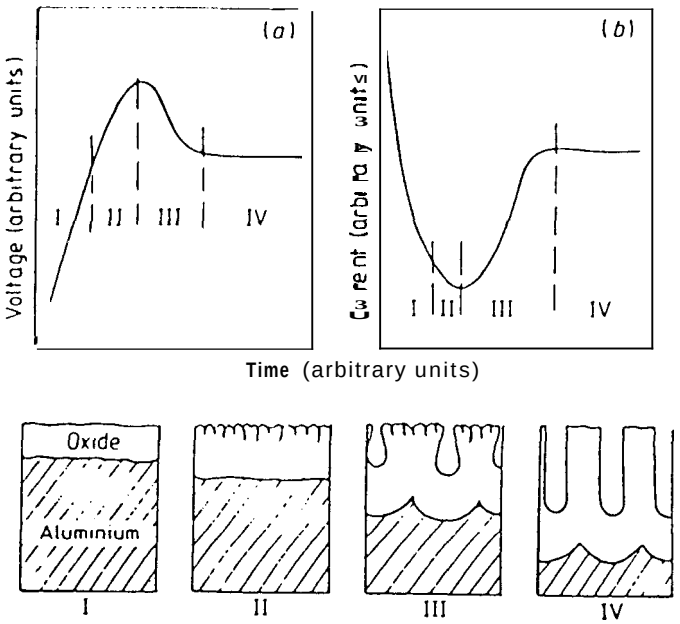


Fig. 6-2. Schematic diagrams showing the development of a porous anodic film on aluminium under (a) constant current conditions, and (b) constant voltage conditions.'

It also follows that as aluminium is oxidized to form the anodic film, the thickness of the aluminium component will therefore decrease. However, this is compensated by the bulkier oxide produced, and the component dimensions usually only increase slightly as the result of anodizing. The way in which the film thickness and the thickness of the basis metal vary with time" is shown in Fig 6-3, where curve **A** refers to the total change in thickness of a sheet anodized on both sides to the coating thickness referred to by curve B, while the curve **A'** refers to the dimensional change for one-sided anodizing. In this example, the coating reaches its maximum thickness in just under two hours and it may be seen that up to this point, for every 3 μm of coating formed, the metal retreats approximately 2 ym and the exterior surface advances about 1 ym.

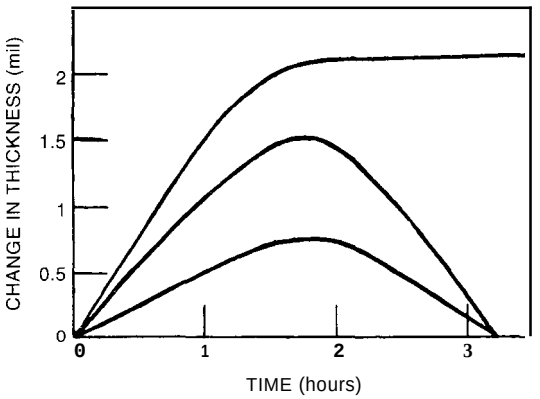


Fig. 6-3. The change in thickness of metal sheet, **A,** anodized on both sides to the coating thickness indicated by curve B, and **A',** anodized on one side only, in sulphuric acid at 20°C and at 1.5 A/dm^2 direct current.[4] (1 mil = 25 ym)

Barrier layer formation

In furthering the understanding of anodizing processes, it has been important to determine the location where film growth takes place. For barrier films, is this at the metal/oxide interface, at the film/solution interface, or both, or somewhere in between? And what happens when a porous layer is developing and dissolution of the barrier layer is taking place to enable the pores to propagate? The investigation of these questions has involved barrier films produced in electrolytes believed to have no solvent action on the film, as well as porous films. However, as described above, the demarcation between the two film types was not clear. In fact, some workers have assumed that their experiments involved barrier films, although it is now appreciated that these may have been thin porous outer layers. This has to be considered when evaluating previous work.

Barrier layer thickness

The barrier layer thickness is proportional to the anodizing voltage with small variations determined by the nature of the electrolyte. Holland and Sutherland[5] obtained film thicknesses of 1.3 nm/V in 3% ammonium tartrate solution used in the protection of vacuum-coated aluminium mirrors. Capacitance measurements of barrier layers by Ginsberg and Kaden[6] have given values of 1.4nm/V for films formed in barrier film-forming electrolytes and 1.15nm/V for the barrier layers of porous anodic coatings. Fig. 6-4[7] shows that some porous oxide may be formed in a supposedly barrier film-forming electrolyte, when anodizing at constant voltage, after the limiting barrier thickness has been achieved.

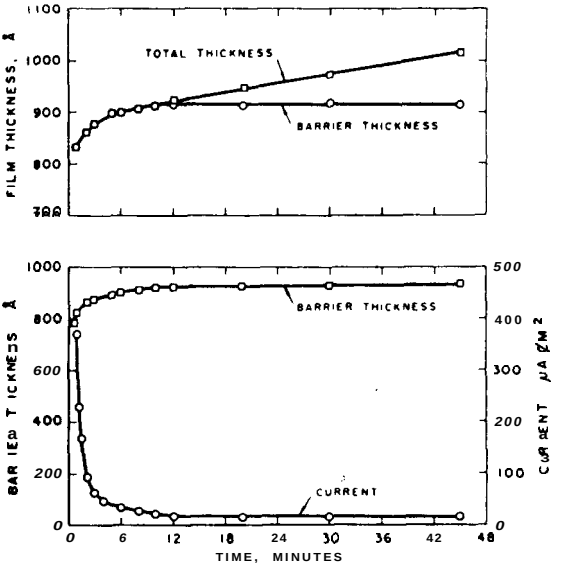


Fig. 6-4. Film growth and current density as a function of time during anodizing in ammonium tartrate solution.[7]

In the research laboratories of the Aluminum Company of America (Alcoa)[8,9,10,11], a method was developed for measuring the barrier layer thickness using the apparatus shown in Fig. 6-5. In this method, the current flow through the coating is monitored with increasing voltage in an electrolyte that forms a barrier-type coating. As the voltage rises, the leakage current increases very slowly until the voltage corresponding to the thickness of the barrier layer is approached. Once appreciable current starts to flow, small increases in voltage cause the current to rise rapidly. The approximate barrier film thickness in nm was said to be 1.4 times the highest voltage that does not produce a pronounced rise in current.[7] This method is based on the proportionality between barrier thickness and anodizing voltage, and is equally applicable to the measurement of barrier layer thicknesses of porous films.

The method was used by the Alcoa workers to study the evolution of the barrier layer during anodizing in 15% sulphuric acid at 20°C. The thickness increased rapidly at first until approximately 4.5s when a maximum was attained. It was said that at this stage, solvent action of the electrolyte exceeded the rate of growth. The fluctuations in thickness ceased after approximately 25s, and the thickness was unchanged over the remainder of the 45 min total anodizing time, during which the porous coating grew in thickness. An interesting incidental result reported by these authors was that hot-water sealing appeared to decrease the barrier layer thickness at a rate of 0.04 nm/min. It has been proposed elsewhere

that hot-water sealing causes dissolution of the anodic film material prior to exceeding the aluminium solubility product, when precipitation of sealing product occurs. (See Chapter 11).

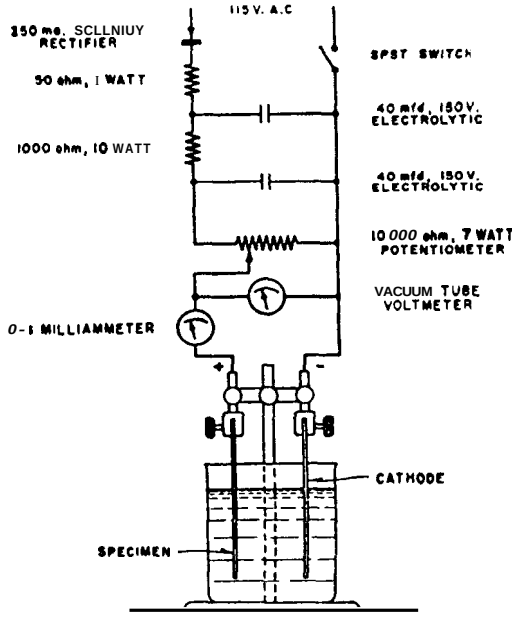


Fig. 6-5. Electrical arrangement for determining barrier layer thickness.[8,9,10,11]

The effect of anodizing electrolyte concentration is seen in Fig. 6-6. At constant voltage and temperature and with very low sulphuric acid concentrations, the unit barrier thickness approaches a maximum of 1.4 nm/V as, at this concentration, the solvent action is very low. Increasing the concentration causes a drop in the unit barrier thickness which reaches a minimum at between 35 and 65 wt% sulphuric acid. This is followed by a marked increase up to 90% where it changes sharply to an almost negligible value. As seen when comparing Fig. 6-6 with Fig. 6-7[11], the decrease in unit barrier thickness at higher concentrations is by no means related to the rate of dissolution, nor is it directly related to the degree of dissociation of sulphuric acid as indicated by electrical conductivity. This suggests that some other factor influences barrier thickness at high acid concentrations.

In other electrolytes, such as chromic, oxalic or phosphoric acids, the barrier thickness is influenced by the same factors to a very similar extent.

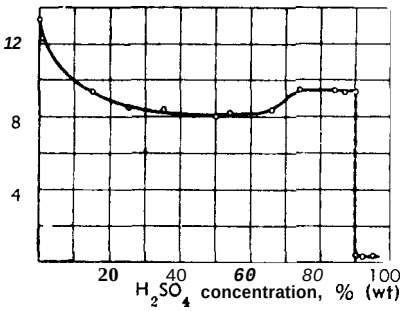


Fig. 6-6. The relationship between unit barrier layer thickness and sulphuric acid concentration for anodizing 99.99% aluminium at 20°C and 15V.[11]

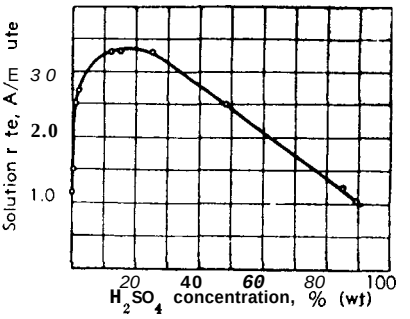


Fig. 6-7. The relationship between the dissolution rate of anodic film material and sulphuric acid concentration at 36°C."

High field conduction

Although the barrier layer is compact and very thin, generally 10-50nm, it is probably not sufficiently thin to allow significant quantum-mechanical electron tunnelling. Therefore ionic conduction is the principal means of electric conduction. However, the film is sufficiently thin that it is subjected to a very high field strength, more than 10^8 V/m. Ionic transport under a high electric field through oxide films is generally explained by thermally activated motion, over discrete energy barriers, of charged point defects.[13] The ionic current and the field are related by the so-called high-field conduction equation:

$$J = Ae^{\beta E},$$

where J is the flux density of an ionic species in the film, E is the field strength across the film, and A and β are temperature-dependent constants.[14] This equation has been presented in different forms by various authors depending on different mechanistic assumptions. Work has been reviewed by Dignam.[15] Palibroda[16] has proposed a variant of the high field conduction equation to describe the current/voltage relationship for steady-state porous anodizing, which includes a limiting value for the voltage, possibly associated with the breakdown voltage of the film.

Theories that have been proposed for ionic conduction can be classified according to their basic assumption: internal control, interface control or internal-interface control. Verwey[17] proposed that the rate limiting step is the rate at which ions move from one interstitial position to another, while other authors have suggested that the high field produces Frenkel defects (pairs of interstitial cations and cation vacancies) by drawing out metal ions into interstitial positions.[18,19] Later, a theory for internal control was developed by Dignam on the basis of a dielectric mosaic model of the anodic film.[20]

Mott and Cabrera[21,22] considered that the rate determining barrier is associated with the injection of defects into the oxide. Subsequently, models were extended to include the effects of space charge due to ions in transit, so that barriers at the metal/oxide interface and within the oxide both have a role in controlling ionic current.[23,24,25,26]

As a first approximation, the high-field conduction equation above and subsequent derivations provide convenient theoretical descriptions of anodic oxidation to produce barrier films. However, a number of factors were not adequately considered. Both anions and cations rather than a single species may be mobile,[27,28] there is a slight non-linearity in the relationship between log J and the field,[29] anodic films are generally amorphous rather than crystalline[30] which makes concepts involving interstitial sites difficult to understand, and there may be an electronic component to the total current."

Anion and cation migration

There has been considerable work investigating whether film growth is due to the migration of aluminium cations across the film to produce oxide by reaction with the electrolyte, or due to oxygen-bearing anions moving across the film to oxidize the metal surface, or both.

Originally, it was believed that oxygen moved across the film.[4,32,33] Schenk[4] appreciated that the ionic diameter of oxygen and the atomic diameter of aluminium are very large, but as the discharge potential of oxygen is low, he postulated that oxygen ions are first discharged at the solution interface, diffuse across the oxide and are then reionized near the metal surface to react with Al^{3+}. Hoar and Mott[34] suggested that the smaller hydroxyl ions carry the current and produce protons at the metal interface, which then move back across the film to combine with O^{2-} from the electrolyte, and subsequently the process repeats. This prompted work to determine the hydration of anodic films.[35,36] It was discovered that only the outer regions of films formed in aqueous tartrate solutions were hydrated, but Brock and Wood[36] found no hydration in films produced in a non-aqueous glycol-based solution. Thus, it was deduced that O^{2-} rather than OH- is mobile.

Lewis and Plumb[37] carried out radiographic studies which they claimed showed that the point of growth of both barrier and porous films lies near the solution interface; only aluminium ions are mobile. However, their technique was criticized by later workers.[38,39] Furthermore, the idea that the oxide of porous films should be produced at the base of the pores is difficult to conceive, when pore propagation takes place at the same site. Later, using sequential anodizing in normal and labelled sulphuric acid, it was shown that the oxide of porous films is produced at or near the metal/oxide interface.[40]

Considerable work has been undertaken using tracer techniques to understand the transport processes taking place. Thus, ionic transport through anodic films has been investigated using radioactive tracers,[27] ion implantation,[41] nuclear microanalytical techniques,[42] and transmission electron microscopy of ultramicrotomed sections.[43]

Davies and coworkers[27] implanted Xe^{125} marker ions onto a slightly anodized aluminium surface and then by monitoring the energy loss of emitted particles, determined their depth below the surface after further anodizing. They were able to show that both oxygen and aluminium ions are mobile during film growth with a cation transport fraction ranging from 0.37 to 0.72 (error 10%) for an aqueous ammonium citrate anodizing electrolyte and 0.58 for sodium tetraborate in a 95% ethylene glycol solution. Also, for the aqueous solution, it was found that up to about 40% of the oxidized metal was dissolved, under the influence of the field, into the solution. Bernard[18] agreed that both anions and cations are mobile, and that metal ion transport predominates. It is now understood that the cation transport number is about 0.4 for film growth at 100% faradaic efficiency[M], but this value falls under conditions of reduced current density and electrolyte pH, where direct ejection of Al^{3+} ions into the electrolyte is possible.[45] As explained later, these conditions include those of porous film formation. It has been confirmed by the direct observation of immobile xenon marker bubbles in the film that both Al^{3+} and O'-/OH- contribute to barrier film formation at the oxide/solution and metal/oxide interfaces respectively.[45]

Amsel and Samuel[42] anodized in an ammonium tartrate solution and subsequently in a similar solution labelled with O^{18}, and found that the order of oxygen in the film was conserved, indicating that its sublattice remains stationary while metal ions move by a mixture of vacancy diffusion and interstitial exchange. Their results do not imply that oxygen does not carry ionic current. In further work by the group at the Université Paris VII,[31] aluminium was anodized at constant current to a preset voltage using citric acid in water either enriched or depleted in O^{18}, and found that at least 98% of the oxygen present in the films formed derived from the water. Thus the principal anodic reaction is:[46]

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-.$$

The Paris workers determined the components of the total current, which were found to be dependent on surface preparation of the aluminium. The electronic current constituted up to 5% of the total, although may reach 90% under conditions of current decay at constant voltage. The ionic current comprised an oxidation current and an electrochemical dissolution current which varied between about 10% and 60% of the total depending on surface preparation and anodizing conditions. This observation confirmed the findings of Davies.[27] The authors concluded that oxygen transfer at the oxide/solution interface, enhanced by field-induced oxygen vacancies, was responsible for the growth of the anodic film.

Francis[47] carried out some elegant experiments to clarify more directly the issue of ionic transport. He anodized in a citrate solution aluminium surfaces with vacancy pits beneath an initially formed oxide film, or with thermally produced oxide crystals beneath the initial film. During anodizing, steps were produced in the newly formed film, demonstrating that both anions and cations contribute to film formation in such electrolytes.

Rectification

It has long been recognized that anodized aluminium has rectifying properties. Anodic polarization gives rise to small currents while cathodic polarization results in large currents. Processes involving alternating current, such as electrolytic colouring, continuously switch between anodic and cathodic polarization. Early workers proposed theories which assumed electronic currents in the oxide and depended on the existence of space charge barriers to explain rectification.[48,49,50] Subsequently, it was suggested that flaws in the anodic film allow inward proton transport and reduction at the metal/oxide interface.[51,52] Recently Takahashi *et al*[53] have presented further evidence showing that rectification only takes place in solution, and is likely to be due to high rates of proton reduction during cathodic polarization. They reported that flaws may not only be due to impurities in the metal surface but can also be derived from the oxide morphology resulting from topographical variations. They proposed a mechanism describing the observed film breakdown and pit formation in a borate/boric acid electrolyte (Fig. 6-8). At low cathodic potentials, proton transport is low and the evolved hydrogen may dissolve in the substrate. When the rate of proton transport is higher than that of hydrogen diffusion, then gas accumulates underneath any oxide film at the flaw site. Subsequently, mechanical stresses can cause breakdown of the film allowing solution ingress and current concentration to propagate the pit.

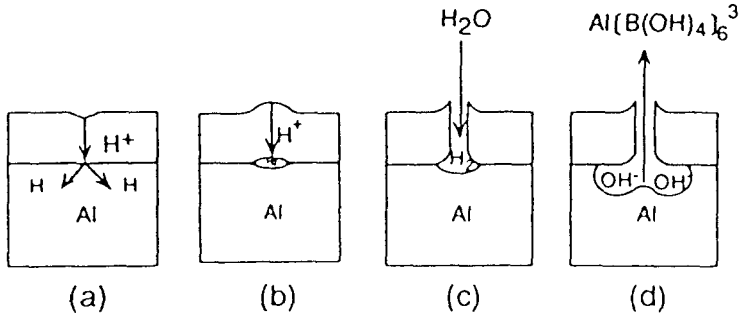


Fig. 6-8. Schematic diagrams showing a mechanism of film breakdown during cathodic polarization: **(a)** at low potentials. and (b) to (d) the sequence of events at high potentials.[53]

Initial film development and pore initiation

It has long been appreciated that anodic films produced on aluminium in acid electrolytes are capable of absorbing dyestuffs. Thus, it was deduced that such films are porous. However, before the advent of the electron microscope, the

nature of this porosity was not at all clear. Consequently, it was also difficult to understand how and why the pores developed. These are important questions in understanding porous anodic films, and, as will become clear, have a significant impact on the effective operation of commercial processes including product quality.

Early work

Setoh and Miyata[54] proposed that the barrier layer is more or less porous, the pores arising from attack by the electrolyte anions. Nascent oxygen is occluded in these pores and is responsible for further barrier layer formation by reaction with the aluminium. Rummell[32] suggested that the barrier layer is holed through by the current with the formation of pores; a new layer then begins to form underneath the porous film. Baumann[55] postulated that a vapour film exists at the base of the pores, and that oxygen ions are produced at the gas/electrolyte interface, which produce oxide kernels. Pores were said to form by breaks through the barrier layer due to atomization of the material in the pores. Schenk[4] envisaged that pore formation is the result of breakdown promoted by the anions. Murphy and Michelson[56] simply ascribed the formation of pores to the drying out of the rather gelatinous film material.

Keller, Hunter and Robinson' extended the Baumann theory and proposed that pore propagation is due to dissolution of the barrier layer promoted by Joule (resistive) heating. There was considerable debate whether the temperature at the base of the pores could become sufficiently high to account for the pore propagation (film growth) rates observed.[7,57] Hunter and Towner[7] pointed out that anodizing in sulphuric acid produces a growth rate of about 0.4 μm/min, while open-circuit dissolution in the same electrolyte only proceeds at 0.084 nm/min. 50% sulphuric acid at 125°C would be required at the base of the pores to give the required 'growth rate' during open-circuit dissolution. Kaden[58] showed that this concept is untenable. He deduced from calculations that the temperature at the film growth site is nearly equal to the bulk solution temperature.

Hoar and Yahalom[59] considered the anodizing current/time curve to represent two overlapping processes, the exponential decrease in the current producing barrier film and the pore formation current (Fig. 6-9). They assumed that proton entry into the barrier layer produces a hydrated oxide which is more susceptible to pore formation. However, this process is checked by the outward migration of Al^{3+} ions which form a positive ionic space charge.

Concepts involving hot acid at the pore bases or local field-inhibited, proton-induced dissolution were rejected in favour of field-assisted dissolution.[34,60] Since Al_2O_3 is mainly ionic in nature, its dissolution involves breaking Al-O bonds in the lattice. Thus, any process which weakens these bonds eases the dissolution process at kink sites by lowering the effective activation energy for dissolution. The presence of the electric field was considered important in this respect as it tends to pull O^{2-} ions into the oxide and push Al^{3+} ions into solution, which may be solvated by H_3O^+ ions and water respectively (Fig. 6-10).

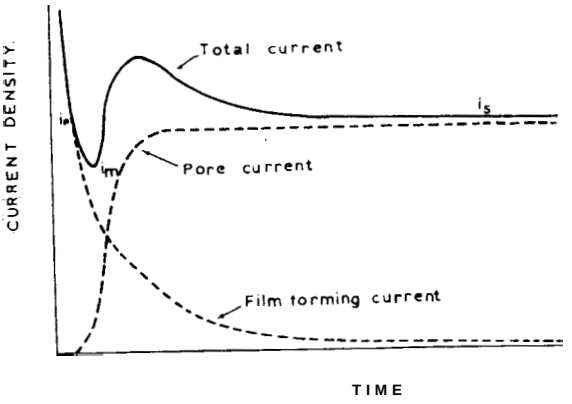


Fig. 6-9. Schematic illustrations showing the concurrent processes contributing to the total current during anodizing at a constant voltage to produce a porous film.[59]

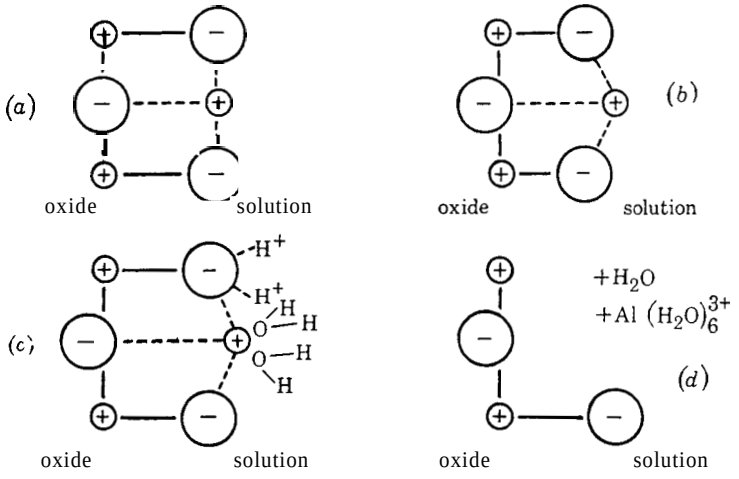


Fig. 6-10. Schematic representation of the field-assisted dissolution of Al_2O_3 (a) before polarization, (b) after polarization, (c) removal of Al^{3+} and O^{2-} ions, and (d) the remaining oxide.[60]

Ionic currents

Based on experiments using O^{18} tracer techniques, Siejka and Ortega[61] found that pore formation does not take place through a simple oxide dissolution process whether chemical or field-assisted. They identified three types of ionic current

during anodizing in sulphuric acid: I_{ox}, $I_{„}$ and I_{dec}. I_{ox} is due to the current of oxygen anions to the metal/oxide interface where new oxide is formed, the value of which is numerically equal to the current efficiency of porous oxide formation. $I_{„}$ is due to the movement of cations passing through the barrier layer directly into solution. I_{dec} is due to the movement of ions generated by field-assisted dissolution, cations (I_c) into solution and anions towards the metal/oxide interface. The total current of cations passing into solution, $I_{dis} = I_{„} + I_c$ (Fig. 6-11). These authors deduced that $I_{„}$ is due to interstitial or interstitialcy mechanisms or as $(AlO)^+$, and although the ions are ejected directly into the solution during porous anodizing, they contribute to film formation at the oxide/solution interface during barrier-type anodizing. The existence of I_c implies regions of oxide susceptible to dissolution. Two models were proposed. If it is assumed that there is a high concentration of oxygen vacancies at the oxide/solution interface, then field-assisted dissolution is a process, the rate of which is determined by the equilibrium between cation transfer into solution and the reaction between oxygen and vacancies at the oxide/solution interface (Fig. 6-12). The second proposed model is a variant of the Hoar and Mott mechanism,[34] except that mobile OH- ions decompose to O^{2-} ions which migrate by vacancy motion to the metal/oxide interface (Fig. 6-13).

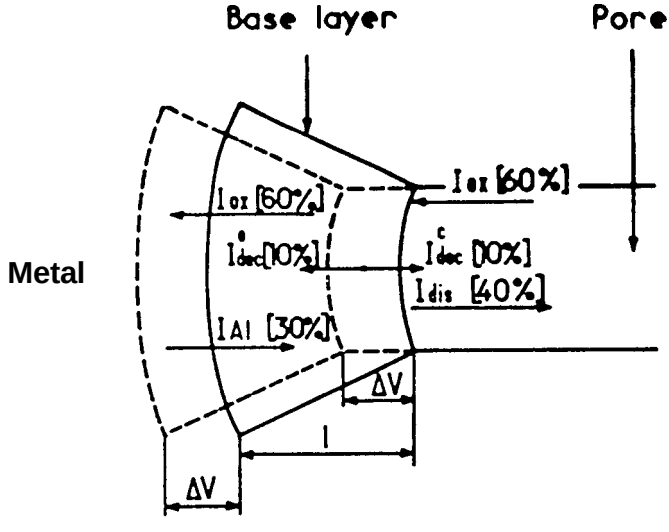


Fig. 6-11. Components of the current expressed as a percentage of the total ionic current flowing through the oxide during anodic oxidation at steady-state conditions; see text for definitions. l and **AV** are the thicknesses of the base layer and the decomposed oxide respectively."'

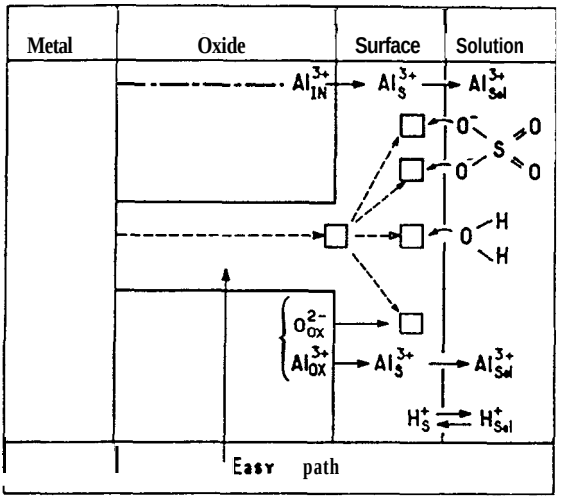


Fig. 6-12. Schematic representation of processes taking place on the surface and in the volume of the base layer during porous film formation. It is assumed that oxygen movement takes place through the base layer via "easy paths", and that aluminium cation movement involves an interstitial or interstitialcy mechanism (Al_{IN}^{3+}). □ is an oxygen vacancy.[61]

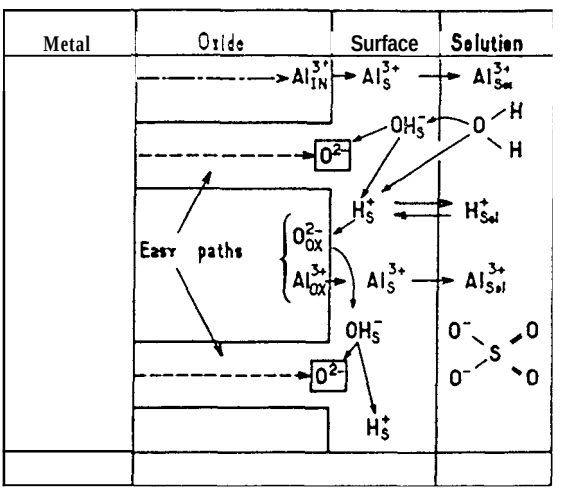


Fig. 6-13. Schematic representation of processes taking place on the surface and in the volume of the base layer during porous film formation. It is assumed that oxygen movement takes place through the base layer via "easy paths", and that aluminium cation movement involves an interstitial or interstitialcy mechanism (Al_{IN}^{3+}). H_S^+ and OH_S^- indicate protons and hydroxyl anions respectively adsorbed on the surface of the base layer. $\boxed{O^{2-}}$ is an oxygen ion just after reaction with a vacancy.[61]

Thompson and coworkers[62] have proposed that the hydrated aluminium ions arising at the oxide/solution interface in high concentrations from direct ejection and dissolution, may deprotonate and aggregate with acid anion species. These may produce negatively-charged colloidal particles, held in solution due to the influence of the incorporated acid anion, which are deposited under the field to produce the anion-incorporated anodic film material as described in more detail below. Effective compaction of this layer may occur by further deprotonation of the impure hydrated alumina by reaction with some of the Al^{3+} ions ejected from the inner layer of relatively pure alumina. This view has been supported by Cabot *et al.*[63]

Pore initiation

Since the work of O'Sullivan and Wood[60] and their detailed measurements and pictorial evidence of the early stages of pore initiation and growth, Thompson, Wood and colleagues at UMIST have extended the knowledge of pore formation a great deal further. This work is well summarised elsewhere.[64]

The ability to understand the early stages of anodizing has been greatly helped by new techniques of film examination, particularly film stripping techniques and ultramicrotomy. Stripping the intact anodic film from the aluminium allows direct transmission electron microscope examination of the very thin films formed in the first few seconds of anodizing. Ultramicrotomy, on the other hand, is a technique that was developed for use in the biological sciences, and allows very thin slices of material to be cut with a diamond knife, which can be used for direct examination of film cross-sections in a transmission electron microscope. In recent years, this technique has been extensively used at UMIST and elsewhere. The benefit of direct examination of anodic films rather than carbon replicas as used previously, is obvious.

Such electronoptical studies have been carried out on films produced in all the major anodizing acids: sulphuric acid,[65] oxalic acid,[66] phosphoric acid[67] and chromic acid.[''] In each case the changes occurring during film growth appear to be similar and, because of the relatively large features involved, they are most easily illustrated with films produced in a phosphoric acid electrolyte at high voltage.

Transmission electron micrographs of stripped films, formed for various times at a current density of 0.5 A/dm^2 in 0.4 mol/l phosphoric acid, are shown in Fig. 6-14.[67] Thompson and Wood, in their description of the film growth,[64] say the following:

'After 15s the film appears relatively structureless, although a developing texture ***of*** similar dimensions and population density to the electropolished structure of the original aluminium substrate can be discerned (Fig. 6-14a & b respectively). Black dots, up to 6nm diameter, representing regions of locally thicker film material and/or different composition, are evident at the

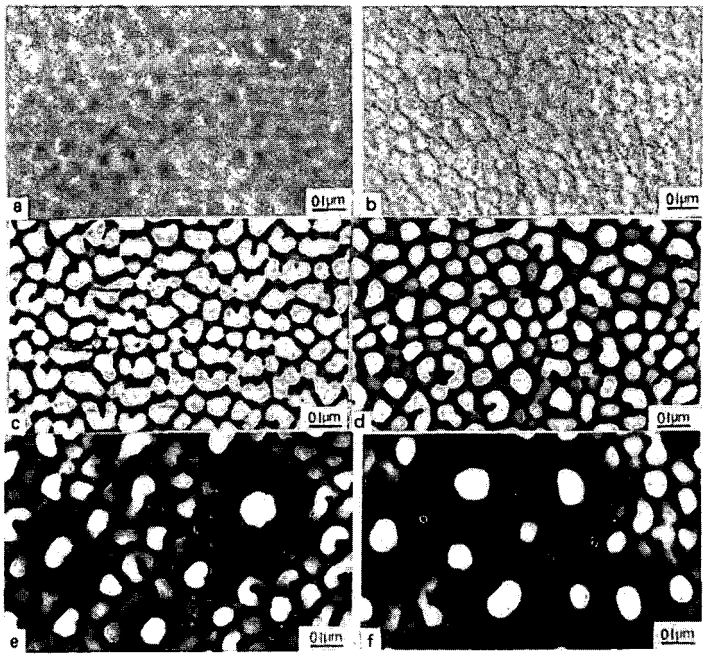


Fig. 6-14. Transmission electron micrographs of stripped anodic films formed on aluminium at 50A/m^2 in 0.4mol/l phosphoric acid at 298K for various times: (a) carbon replica of the electropolished substrate; (b) 15s; (c) 60s: (d) 90s: (e) 120s; (f) 180s.[67]

boundaries between the cellular texture inherent from the electropolished metal substrate, but now separated from the metal by the thickening barrier layer. With further anodizing up to 60s, a general trend of non-uniform film growth is observed (Fig. 6-14c); the locally thicker film material develops preferentially above the growing barrier layer and merges to produce an approximately hexagonal or banded arrangement, which, again, is related to the original electropolishing texture developed on specific aluminium grain orientations. After 90s, it seems that the preferential growth of locally thicker film material has ceased and the locally thinner film between it shows various changes in contrast, depicting regions of differing thickness (Fig. 6-14d) which represent the early stages of pore development. Major pore development is evident after 120s, a time well before the voltage maximum, and the pores are detected by the darker, approximately circular, regions surrounding them (Fig. 6-14e), which represent regions of thickening cell material which are scalloped at the metal/film interface and with the pores at their centres. The extent of the darker regions varies, indicating that some major pores had developed earlier than others and the corresponding diameters grown to larger dimensions. The pores develop within preferred regions of thinner film, which are not always completely surrounded by the

thicker film material, and the pore mouths appear to take the shape of the maze-like thinner film. Occasional star-shaped pore mouths reminiscent of the Keller et al. model[9] for the pore sections are evident, in addition to the more frequently observed oval and circular pore mouths. With further anodizing, the major pore population density increases further until the steady-state true pore morphology of reduced population density develops and remains approximately constant throughout steady-state anodizing (Fig. 6-14f). In order to reduce the pore population density, certain incipient pores do not continue to develop, but are present at the outer surface of the film until partially removed by continued chemical dissolution of the surrounding film material at the film/solution interface.'

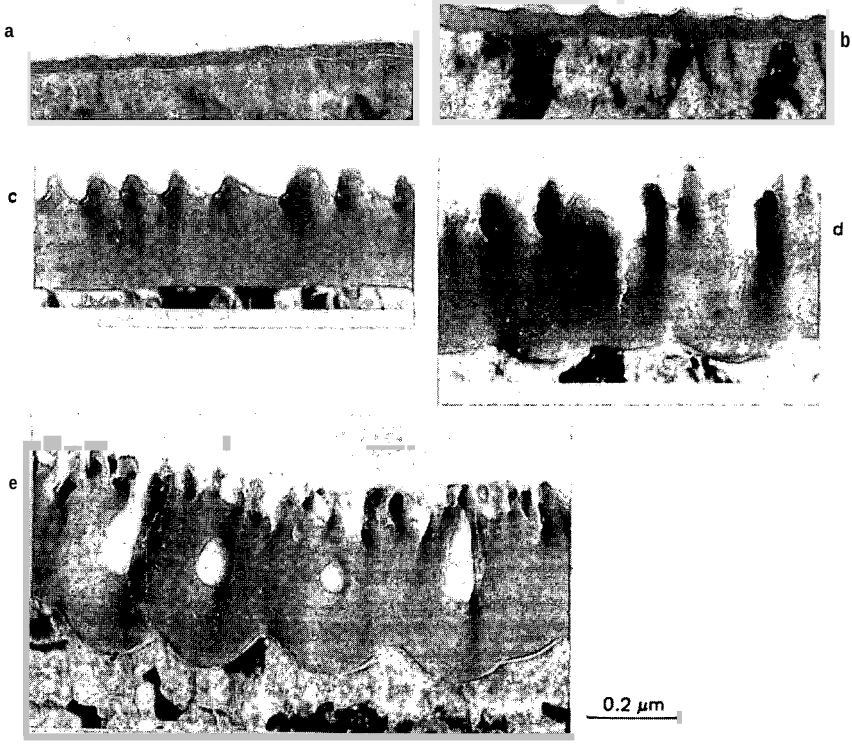


Fig. 6-15. Transmission electron micrographs of ultrainicrotomed sections of the aluminium substrate and the anodic film formed at 50 A/m^2 in 0.4mol/l phosphoric acid at 298K for various times: **(a)** 10s; (b) 40s; (c) 90s; (d) 120s; (e) 160s.[64]

Cross-sections of films of this type examined in the electron microscope show the non-uniform pattern of film growth, and complement the surface examination just described. Again the work is that of Thompson and Wood[64] and is illustrated in Fig. 6-15. In their description of these films, again formed at 0.5 A/dm^2 in 0.4mol/l phosphoric acid, they say:

'After 10s, the pre-existing film thickens relatively uniformly above the finely spaced scalloped electropolished substrate (Fig. 6-15a). With further anodizing, this film thickens, together with the development of locally thicker film at the outer surface (Fig. 6-15b). The separation of the protuberances corresponds to the textured appearances of the electropolished substrate, and they appear to develop above pre-existing metal ridges. This observation is confirmed by the further development of the protuberances, which corresponds with a flattening of the metal/film interface (Fig. 6-15c). The regions of thinner film between the protuberances appear similar to pores but they are not the conventional pores, because none is growing at this stage of film formation. After 120s, further thickening of the barrier layer and protuberances is evident and the development of the major pores can be seen directly, or detected by the relatively pronounced scalloping, which develops at the metal/film interface beneath the major pore (Fig. 6-15d). The spherical scalloped regions are observed to increase in effective diameter, as does the diameter of the pores, until they merge with other scalloped regions and the relatively regular morphology of the steady-state porous anodic film is created (Fig. 6-15e).'

In order to obtain more information on the effect of metal topography on initial porous film formation, workers have deliberately introduced surfaces of controlled cellular structure, often produced by forming a conventional porous film and then removing it by dissolution in chromic/phosphoric acid.[62] This treatment leaves a scalloped topography of controlled dimensions, and phosphoric acid anodizing of such a substrate leads to the cell pattern and oxide structure shown in Fig. 6-16. During subsequent anodizing, initial uniform film thickening is apparent in Fig. 6-16a followed by local thickening of the film material above the metal ridges (Fig. 6-16b). In other cases etched,[69] mechanically polished[65] or deliberately scratched substrates[70] have been used, and similar effects have been observed in the pitted or scratched regions.

Other observations have been reported more recently." The metal/film interface of ultramicrotomed sections has revealed occasional local regions at the top of the metal ridges where crack/heal events appeared to have taken place (Fig. 6-17). Above such regions, protuberances appeared to have been distorted, possibly by the rapid healing of the cracks at the high local current density and, perhaps, with local temperature rises. Further examination also revealed shallow depressions above the metal ridges, perhaps related to cracking. The mechanisms associated with the development of protuberances or local thickening over metal ridges are described in the next section.

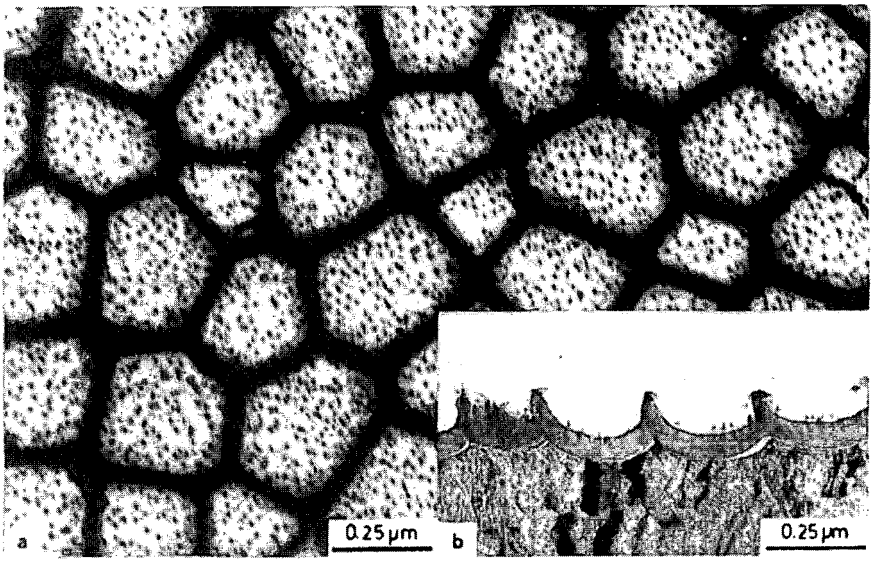


Fig. 6-16. Transmission electron micrograph of the film formed on the preconditioned aluminium substrate at 50A/m^2 in 0.4mol/l phosphoric acid at 298K for 60s: (a) stripped film; (b) ultramicrotomed section.[62]

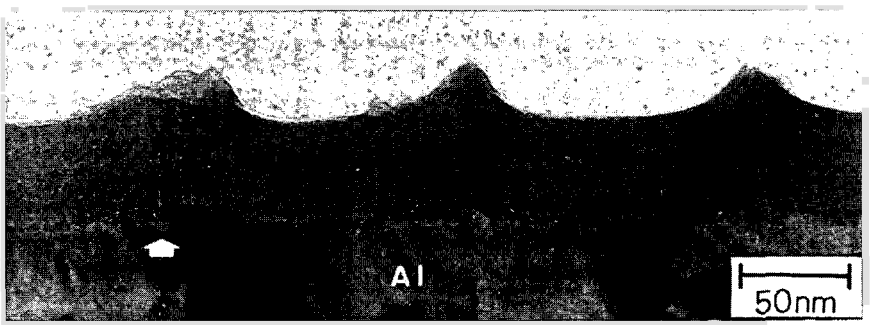


Fig. 6-17. Transmission electron micrograph of an ultramicrotomed section of an aluminium substrate and its anodic film formed to 50V showing local thickening of the oxide at the metal ridges.[71]

During porous anodizing at constant current, the voltage rises linearly associated with the thickening of the barrier layer, then may achieve a maximum and minimum before attaining the steady-state value. The deviation from linear voltage rise is associated with pore initiation. Cabot and Pérez[72] studied the voltage/current relationships obtained during galvanostatic porous anodizing in propanedioic acid. They followed Palibroda[16] and proposed a relationship between current and voltage at the voltage maximum, and suggested an electrolyte-dependent critical voltage corresponding to the breakdown voltage. This was interpreted to indicate the presence of flaws in the barrier layer, which increase in number with increasing current density, and are determined by the influence of the electrolyte on growth efficiency and film composition.

Anodic film thickness depends on the orientation of the aluminum substrate,[73] where the maximum thickness is achieved on (111) planes and the minimum on (100).[74] Following previous work[75] Ueda and coworkers[76] have reported that the direction of the cellular structure of anodic films is perpendicular above (100) and (111) planes but tilted above (110) planes, therefore affecting surface topography. These effects may only be detected for thin films grown under specially controlled conditions, and for thick films, they are unlikely to be significant.

Non-uniform current distribution

There is a non-uniform current distribution during initial film growth and pore development, with initial current concentration at the thickening regions, but eventual concentration at the thin areas where the steady-state pores finally develop. An explanation has been given by Shimizu and coworkers[71] and is described below.

The non-uniform thickening in the initial barrier oxide is one of the most distinctive differences between porous and barrier-type oxide growth on aluminium. Typical barrier-type films, formed on aluminium in neutral electrolytes, are of uniform thickness, and their thickening leads to a flattening of the metal/oxide and oxide/solution interfaces. Conversely, during anodizing of aluminium at constant current density in acid electrolytes, the initial barrier oxide growth is always accompanied by the emergence of locally thicker oxide regions above the network of pre-existing metal ridges as described in the previous section. Furthermore, the local thickening of the oxide becomes more and more pronounced as the forming voltage rises, until barrier film growth is overtaken by the development of major pores.

Whereas true barrier-type films grow at a current efficiency of about 100%, the efficiency may be considerably less than 100% during the initial barrier oxide development, at constant current density, in acid electrolytes. Assuming the densities of aluminium and anodic alumina are 2.7 and 3.0g/

cm^3 respectively, then the Pilling-Bedworth ratio for anodic oxide growth is 1.7 at 100% efficiency. Where the Pilling-Bedwoth ratio falls below 1.0, as may be the case during anodizing in an acid solution, then the volume of oxide formed is less than the volume of metal consumed. This means that the planarity of the oxide surface becomes unstable with respect to perturbations, and the barrier oxide thickens under tensile stress.

During anodizing in 0.4mol/l phosphoric acid at 298K applying 5mA/cm^2, the efficiency during barrier oxide thickening is 53.5% giving a Pilling-Bedworth ration of 0.91. The inward migration of O^{2-} ions fills the volume of metal consumed, but the outward migrating Al^{3+} ions do not contribute to growth at the metal/oxide interface but pass directly into the solution. As the barrier layer thickness must be maintained proportional to the anodizing voltage, it grows under increasing tensile stress, which eventually causes local cracking of the oxide. Local cracking is most expected at the pre-existing metal ridges where greater stress accumulation in the growing oxide is anticipated. The consequent rapid healing of the cracks at high local current density and, possibly, with local temperature rises, leads to the formation of thicker oxide regions, or protuberances, above the metal ridges (Fig. 6-18). Local thickening may also be associated with ridges due to mechanical damage of the substrate such as may be produced by mechanical polishing.

During anodizing in 0.05mol/l phosphoric acid at 298K applying 5mA/cm^2, the current efficiency is 74.1% with a Pilling-Bedworth ratio of 1.25. No non-uniform thickening of the barrier oxide has been observed.

The local thickening of the oxide above the ridges causes a redistribution and concentration of the current into the residual thin areas between the protuberances. The local film surfaces in these thin areas now exhibit distorted, semi-spherical curvatures of varying radii. As the forming voltage rises and the barrier layer thickens, the protuberances also become wider and thicker, due to the persistent film-cracking/healing events in these local regions. The thickening and widening of the protuberances, causes a continuous increase in the curvature of the local film surfaces between the protuberances, which, in turn, results in a continuous increase in the field there. Eventually, the field at the local film surfaces between the protuberances reaches a level at which the rate of thinning (or dissolution) of the oxide by the increased field-assisted dissolution becomes equal to the rate of thickening of the oxide at the metal/oxide interface, via inward migration of O^{2-} ions. The condition for the development of the major pores is now established. Development of the major pores starts earlier, or at lower forming voltages, at the local thin areas where the curvature of the film surfaces between the protuberances is greater. Since the local thin areas of favourable geometries for pore development are distributed randomly over the surface, a random nucleation of the major pores is expected and has been observed experimentally.

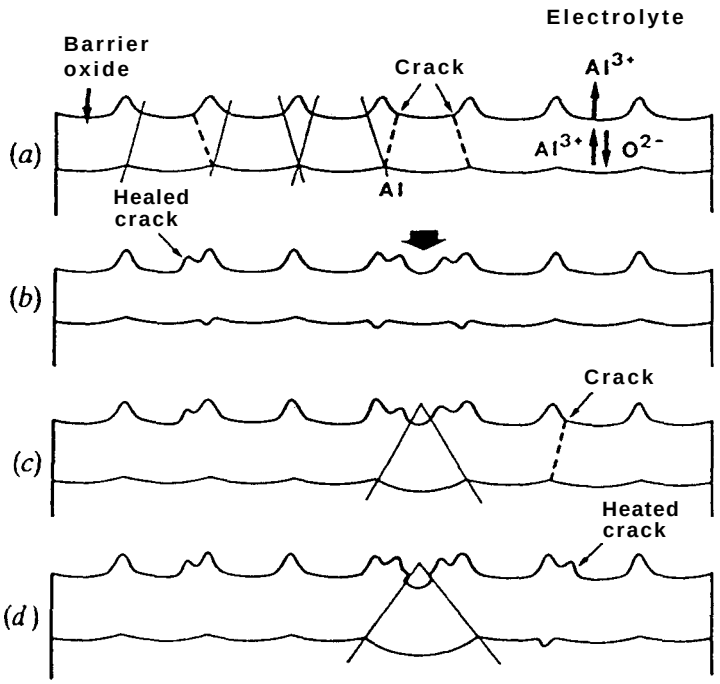


Fig. 6-18. Schematic diagrams revealing the non-uniform thickening of the barrier oxide and eventual development of major pores. Through the development of tensile stresses, cracks in the barrier oxide develop in the regions associated with pre-existing ridges at the metallfilm interface. Current concentration results in the development of protuberances of locally thicker film at the filmlelectrolyte interface. Eventually current concentrates in the local thinner regions of the film defined by the straight lines on either side of the protuberances.[71]

As the forming voltage rises further and the number of developing major pores increases, the initial barrier oxide growth is gradually overtaken by major pore growth. The forming voltage still continues to rise, but at progressively slower rates, and eventually achieves a maximum when the specimen surface is covered by major pores. Then, due to geometrical constraints between the growing major pores, the pores are forced to rearrange into a new, but slightly modified distribution, so that all the surviving major pores are allowed to grow

into the metal. This is accomplished by a reduction in cell and pore diameters which are directly proportional to the forming voltage. Thus, during this rearrangement, the forming voltage gradually decreases with time until the steady-state voltage is attained. The steady-state porous oxide growth continues thereafter, resulting in the growth of the porous oxide film with a regular morphology of characteristic major pores, passing normally to the macroscopic aluminium substrate, but separated from it by the barrier oxide layer of scalloped appearance (Fig. 6-19).

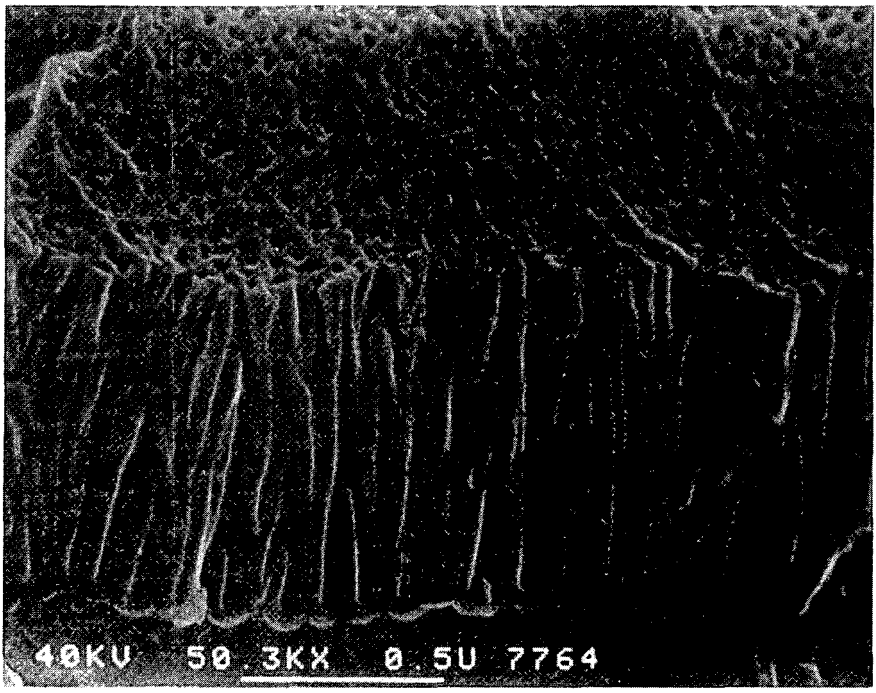


Fig. 6-19. Scanning electron micrograph showing the cross section and surface of an anodic oxide coating.

In order to understand the behaviour observed during pore initiation, the potential distribution has been determined during the stages of initial film growth and development of penetration paths, the precursors to true pores.[45] **A** finite element method of numerical analysis has been adopted to solve the appropriate

mathematical expressions for field distribution.[77] Initially, the field distribution is relatively uniform, but with the development of the penetration paths, although the field lines remain relatively uniformly separated within the compact regions of the film immediately beneath the paths, the potential lines are concentrated, indicating a local increase in field strength. Between the penetration paths there is a weakening of the field. Subsequently, certain paths develop preferentially with a further concentration of the field promoting their activity. The development into pores arises from the strong lateral component of the field beneath the head of the penetration path, resulting in lateral expansion to give an embryo pore, with its characteristic inversely funnelled or pear-drop shape. As ionic current **is** exponentially related to the field, current concentration into the incipient pores takes place.

From mathematical analysis and knowledge of electrostatic pressures at various points within the film material, the electrostriction pressure at those locations may be calculated.[77,78] For positions immediately below the fine penetration paths, values of about 19000kg/cm^2 have been calculated, far in excess of the critical compressive stress of the anodic film (500-1000kg/cm^2). In regions of locally reduced field strength, the electrostriction stress falls to values as low as 21kg/cm^2. Such values and their variation with position within the film were considered to give credence to the bond-breaking mechanism of field assisted dissolution as proposed previously.[34,60]

Recently, Macdonald[79] has offered a different view to account for the apparent non-uniform current distribution that leads to the formation of the porous structure. Previous workers[80,81] have reported the observation of voids in anodic films above the apices of protrusions of the aluminium substrate. Macdonald rejected Ono's concepts that voids could arise from shrinkage due to crystallization of the barrier layer, or may form from oxygen evolution, from tensile stresses in the film, or from electrostriction pressures. He suggested (Fig. 6-20) that voids initiate beneath defective areas of the anodic film, eg at the intersection of grain boundaries, and grow due to the condensation of cation or metal vacancies. The metal/oxide interface recedes during the oxidation process only at regions not in direct contact with a void. Each void tends to become undercut ultimately leading to its detachment from the apex of the protrusion. Subsequently, a new void forms at the apex because the low volume of metal per unit interfacial area has a much lower ability to annihilate or otherwise accommodate vacancies than other regions; the metal at the apex rapidly becomes "saturated" with vacancies. The process then repeats. Macdonald suggested that this process accounts for the hexagonal array of pores. He has not developed his model to account for other features of porous anodic films or their relationship with barrier-type films. At this stage it is probably reasonable to regard voids as a result of porous film formation rather than the cause.

Surganov and coworkers[82] have investigated the rate of aluminium dissolution into a malonic acid electrolyte during the early stages of porous

film formation at constant current density (Fig. 6-21). Point *a* on the potential/time curve relates to pore initiation which proceeds over region II until the steady-state morphology is established. Aluminium dissolution rates of 0.133, 0.020-0.027 and 0.097μg/cm^2.s were found over regions I, II and III respectively. The lowest value, in region II, was attributed to the development and merging of the hemispherical cell bases. The low rates observed during region III were believed to be due to the reduced surface area taking current, reflecting the porosity of the steady-state porous film.

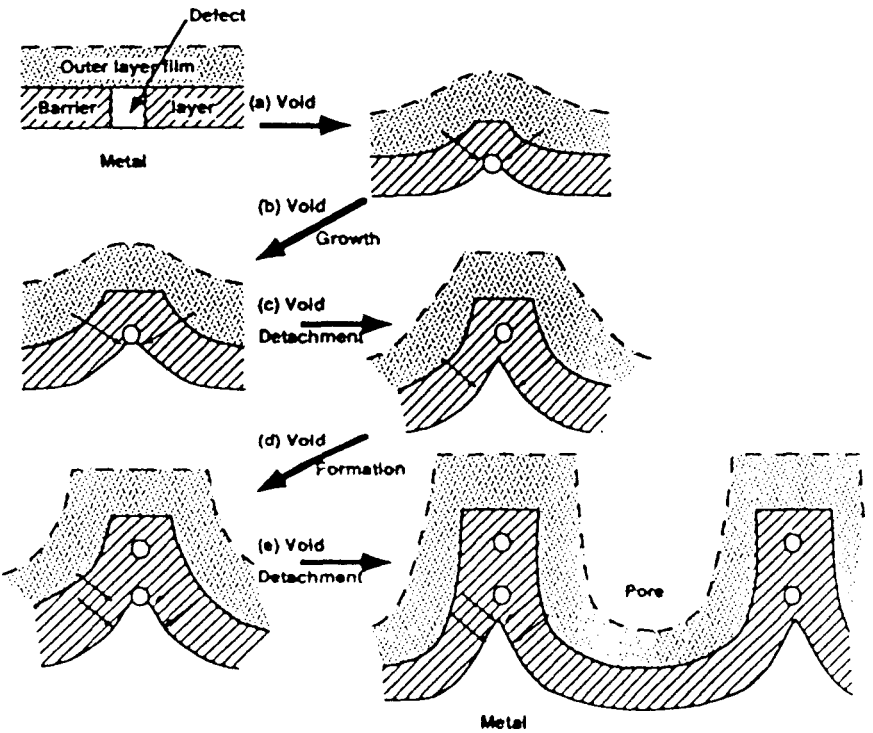


Fig. 6-20. Schematic diagram showing processes proposed for the formation, growth and subsequent detachment of voids in porous anodic films on aluminium. Thin arrows indicate the flow of cation vacancies across the barrier layer."

Jung and Metzger[83] measured the capacitance of films formed in 2.4 mol/l sulphuric acid at very low potentials. They interpreted their results to show that "classical" porous films form at voltages down to $0V_{SCE}$, and "non-classical" porous films form at lower voltages down to $-1.3V_{SCE}$.

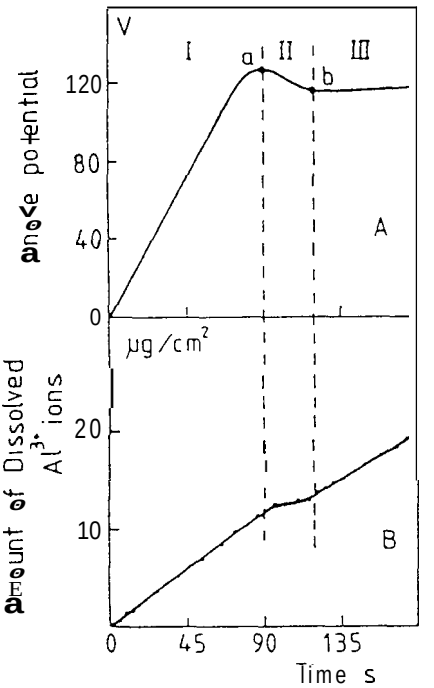


Fig. 6-21. The variation of potential **(A)** and dissolved aluminium ions (B) with time during anodizing in a 0.6mol/l malonic acid solution.[82]

Current efficiency

Often barrier and porous films are regarded as being quite distinct; the former are formed in neutral pH electrolytes while the latter are the result of anodizing in acids. However, a number of workers have shown that porous films can be produced in approximately neutral solutions.[7,84,85] The difference between the two types of electrolyte is one of pore growth rate, this being much slower for neutral solutions.

Xu and coworkers[45] have investigated the transition from barrier-type to porous films. They concluded that during anodizing to form barrier films, Al^{3+} ion egress and O^{2-}/OH^{-} ingress proceed to form film at the film/solution and metal/solution interfaces respectively. This represents growth at 100% efficiency. Efficiency may be calculated using Faraday's Law and the requirement to maintain a constant electric field, E, as the film thickens.[86] Thus,

$$\text{Efficiency} = \frac{6\rho F}{EJM}\cdot\frac{dV}{dt}\times 100,$$

where ρ is the film density, F is the Faraday constant, J is the current density and M is the molecular weight of the film. If it is assumed that the roughness factor of electropolished aluminium is 1.0, the oxide density is 3.0 g/cm^3, and the field in the barrier oxide is 8.47 x 10^6 V/cm,[87] then applying Faraday's Law predicts that at 100% efficiency, the voltage will rise at 149.3 V/min which corresponds well with the value of 147.3 V/min determined empirically[71] by anodizing in 0.05 mol/l ammonium adipate at 298 K, applying 5 mA/cm^2. The barrier thickening stage of anodizing in 0.4 mol/l phosphoric acid at 298 K applying 5 mA/cm^2 gives a rate of voltage rise of 78.8 V/min, on this basis equivalent to 53.5% efficiency, indicating considerable loss of aluminium ions from the onset of anodic oxidation.[76]

Under certain circumstances lower efficiency growth takes place due to direct ejection of Al^{3+} ions into the electrolyte without forming film material. The proportion of ejected Al^{3+} ions compared to film-forming ions, generally increases with decrease in current density such that a critical current density exists below which all mobile Al^{3+} ions are lost to the electrolyte. At current densities below this critical level (Fig 6-22), reactive electrolyte species penetrate the film, representing the initial stages of pore development. This implies that a barrier-type film can be induced to become porous simply by reducing the current density to below the critical level. This is in fact the case, as it is known that when producing a barrier-type film under constant voltage conditions, the film thickens until it achieves the thickness characteristic of the applied voltage. after which the current decays to a low level. During current decay, pores may develop.[43] It was reported that the critical current density for 0.25 mol/l potassium chromate is far below 1 A/m^2, for 0.4 mol/l potassium phosphate **is** between 1 and 10 A/m^2, and for 0.1 mol/l ammonium oxalate is close to 100 A/m^2.

Kato and coworkers[88] have shown that during anodizing in typical barrier-layer forming electrolytes, the interfacial pH falls, attributed to the anodic reaction:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e\text{-},$$

depending on the buffering properties of the solution. They found greater dissolution of the anodic film under lower pH conditions, which was related to lower current efficiency of growth. However, this effect was found to be more marked at higher current densities, contrary to the analysis described above.

Pore filling

Dekker and van Geel[89] developed the so-called "pore-filling process" to obtain information about the morphology of porous anodic films, which was later additionally used to determine transport numbers.[90] The method is based on the observation that if a porous anodic film is reanodized in a barrier film-forming electrolyte, film growth proceeds and includes the production of anodic film material within the pores. Two very thin porous films were produced at different current densities, which achieved different steady-state voltages (Fig. 6-23). When these were reanodized in a borate-based electrolyte at the same constant current, the

voltages increased initially with different slopes and then subsequently with the same slopes (Fig. 6-24). It was stated that the differing slopes reflected the different porosities of the films which thus presented different surface areas to the barrier anodizing. The film with the lower porosity developed barrier layer quicker because the current was distributed over a lower area. The regions where the voltage slopes were similar was because new barrier layer was forming on top of the porous films where the effective surface areas were similar. From a mathematical analysis of their data the authors were able to demonstrate that barrier layer formation occurred at both the metal/oxide interface and at the bottom of the pores, while porous films form only at the metal/oxide interface. They calculated a cation transport number of 0.33 for porous anodizing and 0.24 for barrier anodizing. Porosity depended only on anodizing voltage and decreased with increasing voltage. Pore diameter, cell diameter and barrier layer thickness all varied linearly with the anodizing voltage.

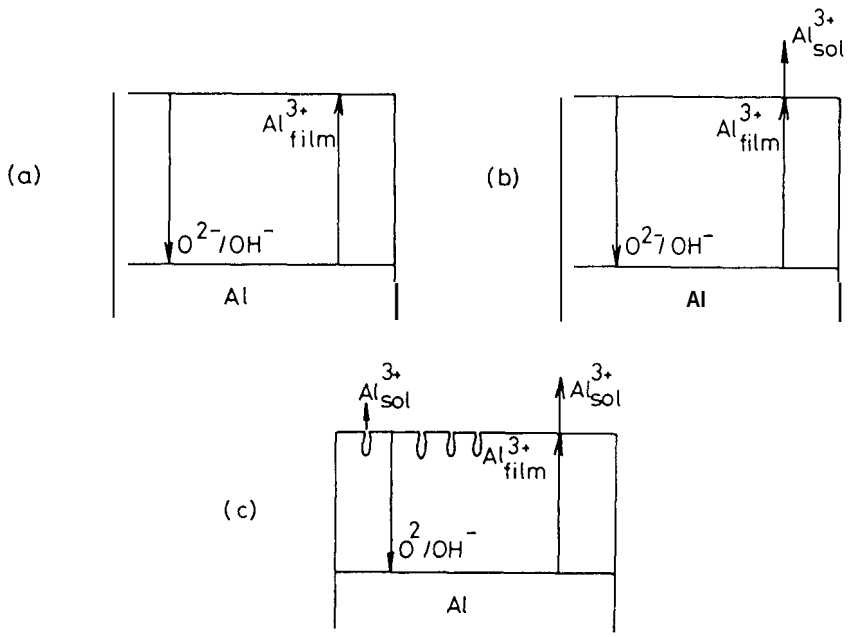


Fig. 6-22. Schematic illustrations of the sections of anodic films, formed at different current densities with respect to the critical current density: (a) relatively high current density, giving a current efficiency of film formation approaching 100%; most of the outwardly moving Al^{3+} ions form solid film at the metal/film interface; (b) applied current density approaching the critical value, most of the outwardly moving Al^{3+} ions are ejected directly into the electrolyte without developing solid film material at the film/electrolyte interface; (c) as (b), but at current densities below the critical value, additional contributions of Al^{3+} ions in the electrolyte are expected as a result of pore development."

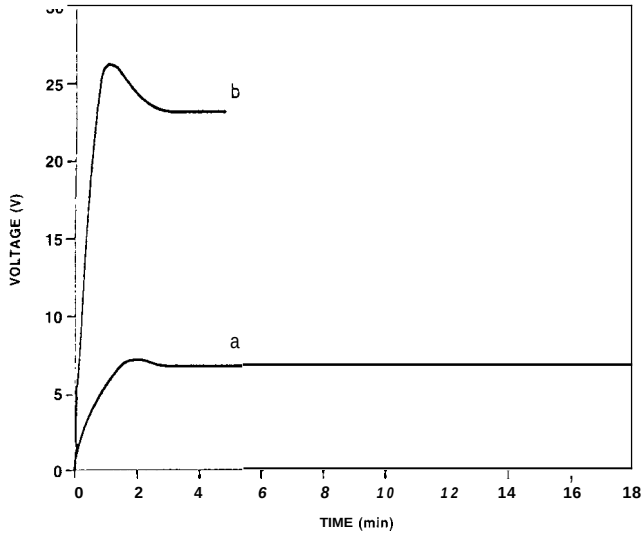


Fig. 6-23. Voltage vs. time during anodizing in 80 g/l oxalic acid at 20°C. Curve (a) corresponds to an over-all current density J_a=0.63 mA/cm^2 for 18 min; curve (b) corresponds to J_b=2.54mA/cm^2 for 4.5 min.[90]

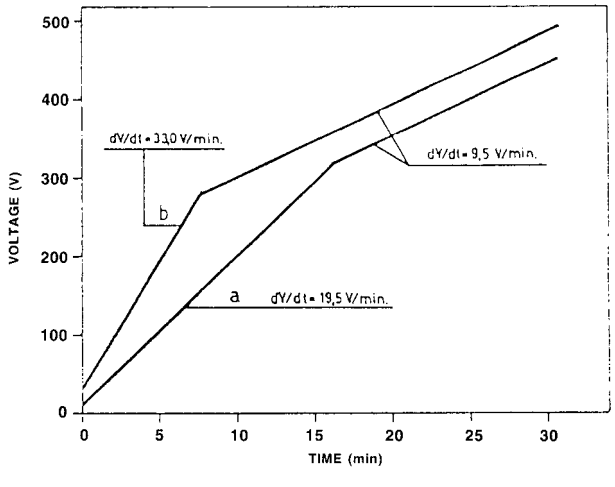


Fig. 6-24. Voltage vs. time during reanodizing in a borate-based solution with 0.38 mA/cm^2 after the oxalic acid anodizing as shown in Fig. 6-23; curves (a) and (b) are for samples anodized with current densities J_a and J_b as given in Fig. 6-23.[90]

Takahashi and Nagayama[91] have also used this method but in a study of anodizing in neutral borate solutions at constant voltage. They found that the current during anodizing in a borate solution decreased exponentially with time to a steady value (the "leakage current"), accompanied by a decrease in efficiency to a value less than 70%. This corresponded to increasing porous character of the outer parts of the film, which was estimated to be 22% for certain conditions used. They were able to demonstrate that the excess current oxidized aluminium that ended up in solution, and that there was almost no electronic current through the oxide to cause oxygen evolution.

The relationship between porosity and anodizing voltage found by Dekker and Takahashi has been confirmed by an analysis of photoluminescence emission spectra.[92] It has also been found that spectroscopic ellipsometry can give quantitative information on barrier layer thickness, porous layer thickness, porosity and interfacial roughness.[93]

The pore filling technique has been used by a number of workers to further the understanding of the morphology of anodic films, and is referred to elsewhere in this chapter.

Porous film morphology

This section covers the steady-state porous structure that arises after pore intitiation when the film has attained thicknesses associated with many commercial products. Consequently, this is the structure subjected to further processing such as colouring, sealing and the deposition of organic coatings. Full understanding of how these further processes may be optimized requires a knowledge of anodic film structure and how it is controlled.

Early work

Anodizing aluminium was first carried out in the laboratory during the 19th century[94] and Ducretet[95] suggested that Al_2O_3 is formed. Norden[96] proposed that the aluminium/film/electrolyte system could be regarded as an electrolytic capacitor, and found that films produced in sulphuric acid contain 13.2% SO,. Fischer[97] produced 300μm thick films in sulphuric acid, which were precursors of hard anodizing technology.

The commercial application of porous anodizing arose from work in the 1920s. Bengough and Stuart[98] patented the chromic anodizing process, and recognized that the porosity was such that the films could take up dyestuffs, while oxalic acid anodizing was patented in Japan.[99,100,101] Later, Setoh and Miyata[102] realized that the properties of porous films could be significantly improved by steam sealing which formed the basis of the Japanese "Alumite" process. Anodizing equipment was installed by VAW (Vereinigte Aluminium Werke) in the mid-1920s using an oxalic acid-based process.[103] The current sulphuric acid

anodizing process originated in Britain due to work by Gower and O'Brien.[104] The use of hard anodizing for engineering applications originated in Russia.[105]

Setoh and Miyata[54] first proposed that porous anodic films have a duplex structure consisting of an inner barrier layer beneath a thicker porous layer. This concept was later accepted,[32,55] and confirmed by Keller, Hunter and Robinson[9] who proposed a model where pores are separated from the aluminium by a barrier layer and are situated at the centres of cloce-packed, approximately hexagonal cells. Murphy and Michelson[56] rejected the concept of discrete pores and suggested instead that the films are composed of oxide microcrystallites surrounded by regions of less ordered material susceptible to hydration, which become progressively more dispersed away from the substrate. This structure could provide the precursors from which pores would develop on drying. The Murphy and Michelson model has not found favour.

The most significant advances in understanding the structure of porous films arose with the advent of the transmission electron microscope,[9,106] particularly the work of Keller, Hunter and Robinson[9] at Alcoa, who were the originators of the main components of the morphological model accepted today. They observed hexagonal cells with a size dependent on the anodizing voltage (Figs 6-25 & 6-26).

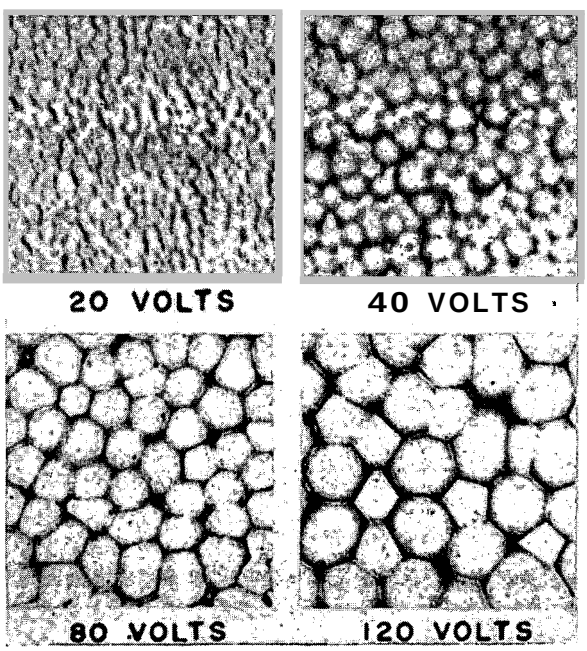


Fig. 6-25. Electron micrographs of oxide film replicas of the cell base patterns produced by anodizing in a 4% phosphoric acid electrolyte showing the increase in cell size with forming voltage (x 35000).[9]

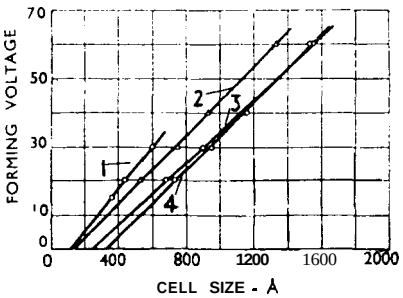


Fig. 6-26. The relationship between cell size and anodizing voltage for different electrolytes:

(1) 15% sulphuric acid at 10°C:
(2) 2% oxalic acid at 25°C;
(3) 3% chromic acid at 50°C;
(4) 4% phosphoric acid at 25°C
($1Å = 10^{-4}\mu m$).[9]

Also, rounded pores were seen in very thin films (Fig. 6-27), but they suggested that in thicker films these changed to give six projections directed at the corners of the hexagonal cells. Their morphological model (Fig. 6-28) included a scalloped barrier layer separating the pores from the metal substrate. As the cell size is proportional to the forming voltage, it was realized that the population density of cells and pores must also be determined by the voltage. Certain aspects of this model were subsequently questioned. Pores are generally rounded rather than star-shaped, and have a size determined by the voltage, but usually modified by the effects of chemical dissolution.

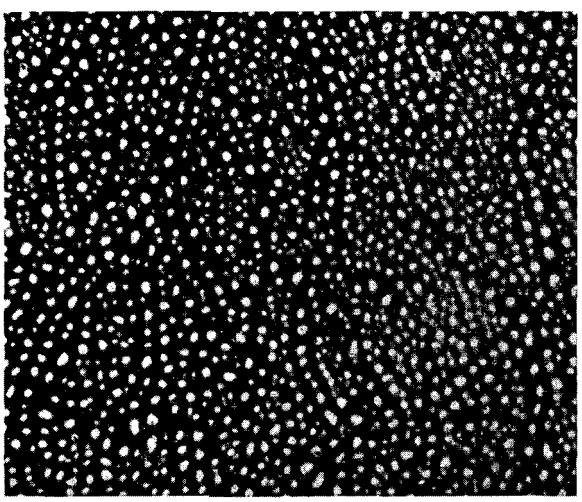


Fig. 6-27. Transmission electron micrograph of an oxide film replica showing the pore structure of a phosphoric acid coating produced at 30V (×35000).[9]

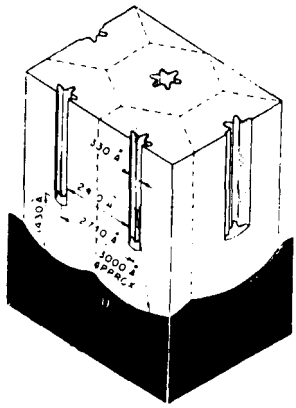


Fig. 6-28. Schematic diagram of the structure and dimensions of an anodic film produced in phosphoric acid at 120V as proposed by Keller, Hunter & Robinson[8] from observations of the cell base pattern (1Å=10^{-4} μm).

Geometrical model

A great deal of speculation concerning the growth and structure of anodic oxide coatings could be resolved if the cross-sections could be observed at very high magnification. Credit must go to the UMIST team for evolving experimental techniques which have portrayed the morphology of the barrier layer and the shape and size of the pores in sharply delineated and unequivocal detail. Their series of photographs completely vindicated for all time the classical (1953) model of film structure, and this must rank as one of the main achievements in the history of anodizing.

The method of Wood, O'Sullivan and Vaszko[107] was to bend the anodized specimen to a V shape to produce a fractured cross-section which tended to follow particular cleavage planes as suggested by Booker and coworkers.[106] After ultrasonic cleaning and drying, a thin layer of carbon was deposited and shadowed by a platinum/carbon mixture deposited at an angle of 60° but in the same vertical plane as the direction of the cracks. The separated replicas covered a complete cross-section including some of the substrate metal at the bottom of the cracks and film surface adjacent to the tops of the cracks. The replicas tended to flatten on drying, facilitating transmission electron microscopy.

Clearly visible in the photographs were the parallel-sided pores, the barrier layer and the often postulated scalloped metal surface (Fig. 6-29). This was assisted by the use of a phosphoric acid electrolyte used at 120V to provide regular cells of large dimensions which are the most readily viewed. These investigators[108] have also used the same techniques to study sulphuric-acid coatings formed under typical commercial conditions.

The cell dimensions measured by Wood and O'Sullivan with phosphoric acid coatings are given in Table 6-1, and their values differ in some respects from those given by Keller and coworkers.[9]

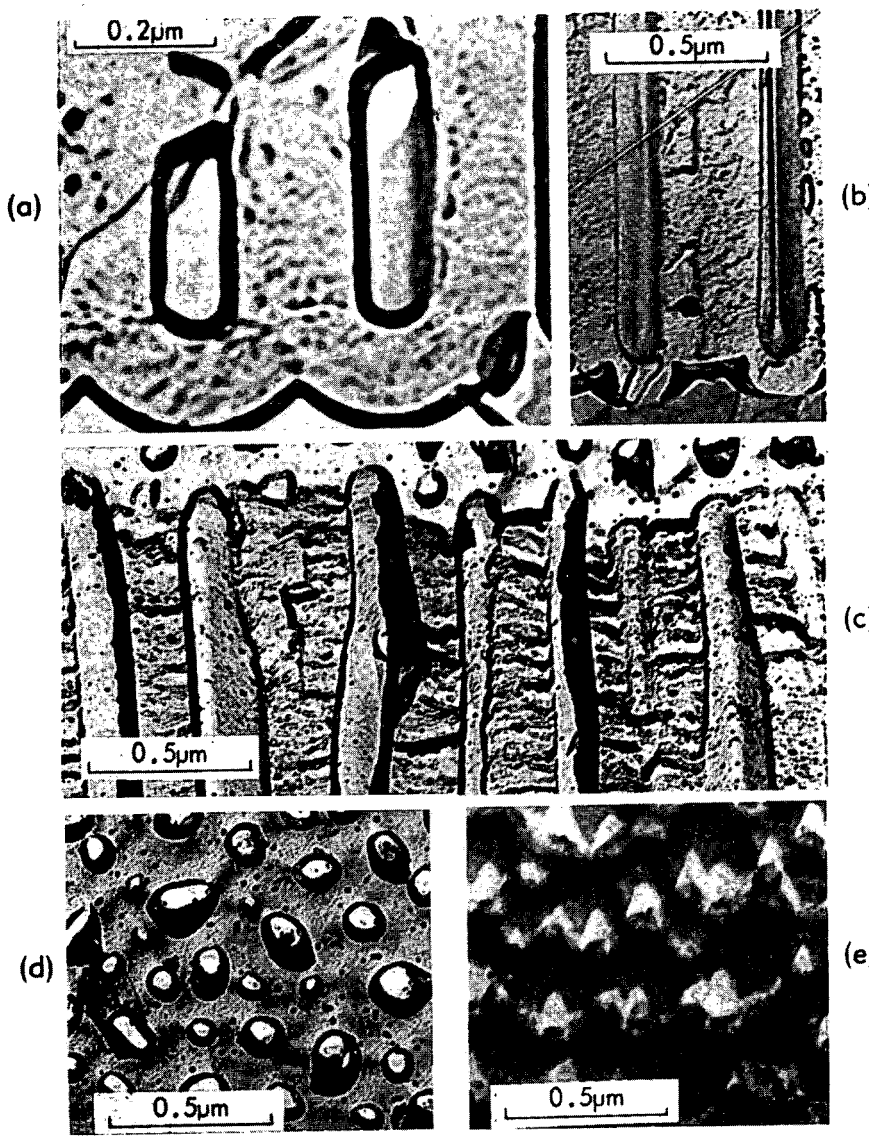


Fig. 6-29. Replica electron micrographs of anodic films formed in phosphoric acid showing general film characteristics: (a) the cross-section near the barrier layer; (b) cross-section with metal attached to the film base; (c) cross-section near the outer surface; (d) the outer surface of the film; (e) the metal surface after the removal of the film. The films were formed at 120V for (a) and (b), 145V for (c) and (d), and 100V for (e).[60]

TABLE 6-1

Cell, pore and barrier layer dimensions in anodic oxide films[107]

Voltage	*Acid concn.* (% *w/v*)	*Barrier thickness* (Å)	*Ratio* (Å/V)	*Cell size* (Å)	*Calculated pore diam.* (Å)
87	4	860	9.9	2360	640
103	4	990	9.6	2800	820
117.5	4	1270	10.8	3330	790
87	15	860	9.9	2400	630
87	25	840	9.7	2250	510

The size and irregularity of the pores increased as the outer surface was approached. Cells became more fibrous in appearance and pores occasionally merged, divided or ceased to function. Replicas from the outer film surface gave pore diameters of 60-140 nm for 4% acid, while pores merged for 15% acid, and an extremely rough surface with cavities was apparent for 25% acid, which was indicative of pore widening and eventual gross dissolution.

The typical cell dimensions given by Wood and O'Sullivan for a film formed at 100V in phosphoric acid are shown in Fig. 6-30. The relationships which they calculated are:

Barrier layer, d	1.04nm/V
Cell diameter, c	2.77nm/V
Cell wall	0.71 d
Pore diameter, **p**	1.29nm/V (p=c-2x0.71d)

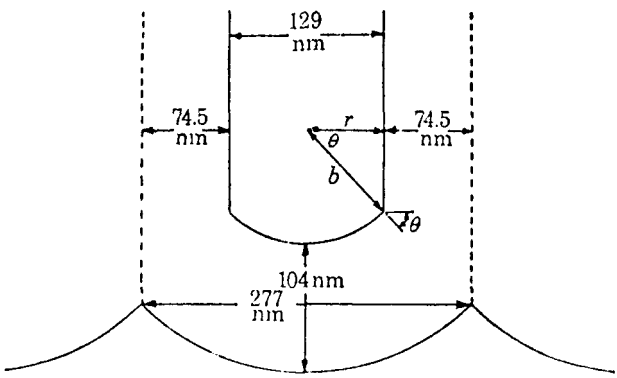


Fig. 6-30. Schematic diagram of the barrier layer, pore and oxide cell of **a** film formed at 100V. r = pore radius; b = radius of curvature of the pore base; $\theta = \cos^{-1} r/b = \cos^{-1}$ (cell wall thickness)/(barrier layer thickness).[60]

The replicas prepared from coatings formed in sulphuric acid are less well resolved. Wood and O'Sullivan[108] were able to carry out some measurements on samples anodized in 1.5 mol/l acid by using transmission electron micrographs. The values obtained are given in Tables 6-2 and 6-3. They found that the pore diameters on the outer surface of the film were not of a fixed value but covered a range, which increased in its spread as the time of anodizing increased. By measuring 400 pores on each of a number of samples they were able to prepare the histogram data shown in Fig. 6-31, and these values are in general agreement with similar findings published by Zavilov *et al.*[109] By considering the peak value in these curves to represent the true pore diameter, this can now be compared with the formation voltage as in Table 6-4 where it is seen that the pore diameter is proportional to the formation voltage. This is in contrast to previous theories and in complete agreement with the behaviour for phosphoric acid anodizing.

TABLE 6-2

Forming voltage, film thickness and pore diameter as a function of temperature for anodizing for 57 min at 25 mA/cm² in 1.5M H_2SO_4[108]

		Pore diameters from surface replicas	
Temperature (°C)	*Voltage (V)*	*Film thickness (μm)*	*Pore diameter (Å)*
0	23	53.6	I70
20	I8	50.1	245
27	15	45.0	300
31	14	39.2	–
35	13	26.6	–

TABLE 6-3

Variation of forming voltage and pore diameter with acid concentration (measurements from transmission electron micrographs). Anodizing at 10 mA/cm² and 20°C[108]

Solution concentration (M)	*Solution pH*	*Forming voltage (V)*	*Pore diameter (Å)*	*Pore diameter/ forming voltage (Å/V)*
0.5	0.3	23.5	230	9.8
1.0	0.06	19.0	180	9.5
I.5	–0.I5	14.3	145	10.1

TABLE 6-4

Pore and cell diameters and pore population as a function of forming voltage (measurements from transmission electron micrographs). Standard anodizing conditions'[108]

Current density (mA/cm²)	*Cell voltage* (V)	*Pore diameter* (Å)	*Pore-diameter/forming voltage* (Å/V)	*Pore population* (number/cm²)	*Cell diameter* (Å)	*Cell diameter/forming voltage* (Å/V)
10	14.5	145	10.1	81.3×10^9	400	28.0
25	17.8	160	9.0	61.1×10^9	460	25.9
50	19.6	180	9.2	45.2×10^9	535	21.3
80	23.5	215	9.1	41.7×10^9	585	24.9

Thus, Wood and O'Sullivan have found that the pores grow so that their diameter remains proportional to the applied voltage as the steady state is approached. The steady state barrier-layer thickness, cell diameter and pore diameter are all directly proportional to the formation voltage. The barrier layer thickness, and behaviour at the pore bases are decided principally by an equilibrium set **up** between the oxide growth in the barrier layer and field assisted dissolution at the pore bases. The dissolution may be accelerated by local heating effects.

Bailey and Wood[110] extended this work by undertaking a detailed study of the morphology of films formed in oxalic acid, which confirmed the geometrical model of steady-state porous films. Morphological parameters from transmission electron micrographs are shown in Table 6-5. They found that during anodizing in oxalic acid at constant current, the voltage exhibits secondary and tertiary rises after extended anodizing times (Fig. 6-32), and that pore (Fig. 6-33) and cell parameters follow these changes. Thus, anodizing at 50 mA/cm² to 500V in 1.0 mol/l acid produced a barrier layer about 0.47 μm thick, a cell size of 0.88 μm with associated pores about 0.3 μm in diameter. Later work investigating the reasons for the secondary voltage rise was carried out by Tu *et al*[111] who ascribed the phenomenon to electrolyte depletion as the film thickens rapidly under high current density conditions. Ueda and Koizumi[112] have found that "hard" anodizing in a sulphuric/oxalic acid electrolyte for long times also shows a secondary voltage rise which was associated with the formation of a layer of abnormally low hardness adjacent to the substrate.

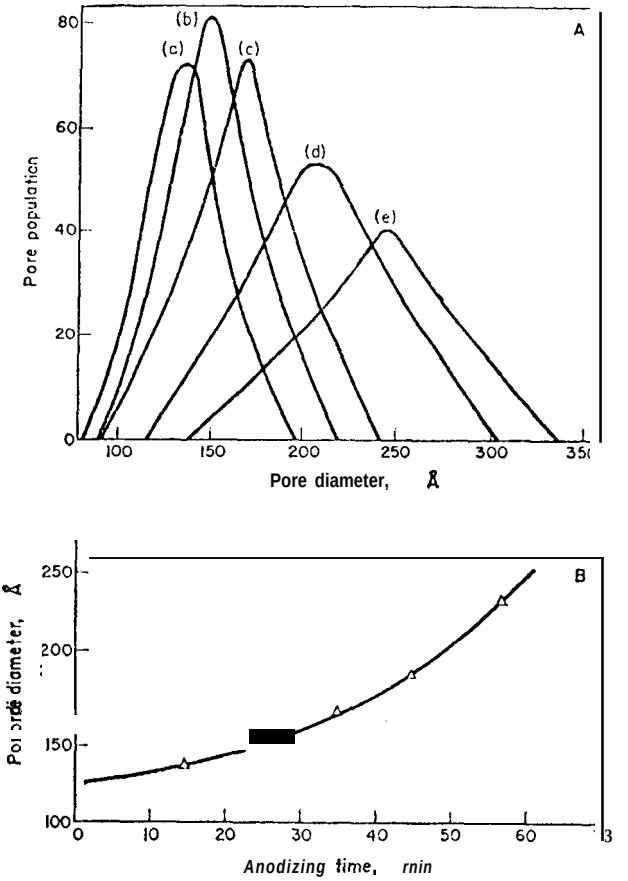


Fig. 6-31. (A) Distribution of pore diameters after anodizing times of (a) 15 min; (b) 25 min; (c) 35 min; (d) 45 min; (e) 57 min, from a total of 400 pores. (B) Average pore as a function of anodizing time. Data from replicas of the surfaces **of** films grown at 25 mA/cm^2 in 1.5 mol/l sulphuric acid at 20°C.[108]

TABLE 6-5

Cell parameters of films formed in oxalic acid at 50 mA/cm^2

Voltage *V*	***Acid*** *Concentration* *mol/l*	*Barrier Layer* *nm*	*Barrier Layer* *nm/V*	*Cell Size* *ntn*	*Cell Size* *nm/V*	*Pore Size* *nm*	*Pore Size* *nm/V*
120	0.25	115	0.96	292	2.4	86	0.12
120	1.0	110	0.91	224	1.9	55	0.46
500	0.25	459	0.92	823	1.6	292	0.58
500	1.0	461	0.93	880	1.8	323	0.65

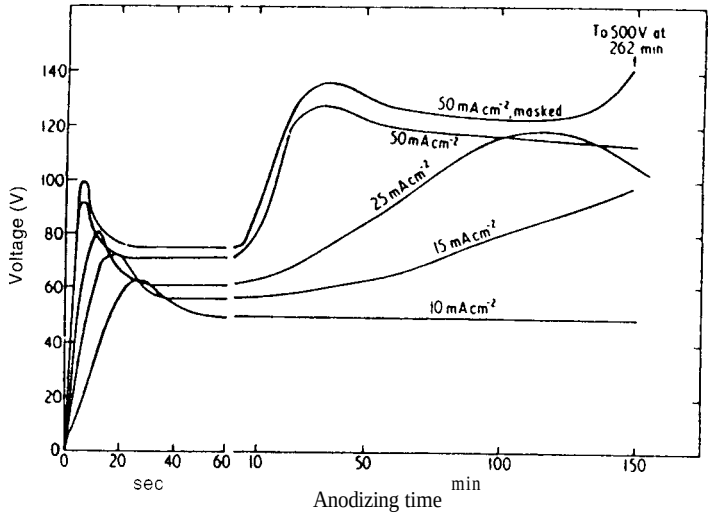


Fig. 6-32. Voltage/time curves for films produced by anodizing at various current densities in 0.25 mol/l oxalic acid at *25°C.*[""]

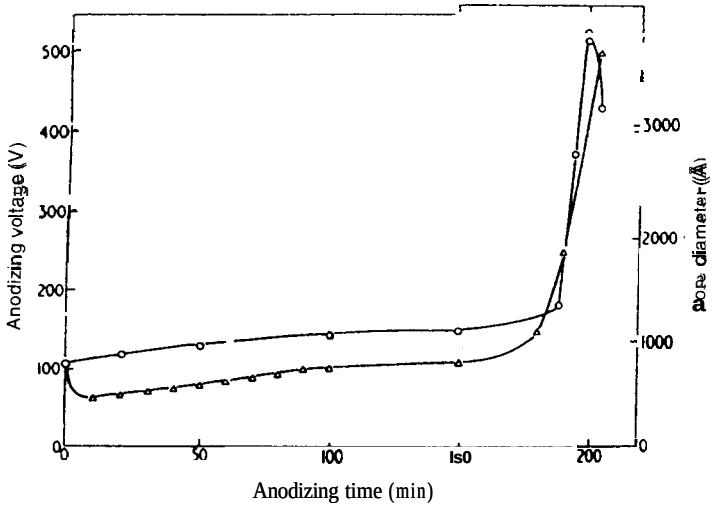


Fig. 6-33. Anodizing voltage and pore size **as** a function of anodizing time for a film formed by anodizing at 50mA/cm² to 500V in 1.0 mol/l oxalic acid at 25°C: **A** voltage, **O** pore diameter.[110]

Ebihara, Takahashi and Nagayama[113] have carried out a comprehensive study of the morphology of films produced in sulphuric acid using a combination of electron microscopy and the pore filling technique. Their work was carried out using electropolished 99.99% aluminium foil samples, anodizing in sulphuric acid solutions of 0.5-4.0 mol/dm^3 at 10-40°C by applying constant current densities in the range 0.5-50 mA/cm^2. For different solution conditions, they showed how pore population density varies with current density and voltage (Figs. 6-34 & 6-35), and the variation with voltage of porosity (Fig. 6-36), pore diameter and cell size (Fig. 6-37), barrier layer thickness (Fig. 6-38), barrier layer thickness to voltage ratio (Fig. 6-39) and oxide density (Fig. 6-40). With the exception of oxide density, all parameters are solely a function of voltage, although the voltage is dependent on solution conditions and current density. It should be noted that the barrier layer thickness to voltage ratio is not constant, but varies between about 0.8 and 1.5 nm/V as the voltage decreases from about 18V to 3V. Cell size, however is linearly related to voltage as found by O'Sullivan and Wood for phosphoric acid anodizing. Over the range of conditions examined, oxide density was more significantly influenced by solution concentration than temperature.

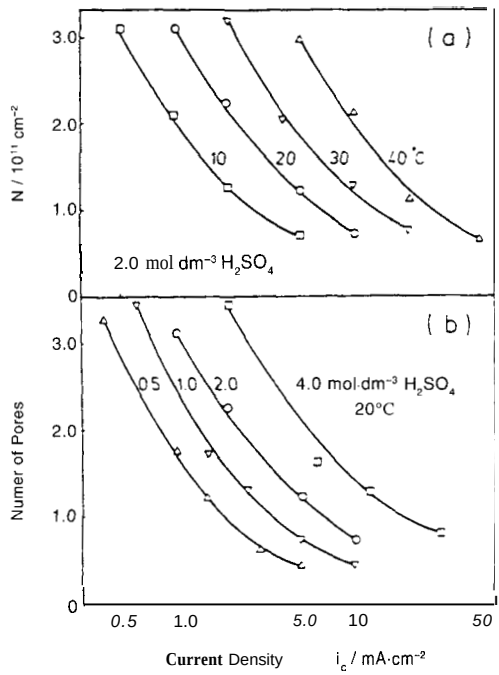


Fig. 6-34. The variation in the pore population density with current density for anodizing in sulphuric acid at (a) different temperatures and (b) different concentrations.[111]

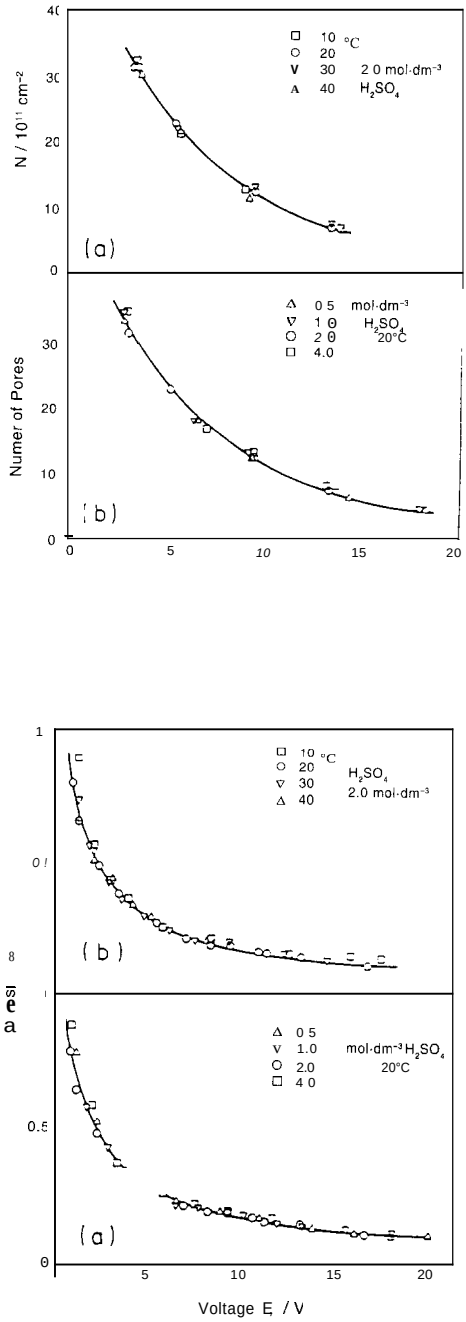
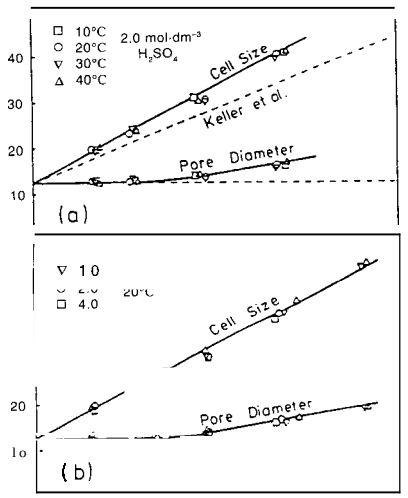
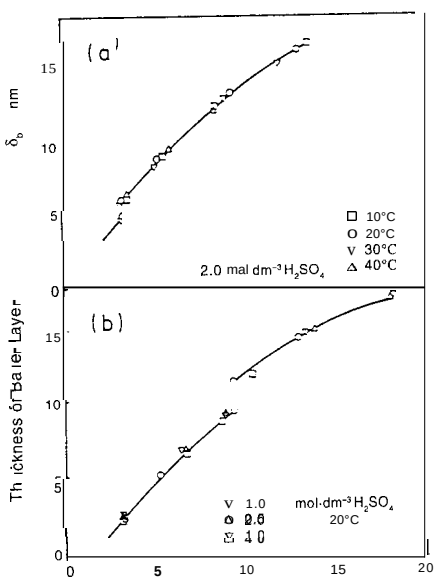


Fig. 6-36. The variation in porosity with voltage for anodizing in sulphuric acid at (b) different temperatures and (a) different concentrations.[113]


10°C
20°C
30°C
40°C
2.0 mol·dm⁻³ H₂SO₄
Cell Size
Keller et al.
Pore Diameter
(a)
10
4.0
Cell Size
Pore Diameter
20
10
(b)


(a)
δo nm
15
10
5
10°C
20°C
30°C
40°C
2.0 mal dm⁻³ H₂SO₄
(b)
Th ickness ofBa ier Layer
1.0
2.0
4.0
mol·dm⁻³ H₂SO₄
20°C
0
5
10
15
20

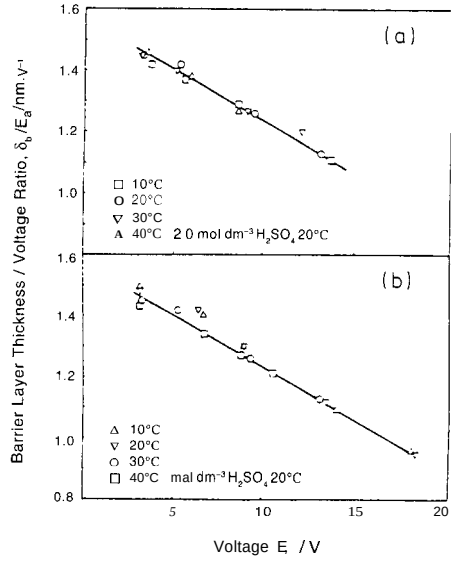


Fig. 6-39. The variation in barrier layer thickness to voltage ratio with voltage for anodizing in sulphuric acid at (a) different temperatures and (b) different concentrations.[113]

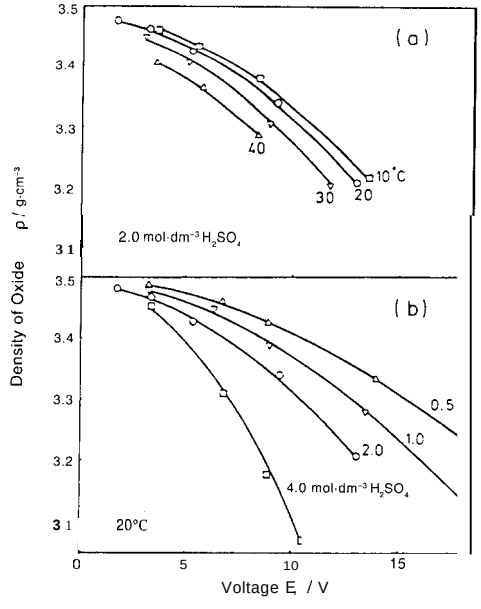


Fig. 6-40. The variation in oxide density with voltage for anodizing in sulphuric acid at (a) different temperatures and (b) different concentrations.[113]

Anodizing under alternating current (ac) conditions in sulphuric acid has been compared with the better studied direct current process by Sacchi and Paolini.[114] Pore population densities were comparable although somewhat more variable, and the pores tended to be larger towards the outer surface for ac films. Barrier layer nm/V ratios were comparable, if the maximum voltage of the ac waveform was used instead of an average voltage.

Parkhutik and Shershulsky[3] have developed a theoretical model of porous oxide growth on aluminium. This also shows a linear relationship between pore size and voltage for particular electrolyte conditions, and a dependency of pore size on solution pH where the pores become progressively larger as the pH is increased.

Recovery

The observation that barrier layer thickness, cell size etc are dependent on the anodizing voltage begs the question: what happens if the voltage is changed during the anodizing process? This has been investigated since the 1960s as a means of improving the understanding of anodizing, but has also validated the voltage dependence referred to above.

Renshaw[115] was the first to record the so-called recovery effect. This is a phenomenon which occurs when, after anodizing at particular steady-state conditions, the voltage is reduced from E, to E,. Simultaneously, the current drops to a very low value, and then after a period of time, is observed to increase to a level lower than the original steady-state current.[116] Renshaw anodized first in a nominally barrier film-forming electrolyte, ammonium tartrate, and subsequently in chromic acid. Hemispherical colonies of pores developed during anodizing in the chromic acid, each colony arising from pore branching from one central pore that opened at the film surface (Fig. 6-41). He recognized that the barrier layer thinning to provide the sites for pore development is too fast to be attributed to chemical dissolution alone, and postulated that pre-existing low resistance pathways exist within the original barrier film, which enable sufficient current flow for incipient pores to form and subsequently develop into colonies. Libsch and Devereux[117] produced pore colonies in neutral ammonium tartrate by first anodizing at 30V, with a period of current decay, and then holding the potential at 10V for 3000 min.

Later Murphy[118] recognized that the readjustment of the barrier layer thickness is due to field-assisted dissolution, and attempted to explain the process by assuming the existence of a proton space charge in the surface regions of the film. Recovery was said to depend on the field-assisted migration of protons out of the film and/or neutralization of protons by field-assisted migration of anions into the film. Diggle, Downie and Goulding[119] suggested that the dissolution process is essentially chemical for a short period, up to a point where the minimum electric field for ionic migration is approached, and thereafter, dissolution increases exponentially and is seen as a field-assisted process, which

was supported by Baba and Imaizumi.[120] O'Sullivan and Wood[60] produced electron micrographs of carbon replicas of films formed in phosphoric acid, showing pore development during recovery at a lower voltage for various periods of time (Fig. 6-42), and Takahashi *et al*[116] described the process schematically (Fig. 6-43) from examination of ultramicrotomed sections of oxalic acid-films subjected to a voltage reduction (Fig. 6-44). At the beginning of recovery (b) thinning of the original barrier layer occurs, during which period very little current flows. As the barrier layer thins, the field strength increases and the anodizing current starts to rise again. During this period new pores (c) are initiating, the dimensions of which are typical of the new anodizing voltage. Finally the current levels off, as an equilibrium pore structure (d), typical of the new voltage, is attained. Similar effects occur if the voltage is increased rather than decreased, but the equilibrium is achieved much more rapidly. Kim et *al*[121] found that during the induction period, barrier layer thinning is accompanied by some new oxide formation at the metal/oxide interface, and deduced that this is determined by aluminium ion removal at the solution interface; this corresponds with current views of the nature of field-assisted dissolution.

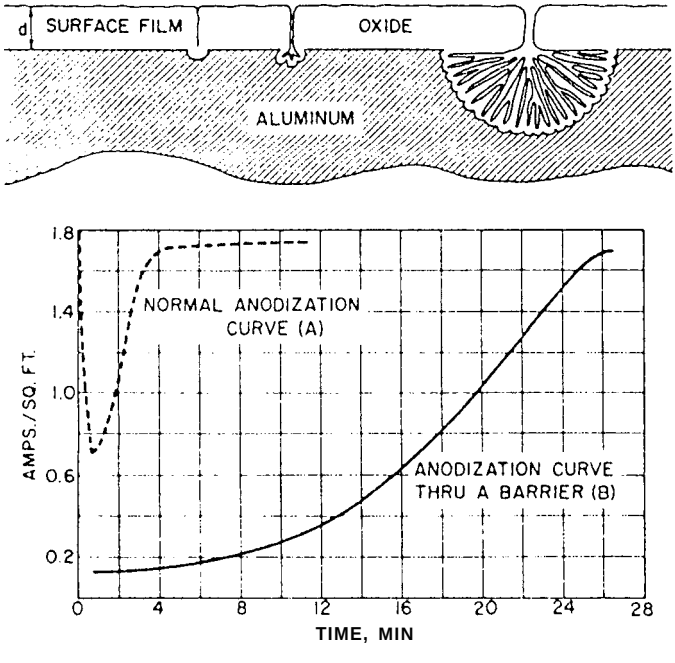


Fig. 6-41. Formation of pore colonies beneath a barrier-type anodic film. The manner in which current flows with time, when anodizing at a constant 35V, through a thick surface oxide film is shown in the graph. The surface film was formed by pre-anodizing the specimen at 40V in ammonium tartrate solution."'

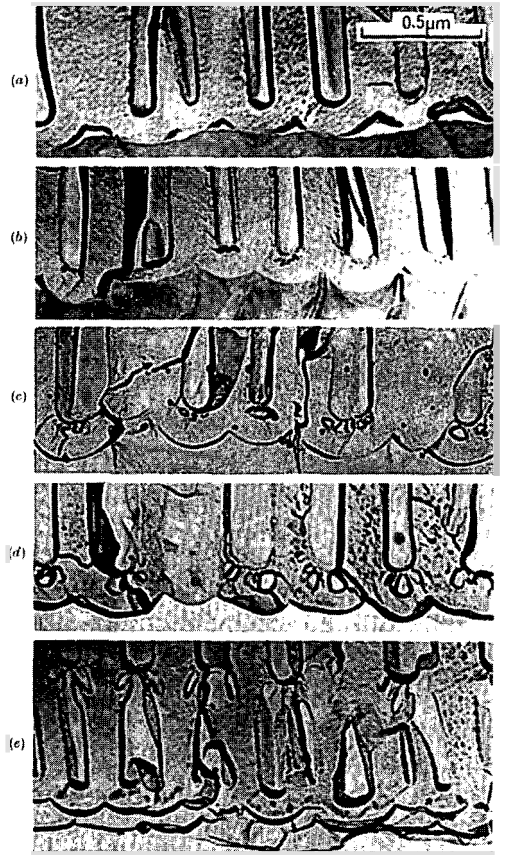


Fig. 6-42. Transmission electron micrographs of carbon replicas of cross-sections of films at various times after a sudden voltage drop from 115 to 85V during anodizing in 0.4mol/l phosphoric acid at 25°C: (a) 1 min; (b) 5 min; (c) 7 min; (d) 9 min; (e) 13 min after the change.[60]9.59.5

Another manifestation of the recovery phenomenon is using voltage manipulation to cause detachment of the anodic film from the aluminium. Lacombe and Beaujard[122] detached porous films by anodically polarizing the anodized metal in an electropolishing solution, a method which was later exploited by Spooner.[123] Thomas[124] separated porous films using a sulphuric acid electrolyte by slowly reducing an alternating voltage to a very low value and then allowing a period of chemical dissolution. He pointed out the slight possibility that this sequence of events could occur at the end of alternating current anodizing or during continuous anodizing or electrolytic colouring procedures. More recently, computer-controlled step-wise voltage reduction under direct current conditions has been used to separate films grown in phosphoric acid to produce membranes for use as micro-filters.[125,126]

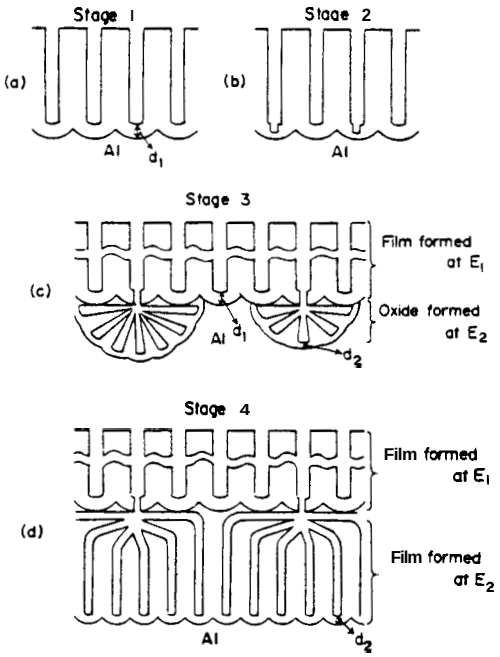


Fig. 6-43. Schematic diagrams showing how film morphology changes over the recovery period after a sudden voltage drop from E_1 to E_2.[116]

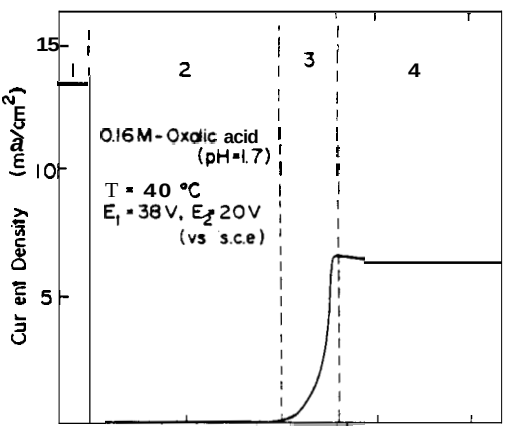


Fig. 6-44. The variation of current density with time during: (1) anodizing at 38V; (2) & (3) the recovery period after a sudden voltage drop to 20V; (4) steady-state anodizing at 20V after recovery.[116]

Chemical dissolution

The chemical dissolution of non-porous films generally will result in a thickness reduction at a constant rate. During the dissolution of porous coatings, considerable mass loss can occur without significant change in thickness. This property is significant for the practical application of anodic films, as is described below.

Nagayama and Tamura[127] suggested that anodic films dissolve by a pore-widening mechanism. As the thickness of material between two pores is approximately twice the thickness of the barrier layer, this implies that very significant mass loss would occur during dissolution with the detection of thickness loss delayed until the widening pores start to merge, the film loses integrity and film collapse occurs. Diggle and coworkers[128] using radiotracer methods showed that concurrent pore widening and pore shortening takes place due to the initial "truncated" pore shape. The truncated pore is wider at its mouth than adjacent to the barrier layer.[129] Manhart and Cochran[130] have observed this behaviour during the development of the chromic/phosphoric acid accelerated test for sealing quality (Fig. 6-45).

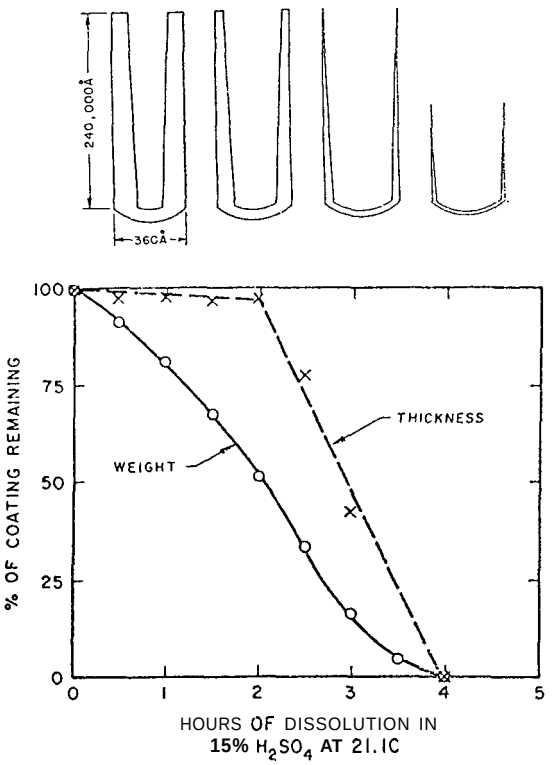


Fig. 6-45. Schematic representation of the mechanism (a) and a comparison of weight and thickness changes (b) during the dissolution of unsealed anodic films formed in sulphuric acid.[130]

Patermarakis *et al*[131] have developed a mathematical model describing the kinetics of thickening and mass increase of porous anodic films produced galvanostatically, taking account of the electrochemical processes and chemical dissolution of the pore walls. The model explains the development of truncated conical pores. The authors reported that pore-wall dissolution in 15% w/v sulphuric acid is a first order reaction, thermally activated, with an activation energy of 78.6 kJ/mol and a rate of 0.052-0.4 nm/min depending on temperature of 20-40°C. Further work[132] developed the kinetic model and applied it to a range of sulphuric acid concentrations. The existence of a critical concentration near 5% w/v was revealed, above which the normal mechanisms of oxide growth are valid, but below which a deficient growth of oxide is observed. Electrolyte concentration influences parameters such as mass and porosity of the anodic films, but in different ways depending on whether the solution is stirred or not. Similarly, solution concentration varies with depth into the pores. Pore shape was described as an elongated spinning top, a truncated cone for a non-stirred bath, or a trumpet for high electrolyte concentrations. Pore shape may be an important influence on hydrothermal sealing processes, organic dye uptake and service performance defined by soft films (see below).

Dissolution of the pore walls also takes place during anodizing itself, and the extent of pore widening depends on the length of time in contact with the acid solution. Consequently, the first-formed anodic film material which is at the outer surface of the film, suffers most attack. Although film growth is coulombic, when the extent of chemical dissolution is such that the pore diameter at the outer surface equals the cell diameter, further film thickening ceases. Thus, there is a limiting film thickness depending on anodizing rate and solution conditions.

Increased porosity may be desirable to increase physical keying of organic coatings to the anodized surface, or to increase the amount of dye adsorption to achieve more intense colouration. However, there are potential disadvantages from high porosity, particularly for anodized finishes to be subjected to weathering.[133] For such applications it is important to limit chemical dissolution, particularly for thicker films which require longer anodizing times, by properly controlling bath temperature and agitation, and eliminating unnecessary contact time with acid solutions. Otherwise, the open structure produced leads to soft outer layers within the film after sealing. These layers tend to craze and flake off during weathering, producing an unsightly bloom or iridescence on the surface and causing a reduction in coating thickness.

Diggle[134] used capacitance techniques to quantify barrier layer thinning during dissolution as a function of solution pH, ionic strength and type, and other factors. Zero-order kinetics were found for acid solutions below a critical pH value. Above the critical pH of 3.0 for sulphate solutions, results were interpreted to show deposition of solid product in the pores, at the same time as dissolution of the barrier layer occurred. This relates to the need for an adequate acidic rinse before electrolytic colouring to dilute solute aluminium within the pores, thus minimising precipitation and ensuring subsequent good colour uniformity.

Burning

Burning can occur in certain electrolytes under relatively high current density anodizing conditions. If heat cannot be adequately dissipated from the metal article by conduction into the electrolyte or more likely by conduction through the metal itself, then local electrolyte heating allows the current to increase locally. Subsequently, further resistive heating occurs leading to current "run away". This results in the formation of regions of very thick anodic film on both sides of the aluminium, which can reduce considerably the local thickness of the metal. The film in the region of burning is highly degraded due to dissolution by the hot electrolyte (a soft film). It may exhibit a different colour from other areas.

Hoshino ***et al***[135] have described mathematically the region of the current density / film thickness map where burning takes place during sulphuric acid anodizing under certain hard anodizing conditions. They have developed a computer controlled system to maintain the current density below the critical level as the film thickens. This, they claim, enables high speed anodizing without burning. Subsequently, they carried out a semi-empirical analysis, which predicted that the critical film thickness achievable by high speed anodizing, without burning, is 613 μm and 280 μm for oxalic and sulphuric acid anodizing respectively under specific solution conditions.

A detailed study of burning during high rate anodizing (750 A/m^2) in 0.25 mol/l oxalic acid at 20°C has been carried out by Tu and co-workers."' They found that burning is accompanied locally by increases in the substrate and electrolyte temperatures to about 60°C, and relative to other parts of the surface, **a** higher rate of film thickening, and changes in the intensity and colour of electroluminescence. Also, the anodizing voltage increased, which was followed by the dimensions of the film morphology at both burnt and non-burnt regions. However, unit dimensions (nm/V ratios) for the pore and cell sizes and the barrier layer thickness were lower within the burnt region. In addition, they found that the current density controls the time before the occurrence of burning, while electrolyte concentration is critical in influencing whether uniform burning over a region of the surface, or many discrete, dark islands of thick film material, develop. The authors concluded that there are two criteria for the initiation of burning: a critical barrier layer thickness and a localized critical rise in the film and electrolyte temperature at the pore base. They proposed that in addition to Joule heating effects, electron avalanching and dielectric breakdown are promoted by, and contribute to, the locally increased temperatures. The increase in the anodizing voltage was said to be due to electrolyte depletion at the cell bases in the burning region, caused by high rates of anion incorporation into the film material at the high current densities, and low diffusion rates of species down the pores.

3 FILM COMPOSITION AND STRUCTURE

Understanding the composition and structure of the anodic film material has tended to be pursued for academic interest. However, such questions are significant when comparing the properties of films formed in different acids and appreciating how anodic films differ from other aluminium oxide- and hydroxide-based coatings. In this context "structure" refers to the atomic arrangement of the species present in the film material rather than the pore structure or morphology. Clearly, anodic films on aluminium contain some form of alumina, but before considering the detail of this structure, below is a review of information on other constituents of the films, namely acid anions and water.

Effect of electrolyte species

Many anodic film properties are known to be modified or controlled by the nature of the acid anion incorporated during anodizing. Such properties include ionic[136] and electronic[137] conductivities, recystallization,[136,138] rate of chemical dissolution,[139] luminescence during anodizing[140,141] and the take-up of organic dyes. Also, it is well known that phosphates inhibit sealing, and this effect is evidenced during the hydrothermal treatment of films grown in phosphoric acid.[142]

Acid anions in anodic films

Early investigations quite consistently reported about **13%** SO, or 15% SO, **in** films produced in sulphuric acid.[57,96,143,144,145,146,147,148,149] Mason[57] pointed out that the level increased with lower operating temperature and higher current density, while Spooner[147] found that it decreased by about 2% on sealing. If hydrothermal sealing proceeds by a dissolution / precipitation mechanism, then there is an opportunity for some sulphate to be lost as the anodic alumina is dissolved.

Using radio-active tracer techniques, Brace and Baker[149] confirmed incorporation at about 15% sulphate, which slowly falls as anodizing proceeds. These data suggest that as film dissolution takes place during anodizing, sulphate is more accessible or more readily removed. Raub and coworkers[150] have determined the amount of sulphate incorporated into films produced in electrolytes based on sulphosalicylic or malic acids which contained 0.35% and 0.5% sulphate respectively. Interestingly, the coatings contained 5-10% sulphate, suggesting that the sulphuric acid had a disproportionate role in the anodizing process.

There has been less agreement on the amount of anion incorporation during oxalic acid anodizing. This has been reported as about 3%[143,146,148] or about 8%[151,152] oxalate. Considering the steric factors involved in fitting acid anions into an alumina lattice, Brace and Baker[149] suggested that about four times as much sulphate as oxalate should be present in anodic films; this appeared to correspond with the findings of 15% sulphate and 3% oxalate. Shimura[153] recognized that,

during anodizing, oxalic acid films exhibit luminescence. He extracted the luminous material, analysed it using electron spin resonance, and identified it as $Al[Al(C_2O_4)_3]nH_2O$ (n=3 or 4). He attributed the luminescence to the formation of $C_2O_4^-$ radicals by charge transfer between the low valency aluminium ion and the oxalato ligand in the complex. Hydrogen ions would also be formed, which could reduce oxalic acid to glyoxylic acid at the anode; this acid was detected in the anolyte. He has similarly examined anodizing in maleic acid.[154]

Fukuda and Fukushima[155] reported that porous films formed in oxalic acid incorporate oxalate in a manner that corresponds with the voltage/time curve (Fig. 6-46) which in itself reflects the initiation and development of pores. They also found that the anion content increased (from about 2.5% to about 4.5%) and the forming voltage decreased with increasing acid concentration at constant pH (adjusted by additions of sodium hydroxide).

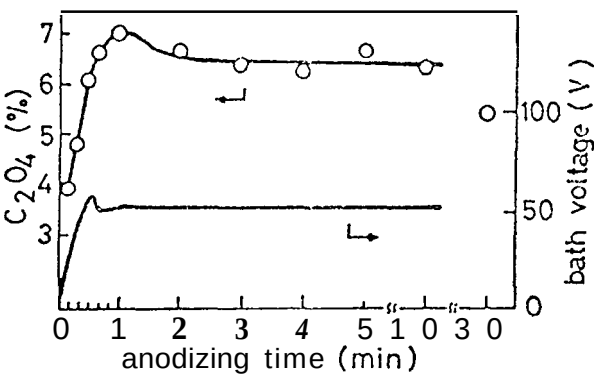


Fig. 6-46. The variation in the anion content of an anodic film and the voltage with time during anodizing in 0.2mol/l oxalic acid at 25°C at 0.94 A/dm^2.[155]

For films formed in chromic acid, values of 0.4-0.7% chromic acid[156] and less than 1% chromium[146,148] have been reported. Although McNiel and Guss[157] found 46% phosphate in a barrier film produced in sodium phosphate, values of 6%[158] and 6-8%[159] have been reported for porous phosphoric acid anodizing. More recent measurements made by Alvey[160] for the four main film types gave 11.1% sulphate, 7.6% phosphate, 2.4% oxalate and 0.1% chromate.

In many cases it has not been clear in what form acid anions are incorporated into anodic films. Using XPS (X-ray photoelectron spectroscopy) Treverton and Davies[161] showed both sulphate and sulphide in films formed in sulphuric acid under both dc and ac conditions. The presence **of** sulphide in films formed using

ac is well known,[162] but its existence in dc films is more surprising. Murphy and others[163] have found that the presence of sulphide for dc films is an artefact due to ion beam sputtering. For ac films, the maximum sulphur content has been found to be 5-6% (as sulphide and sulphate) which is similar to the level in dc films.[164] The presence of sulphide causes the yellow colouration of ac films, but the intensity of colour can be modified via the anodizing voltage or the presence of ferric ions. It was believed that the sulphide is present as Al_2S_3 which may be inside the pores or within the film material.

Tajima and coworkers[165,166] found no significant difference between the differential thermal analysis spectra and infrared spectra of oxalic acid films formed under a range of dc and ac conditions. Films formed in sulphosalicylic acid with low levels of sulphuric acid showed SO, and SO, radicles. Other infrared studies[152,167,168] considered that the incorporated species are sulphate and oxalate for films formed in the respective acids. Using X-ray absorption techniques, Robinson and coworkers[30] have shown that a barrier film formed in a phosphate solution, and a sulphuric acid-formed porous film, contain orthophosphate and sulphate anions respectively, and that molybdate and tungstate are incorporated into anodic films as those anions. However, films formed in potassium chromate contain a small amount of absorbed tetrahedrally-coordinated Cr^{6+} (chromate), but Cr^{3+} is incorporated into the film[169] as if it were present as $Cr(OH)_3$ rather than amorphous Cr_2O_3. Chung *et al*[169] proposed that the reduction of Cr^{6+} may be associated with structural rearrangement of the alumina film and/or electron injection at the film/electrolyte interface during anodizing.

The distribution and incorporation of acid anions

The values for the amount of incorporated anion give no indication of the chemical composition of the film because it is now known that the anions are not uniformly distributed throughout the film. Early work established that barrier films are duplex in nature with electrolyte anions such as borate or phosphate being confined to an outer layer of film material adjacent to the solution interface.[38,170,171] However, Konno and others[172] used a chemical sectioning technique combined with X-ray photoelectron spectroscopy to study films produced in a borate solution, and found boron in both layers; this observation has not been confirmed subsequently using direct techniques. Chemical sectioning combined with the Hunter and Fowle reanodization method, has been applied to films grown in phosphate solutions.[173] Although no results were produced on anion distribution, the duplex nature of the films was confirmed, and results implied that for each layer and the whole film, the product of the permittivity, e, and electric field, E, is constant. ie

$$\varepsilon_1 E_1 = \varepsilon_2 E_2 = \varepsilon_T E_T.$$

Nagayama and Takahashi[174] considered that the cell material consists of three regions in terms of anion incorporation. The first is in the region of the pore wall, with relatively high anion concentration (e.g., 9% oxalate in a film formed in oxalic acid). There is then an intermediate region with even higher anion incorporation (12% oxalate), and the final region is at the extremity of the cell, where the anion is present at relatively low levels. These workers and Fukuda[152] used dissolution and chemical analysis techniques and obtained similar distributions for phosphate ions, and Fukuda and Fukushima[167] confirmed the pattern for sulphate containing films. However, they found that the extent of the regions varied with the electrolyte used. Nagayama and Takahashi[175] carried out step-wise dissolution experiments in sulphuric acid on films formed in phosphoric acid and tritiated water. Analyses of the resulting solutions (Figs. 6-47, 6-48) for aluminium and phosphate showed that the concentration ratio of phosphate to aluminium was 0.19 adjacent to the pores, reached a maximum of 0.22 and decreased sharply to zero for the inner part of the pore wall. Bound water, detected as tritium, was confined to the outer part of the pore wall, with a total incorporation, expressed as the ratio of the amount of water to that of aluminium, of 0.35×10^{-3}. The layers became more resistant to dissolution as they were more remote from the pores.

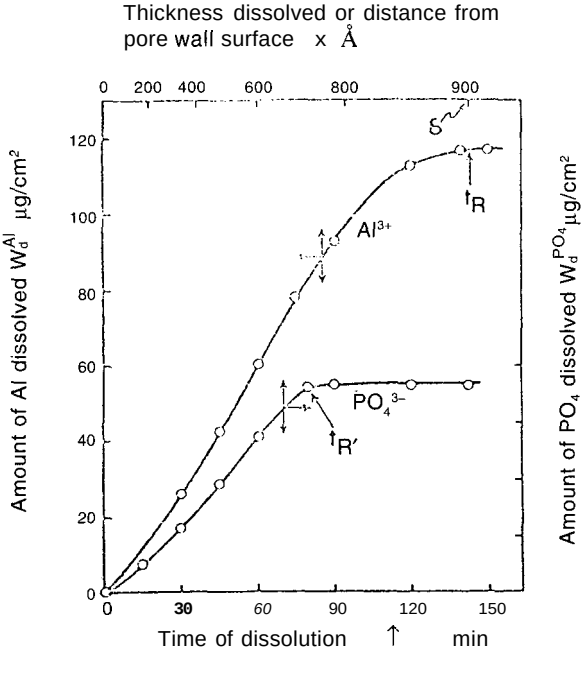


Fig. 6-47. The variation in the amounts of aluminium and phosphate dissolved during the dissolution in sulphuric acid of a porous anodic film produced in phosphoric acid.[175]

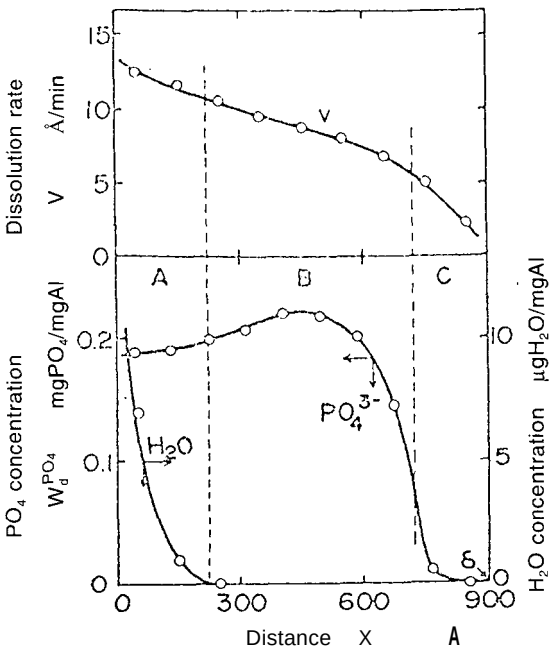


Fig. 6-48. The distribution of phosphate and water across the pore wall and the change in dissolution rate with pore wall thickness dissolved for the dissolution of **a** porous anodic film produced in phosphoric acid and tritiated water, and dissolved in sulphuric acid.[177]

Using the pore filling technique to study dissolution behaviour, Ono and Masuoko[176] also found three layers in barrier layers formed in phosphoric acid, but only two layers for oxalic-acid formed films. In both film types, the inner layers, nearest to the metal, gave dissolution rates independent of the anodizing voltages, while the outer and middle layers dissolved at rates that increased with voltage. The middle layers of the phosphoric-acid formed films dissolved fastest. These differences were attributed to differences in anion incorporation, although the thicknesses of the layers do not correspond well with electronoptical examinations of phosphoric acid films by other workers, and to the presence of defects, the volumes of which increased with increasing forming voltage. Electron microscopy revealed the defects after some dissolution of the film had taken place. Long, narrow (25 nm) holes passed from triple cell junctions towards the pores, while voids at triple points were seen for both phosphoric (about 15 nm in size) and oxalic (about 2 nm) acid-films. Previously, Alvey and coworkers[177] had observed that the pore wall of phosphoric acid-films becomes opened up revealing an array of micropores or fissures due to the effects of chemical dissolution. Ono

and Sato,[178] from a study of anodizing in the Ematal bath, have suggested that these defects arise from breakdown events with accompanying electroluminescence, and promote pore branching. Other work about voids is described on p.352

Other workers[179] stated that the outer two layers constitute the anion-containing region of the film, and found that the dissolution rate for these layers increases with pH; they proposed that increased dissolution rates correlate with higher anion contents for a particular film type.

The first direct indication of cell wall variations, and "cell boundary bands", was in work by Thompson and colleagues at UMIST.[67,180,181] They ion-beam thinned anodic films and examined them in an electron microscope; typical results are shown in Fig. 6-49. They found that, for the relatively large featured films formed in phosphoric and oxalic acids, relatively electron opaque bands developed during the examination. These were readily visible where the cells meet (Fig. 6-49 a & b) and were separated from the open pore by film material of a different texture. No similar bands were evident for films produced in chromic and sulphuric acids (Fig. 6-49 c & d), but more recent work has apparently shown cell boundary bands with high voltage sulphuric acid films.[64]

Point chemical analysis of the ion beam thinned films confirmed that, for films formed in phosphoric acid, the cell boundary band is relatively pure alumina, with the adjacent, differently textured, film containing significant amounts of phosphorus.[182] Similar results, again indicating the presence of relatively pure alumina cell boundary bands, were found for films formed in oxalic and sulphuric acids. With chromic acid produced films, the cell wall seemed to be only alumina, but Thompson *et al.*[183] suggested that a relatively narrow chromium-containing region may be present in the cell material adjacent to the pores.

The extent of the cell boundary bands decreases in the order:

chromic acid > phosphoric acid > oxalic acid > sulphuric acid,

and diagrammatic representations of the pore structures, as suggested by Thompson and Wood,[184] are shown in Fig. 6-50. The solid areas of the diagrams represent the pure alumina and the textured areas indicate the anion-contaminated regions.

The extent of the anion-incorporated region was revealed directly and confirmed by energy dispersive analysis of X-rays (EDX) for films formed in phosphate,[185] borate[186] and tungstate[187] solutions. Subsequent work involving a wider range of inorganic electrolytes also used Rutherford backscattering spectroscopy (RBS) and X-ray absorption spectroscopy.[169,188,189]

Cocke and coworkers[190,191] used Rutherford backscattering with alpha and argon ion beams and observed oscillatory incorporation of WO_4^{2-}, MoO_4^{2-}, and MnO_4^{2-} but not CrO_4^{2-} into barrier-type anodic films using mixed electrolytes containing borate and the sodium salt of the anion of interest. There was a

complimentary periodicity in the aluminium oxide spectra such that minima for the aluminium, including the case of the chromate-containing electrolyte, corresponded with maxima for the anion. This phenomenon has not been fully explained, nor observed by other workers.[188]

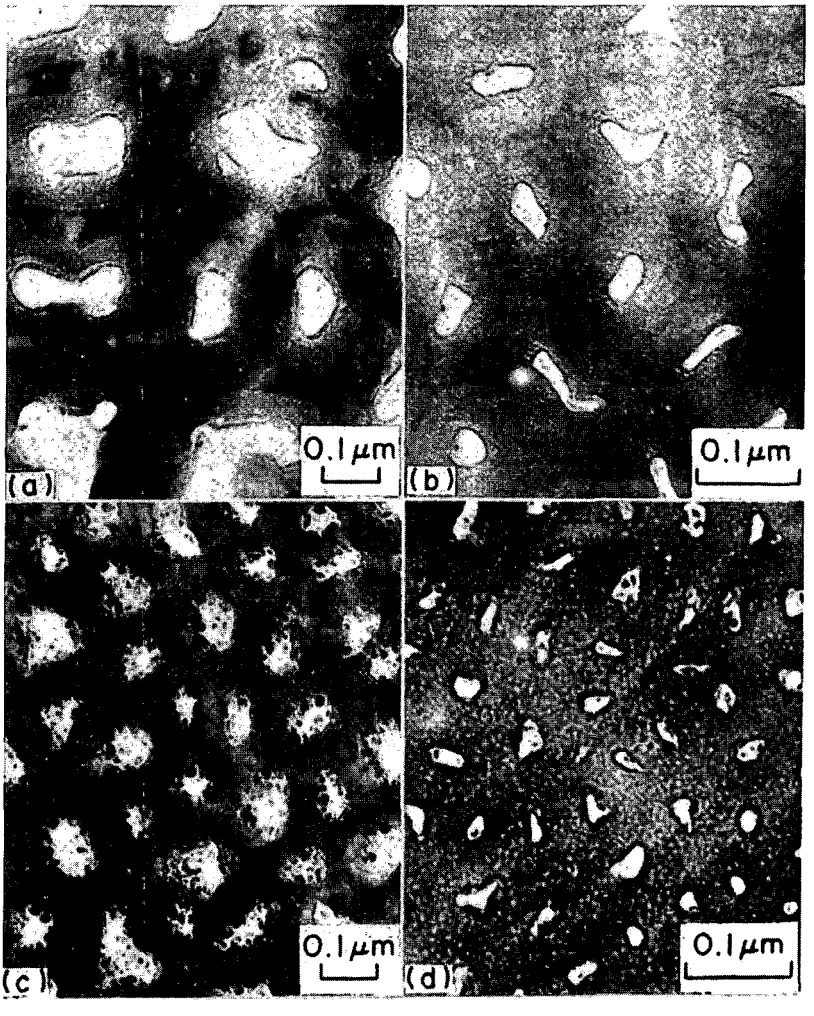


Fig. 6-49. Transmission electron micrographs of thin layers of anodic films prepared by ion beam thinning the stripped films in plan from both sides, and showing the irregular cell and pore patterns: (a) film formed at 150V in 0.4 mol/l phosphoric acid at 293K for 70 min; (b) film formed at 100A/m^2 in 0.25 mol/l oxalic acid at 293K for 30 min; (c) film formed at 100 A/m^2 in 0.25 mol/l chromic acid at 333K for 30 min; (d) film formed at 18V in 1.5 mol/l sulphuric acid at 293K for 30s.[180]

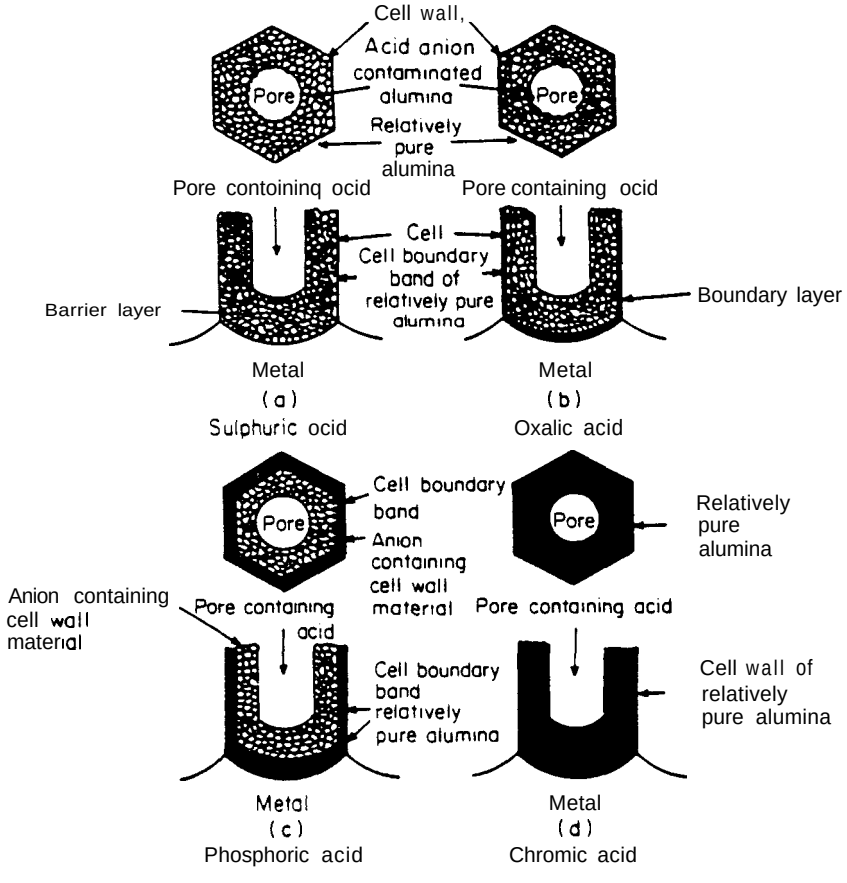


Fig. 6-50. Schematic diagrams showing the plan and cross-sectional views of a pore and its adjacent cell formed in each of the major anodizing acids: (a) sulphuric; (b) oxalic; (c) phosphoric; (d) chromic. The cell comprises acid anion contaminated film material adjacent to the pore and relatively pure alumina where cells meet.[184]

It is currently believed that anions from the electrolyte are incorporated into growing anodic films by adsorption at the film surface during the formation of the ionic double layer.[46] It has been shown that adsorption does not depend on the anodizing field, as the surface enrichment of tungsten atoms arising from anodizing in a tungstate electrolyte is similar to that from simple immersion.[188] During film growth at constant current density, electrolyte-derived species are normally incorporated into the film at a constant rate and uniformly contaminate a layer of film material at the film/electrolyte interface.[170,188] It has been shown that during film growth, electrolyte species may be immobile or migrate inwards or outwards

at various rates. Immobile markers, eg ion-implanted xenon[192,193] (Fig. 6-51) have been used to show this. Also, the fate of mobile tracers has been followed in barrier films which had been reanodized after separation from their original aluminium substrates, and new substrates had been deposited on the film surfaces that had originally been in contact with the electrolytes.[194] Other workers made direct observations by transmission electron microscopy.[185,187] Outwardly migrating electrolyte species result from the field stripping oxygen ions from incorporated oxide species, eg WO, becomes WO_2^{2+} or W^{6+}. Immobile species possibly result from the incorporation of an oxide or salt without forming a charged entity. Where barrier-type films form at 100% efficiency, the relative transport of Al^{3+} and O^{2-}/OH^- ions results in about 40% of the film thickness being formed at the film/electrolyte interface. Thus, electrolyte species contaminate the outer 40%, >40%, and <40% of the film thickness depending whether they are immobile, migrate inwards or migrate outwards respectively. It appears that the mobile electrolyte species participate in a co-operative transport mechanism that also involves the Al^{3+} and O^{2-}/OH^- ions.

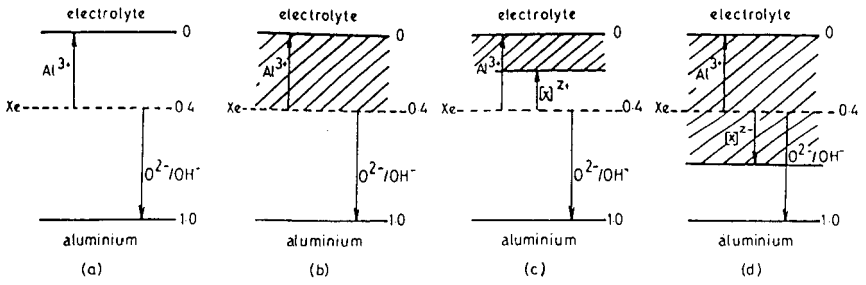


Fig. 6-51. Schematic illustrations of marker experiments to determine the mobilities of electrolyte species during the formation of anodic alumina films at 100% faradaic efficiency. The mobilities are referenced to an inert immobile marker layer such as provided by ion-implanted xenon. All films are formed at constant current density to the same voltage. The arrows on the figures indicate the relative distances moved during film growth of ions that were located at the marker layer implanted into an initial negligibly thick film. (a) Relatively pure anodic alumina film, as formed in hydroxide electrolyte. The marker is buried at a depth of 0.4 of the film thickness. (b) Anodic alumina film containing an immobile electrolyte species (hatched area). The electrolyte species contaminate the outer 0.4 of the film thickness. (c) Anodic alumina film containing an outward-migrating electrolyte species $[X]^{2+}$. The electrolyte species contaminate a layer of <0.4 of the film thickness. (d) Anodic alumina film containing an inward-migrating electrolyte species $[X]^{2-}$. The electrolyte species contaminate a layer of >0.4 of the film thickness."'

Wood and coworkers[195] have recently consolidated this data and presented a model for the incorporation of electrolyte species into barrier films formed galvanostatically in aqueous electrolytes. Wood's model predicts that the proportion of electrolyte species to aluminium atoms, N_x/N_{Al}, in the whole film is independent of the faradaic efficiency of film growth where the species is inwardly mobile, but dependent on the efficiency where the species is immobile or outwardly mobile. Values of this ratio are about 10^{-2} depending on direction of mobility and charge on the species. In all cases, the proportion of the film thickness occupied by the electrolyte species increases as the faradaic efficiency increases. Therefore, the local ratio of electrolyte species to aluminium atoms in the contaminated layer increases with lower faradaic efficiency, although this may be mitigated by other factors.

Experimental data were used for comparison with the model (Table 6-6). Rutherford backscattering spectroscopy (RBS) provided analyses from which average film compositions were determined and subsequently N_x/N_{Al} values were calculated. Actual values for the concentration of electrolyte species within the films was typically about 70% of the predicted values. Manganese and vanadium were effectively not incorporated into the oxide film. Only antimony and sulphur were present to greater extents than predicted. Other aspects of the model were qualitatively confirmed.

As described above, current efficiency is a key parameter in determining whether anodizing will produce a barrier-type or porous film. Consequently, the model has relevance to porous anodizing. However, during porous anodizing, there is no net film formation at the film/electrolyte interface. Thus, only electrolyte species that are inwardly mobile may be expected to accumulate in the film.

Ono and Masuko[196] have examined the effect of anodizing voltage with a phosphoric acid solution on the thickness of the anion-containing and anion-free layers, and the amount of phosphate present (Table 6-7). Below 20V the duplex structure could not be detected, while above this voltage, the fraction of the cell wall thickness containing anion increased with voltage. Similarly, but except for a high level of phosphate in a 2V film, the concentration of phosphate in the anion-containing regions increased with voltage.

Water

Norden[96] reported that sulphuric acid films contain 14.8% water. Baumann[197] found 5-7% water in sulphuric acid and oxalic acid films, while Edwards and Keller[198] reported 1-6% water in the former. Phillips[199] gave a water content in oxalic acid-formed films equivalent to $2Al_2O_3 . H_2O$. Spooner[147] reported that unsealed films produced in sulphuric acid have 0.5% $Al_2O_3 \cdot H_2O$ and 0.4% H_2O which increase to 7.6% and 2.8% respectively after sealing. This well demonstrates the contrast between the probably gelatinous hydrous alumina produced by hydrothermal sealing to fill the pores of the anodic film, and the essentially anhydrous material developed during anodizing.

TABLE 6-6

Measured and predicted composition of films formed at 50 A m^{-2} and 293K[195]

Electrolyte	*pH*	*Voltage (V)*	*Efficiency (%)*	*Averaged film composition*	*Mobility of electrolyte species in film*	*Predicted adsorbed anion*	$(N_x/N_{Al})_{meas.}$	$(N_x/N_{Al})_{pred}$	$\frac{(N_x/N_{Al})_{meas.}}{(N_x/N_{Al})_{pred.}}$
Silicate	12.6	250	102	$Al_2O_{3.00\pm0.02}Si_{0.014\pm0.003}$	Immobile	SiO_3^{2-}	$7.0 \pm 1.5 \times 10^{-3}$	9×10^{-3}	0.78
Antimonate				$Al_2O_{3.12\pm0.01}Sb_{0.058\pm0.001}$	Out	SbO_3^-	$2.9 \pm 0.1 \times 10^{-2}$	1.9×10^{-2}	1.53
Chromate	10.0	125	100	$Al_2O_{3.03\pm0.02} \cdot Cr_{0.0100\pm0.0002}$	Out	CrO_4^{2-}	$5.0 \pm 0.1 \times 10^{-3}$	9×10^{-3}	0.56
Permanganate	9.5	65	63	$Al_2O_{2.98\pm0.02} \cdot Mn_{<0.0013\pm0.0002}$	–	MnO_4^-	$<7 \times 10^{-4}$	4.7×10^{-2}	<0.01
Phosphate	9.4	162	108	$Al_2O_{3.17\pm0.02} \cdot P_{0.072\pm0.006}$	In	$H_2PO_4^-$	$3.6 \pm 0.3 \times 10^{-2}$	4.7×10^{-2}	0.77
					In	HPO_4^{2-}	1.7×10^{-2}	2.4×10^{-2}	0.71
					In	$H_2PO_4^-$	3.5×10^{-2}	4.7×10^{-2}	0.74
Arsenate	9.3	250	100	$Al_2O_{3.06\pm0.02} \cdot As_{0.0298\pm0.0002}$	Immobile	$H_2AsO_4^-$	$1.5 \pm 0.1 \times 10^{-2}$	1.9×10^{-2}	0.79
Tungstate				$Al_2O_{3.05\pm0.01}W_{0.015\pm0.001}$	Out	WO_4^{2-}	$7.5 \pm 0.1 \times 10^{-3}$	9×10^{-3}	0.83
Borate				$Al_2O_{3.07\pm0.03}B_{0.06\pm0.01}$	Immobile	$HB_4O_7^-/B_3O_5^-$	$3.0 \pm 0.5 \times 10^{-2}$	$7.6 \times 10^{-2}/5.7 \times 10$	0.40/0.53
Selenate	7.5	60	65	n.d.	In	SeO_4^{2-}	$1.3 \pm 0.1 \times 10^{-2}$	2.4×10^{-2}	0.54
Molybdate				$Al_2O_{3.06\pm0.01}Mo_{0.013\pm0.001}$	Out	MoO_4^{2-}	$6.5 \pm 0.1 \times 10^{-3}$	9×10^{-3}	0.72
Vanadate	6.5	250	84	$Al_2O_{2.99\pm0.02} \cdot V_{<0.0002\pm0.0002}$	–	$H_3V_2O_7^-$	$<1 \times 10^{-4}$	3.8×10^{-2}	<0.01
Sulfate	5.8	44	68	n.d.	In	HSO_4^-	$7.4 \pm 0.6 \times 10^{-2}$	4.7×10^{-2}	1.57

n.d.: not determined

TABLE 6-7

The change of thickness fraction of the anion-contaminated outer layer to cell wall, and anion concentration with increasing forming voltage[196]

Forming voltage (V)	*Current density (A/m^2)*	*TEM observation*		*EDX analysis*	
		Anodizing time (min)	*Fraction of outer layer*	*Anodizing time (min)*	*Wt.% of PO,*
2	8	30	–	30	5.6
5	9	30	–	10	1.8
10	11	10	–	10	2.2
20	15	10	0.62	5	3.7
40	21	10	0.69	5	5.4
60	27	10	0.71	5	6.3
80	32	5	0.77	5	6.9
100	45	5	0.78	5	7.4

A nuclear reaction technique has been used to profile anodic films for hydrogen.[200] Barrier-type films formed in phosphate and glycol-borate solutions, 210 and 170 nm thick respectively, had trace levels of hydrogen to a depth of about 60 nm. This was equivalent to 0.04% H_2O if the all the hydrogen was present as water. It was unlikely that the hydrogen was associated with the phosphate anion as HPO_4^{2-} or $H_2PO_4^-$, because there was about four times the amount of anion than that necessary for the amount of hydrogen. Also the thickness of this hydrogen-containing layer did not correspond with the thickness of the anion-containing layer. Films formed in tartrate solutions at much less than 100% efficiency had hydrogen-enriched surface layers. This was attributed to a surface precipitate.

It is now generally accepted that anodic films are essentially anhydrous when freshly formed. Clearly, as they are produced in aqueous electrolytes, there is surface hydration and this is discussed below. Also, subsequent to anodizing, the film material may become hydrated, which is one of the processes occurring during hydrothermal sealing. It is interesting to note that the mechanical properties of anodic films are very dependent on environmental humidity. Grosskreutz[201] has shown that separated films grown in tartaric acid have a Young's modulus comparable to that of bulk alumina, 39×10^{10} N/m^2, at an absolute humidity of 10^{-6} g/m^3 falling to 3×10^{10} N/m^2 at 1 g/m^3. Bradhurst and Leach[202] have commented that the low modulus under ambient conditions reflects the amorphous structure of the anodic alumina. Further information on this is included in the section on film structure.

Mixed electrolytes

It is known that during porous anodizing in mixed electrolytes, the voltage and current characteristics typify those of one component rather than the other. Thus, sulphuric acid has to be controlled as a contaminant in chromic acid, otherwise the anodizing characteristics will follow those found during anodizing in sulphuric acid alone and the coating will be transparent rather than opaque.[203] Similarly, for integral colouring processes using organic-acid based electrolytes with low levels of sulphuric acid, the anodizing behaviour may be determined by the sulphuric acid component.[204] Sulphuric acid may be a dominant anodizing electrolyte, but other acids may dominate in other respects. For example, small additions of oxalic or phosphoric acids to a conventional sulphuric acid bath have no significant effect on the anodizing process per se, but do modify the extent of chemical dissolution of the film during the process. Phosphoric acid is a powerful solvent for anodic alumina, while oxalic acid is able to inhibit the dissolution. The effect of sulphate additions to an oxalic acid electrolyte has been investigated by Fukuda and Fukushima[155] (Fig. 6-52). These data may suggest competitive adsorption processes at the film/electrolyte interface. However, mechanisms are unclear, as such processes are also significant in controlling anion incorporation which determines the anodizing characteristics.

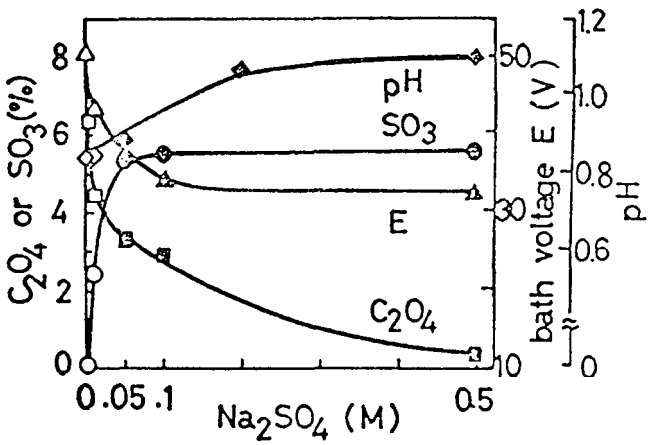


Fig. 6-52. The variation in anion content (oxalate and sulphate), bath voltage and pH with the amount of sodium sulphate present in a 0.2 mol/l oxalic acid solution at 25°C, anodizing at 1A/dm^2 for 30 min. Uniform white anodic films (open symbols) or black films with pitting (closed symbols) were produced.[155]

Skeldon and coworkers[205] have used Rutherford backscattering spectroscopy to investigate the selective interfacial processes during barrier film growth in mixed electrolytes. They proposed that the normalized atomic ratios for the electrolyte species can be used to assess film compositions, and deduced an order of dominance during competitive adsorption processes: silicate > phosphate > arsenate > tungstate > molybdate > chromate. Borate ions did not fall simply into this sequence. However, it is not clear what specific electrolyte species are adsorbed onto the surface and subsequently incorporated into the growing film. The authors point out that any of a range of different processes may take place at the film surface including reaction with hydrogen ions and hydrogen stripping under high field conditions (Fig. **6-53).** If the interfacial reactions produce a neutral entity, such as a hydrated oxide, then this may aggregate to form a gel layer above the surface of the anodic film or may precipitate.

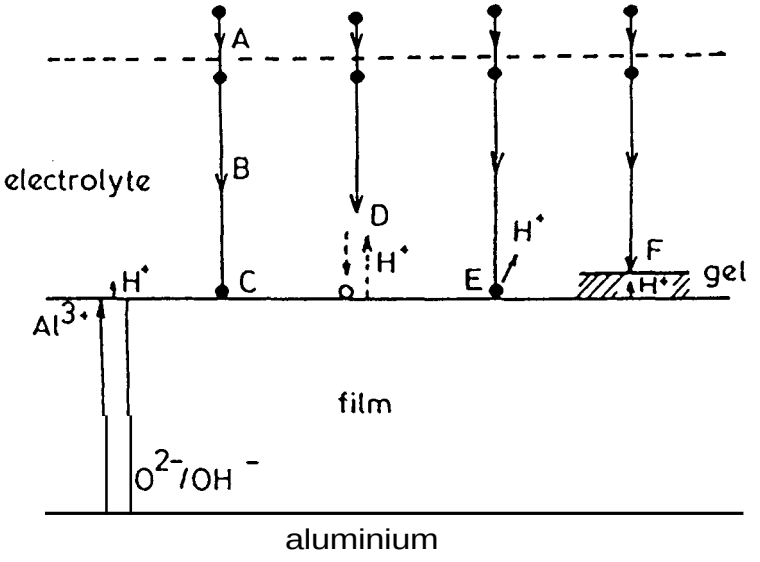


Fig. 6-53. Schematic illustration of the possible processes leading to incorporation of electrolyte species into an anodic film: entry of anions into the diffusion layer, **A;** transport of anions across the diffusion layer, B; adsorption of anions on the film surface and incorporation into the film, C; reactions of anions with hydrogen ions, D; stripping of hydrogen ions from anions in the region of high electric field, E; formation of gel layer, F.[205]

Anodic film structure

Crystalline or amorphous

During the development of the science associated with the structure of anodic films, they have variously been described as amorphous, microcrystalline, γ-Al_2O_3, γ'-Al_2O_3 or η-Al_2O_3. Material is amorphous if it is X-ray indifferent, ie no spotty diffraction pattern can be obtained. Microcrystalline describes such material where the crystallite is less than about 10 nm. γ-Al_2O_3 is a transition alumina produced during the thermal transformation of boehmite to corundum.[206] It has a tetragonally deformed spinel-type structure and contains cation vacancies and several percent hydroxyl ions. η-Al_2O_3 is also a transition alumina but arises from the decomposition of bayerite. According to Verwey,[207] the O^{2-} ions in γ'-Al_2O_3 are arranged in a face-centred cubic lattice, and the smaller Al^{3+} ions are distributed statistically in the interstices between the oxygen ions with about 70% of the aluminium ions having a coordination number of six, the rest having four.

γ-Al_2O_3 has been found by X-ray diffraction in films produced in oxalic acid,[208] concentrated sulphuric acid[209] and boric acid.[210] Recently, Ono and coworkers[211] have determined lattice parameters from electron diffraction patterns of films formed in chromic, phosphoric and sulphuric acids, which had undergone crystallization under the electron beam. They concluded that the film material is comparable to η-Al_2O_3.

Harrington and Nelson[212] found coatings produced in sulphuric, phosphoric and oxalic acids, trisodium phosphate, borax and ammonia to be amorphous, while Edwards and Keller[198] found electron diffraction patterns of high voltage boric acid films to be crystalline with a γ-Al_2O_3 structure. Taylor, Tucker and Edwards,[213] using X-ray diffraction on anodic coatings produced on 99.8% aluminium foil, made no distinction between the γ-Al_2O_3 and γ'-Al_2O_3 forms. These authors investigated a large number of coatings produced by various methods and found all of them to consist largely of amorphous oxide, with a percentage of the γ-Al_2O_3 form in some cases. In general, high potential was found to favour formation of the crystalline lattice, which also tended to form in dilute solution, ie at less than 0.1% oxalic acid, 0.1-0.5% chromic acid or 0.05% sulphuric acid. Larger amounts of the crystalline oxide were found using alternating current, as well as at higher temperatures. The largest amounts were obtained with dilute citric acid at 670 volts and 95°C. In molten electrolytes γ-Al_2O_3 has been produced.?'''

Trillat and Tertian,[214] investigating by electron diffraction coatings of 1 μm and 20 μm thickness obtained in sulphuric acid on 99.99% aluminium, found a crystal structure consisting of a mixture of the monohydrate and either the y-oxide or a non-classified transition form at the extreme top layer. The lower layers of both coatings were amorphous. It must be remembered, however, that in the presence of moisture, the amorphous oxide coating is gradually transformed into the monohydrate, as during hydrothermal sealing, which may provide some explanation of the results of Trillat and Tertian.

Franklin[215] found at least three types of oxide in films formed in a boric acid-borax solution: (1) a hydrated layer at the outside of the film, (2) irregular patches of crystalline γ'-Al_2O_3 within the coating, and (3) amorphous oxide as the bulk of the film.

It is worth noting at this stage that the dielectric breakdown of anodic films and other phenomena lead to the formation locally of crystalline material. The results from some workers may have detected such effects. Breakdown is discussed further in a subsequent section of this chapter.

From the electron diffraction patterns obtained on freshly-formed coatings, Harrington and Nelson[212] calculated a grain size of approximately 1.2 nm. Brummough and Cooke are quoted by Phillips[199] **as** finding **a** rather lower value, 0.5-1.0nm, which increased on sealing in boiling water to 10-25 nm, the boehmite pattern being obtained. Phillips also reports that other electron diffraction patterns, which could not be assigned to any known form, were found by Baker and Pearson[216], who estimated a microcrystallite radius of 2.4nm, whilst Alvey[160] suggests dimensions of 9.0, 9.5 and 4.0 nm for oxalic, phosphoric and chromic acid films respectively. Most recently, Thompson and others at Manchester[180] have reported cell wall textures suggesting microcrystallites of 2.0-2.5nm, but this may be an artefact caused by the ion beam thinning method used in the examination.

Fine structure

The descriptions of anodic films as amorphous, microcrystalline or glassy have been used rather imprecisely, and only recently has significant progress been made. In the 1950s Wilsdorf[217] and Kerr[218] proposed a molecular model based on diffuse haloes from electron diffraction patterns, with a basic unit of Al_4O_6 in the form of an octahedron of O^{2-} ions with Al^{3+} ions bonded to three O^{2-} ions on four of the faces. Results from angular and energy dispersive X-ray diffraction have indicated that the basic unit is two AlO_4 tetrahedra sharing a common corner.[219] Oka *et al*[220] suggested that a model using a disordered γ'-Al_2O_3 crystalline base best fitted their X-ray scattering data. More recently, it was shown that Al^{3+} cations are both octahedrally and tetrahedrally coordinated to O^{2-} ions.[221] El-Mashri and coworkers[222] attempted to explain the distribution of A1-0 coordination by arranging Al_4O_6 molecular units into sheets which, when stacked together, resulted in the appropriate number of the different sites occupied by aluminium. By applying a radial distribution function method to electron diffraction haloes from films formed in sulphuric acid, Kobayashi and Niioka[223] concluded that the short range order structure is not similar to γ'-Al_2O_3, but is more akin to the natural air-formed film on aluminium or the film produced by electropolishing.

Four- and six-fold coordination of Al^{3+} with O^{2-} ions have now been confirmed, but additionally five-fold coordination has been discovered.[224,225,226] These workers used magic-angle spinning nuclear magnetic resonance **(MAS** NMR) which is sensitive to aluminium ions in a short-range ordered environment (Fig. 6-54). As shown in Table **6-8,** the fraction of aluminium detected varied greatly with

chromic acid-formed films showing the greatest order, and films formed in sulphuric acid being the most disordered. The proportions of 4-, 5- and 6-fold coordination of the aluminium ions varied among the different film types.

TABLE 6-8

Anodizing conditions and NMR data

Electrolyte	*Anodizing Temperature (°C)*	*Aluminium Determined (Fraction)*	*Spectra Peak Positions for Different Coordinations (±2ppm)*		
			4-Fold	*5-Fold*	*6-Fold*
Sulphuric acid	25	0.37	61.5	29.0	1.5
Oxalic acid	25	0.43	63.5	34.0	4.0
Phosphoric acid	25	0.62	64.0	33.0	–
Chromic acid	60	0.94	–	–	6.5

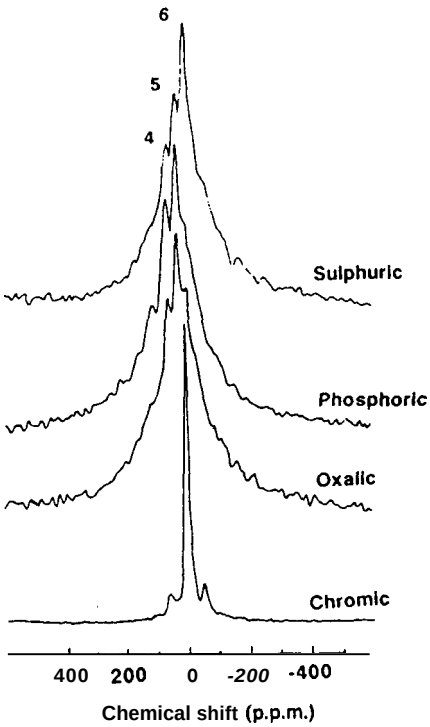


Fig. 6-54.[27] Al magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra of anodic films formed in different acid electrolytes. The numbers indicate the aluminium-oxygen co-ordination associated with the narrowed resonances.[226]

The data was interpreted to confirm that discrete microcrystallites are present within disordered, distorted material. This even applies to the films produced in chromic acid, but, as they are X-ray amorphous, the disordered regions contain much less aluminium and may constitute a much lower fraction of the total volume. It was pointed out that the microcrystallites in the chromic acid-formed films are not α-Al_2O_3, nor γ-Al_2O_3 or any intermediate alumina, but are more similar to boehmite, which exhibits 6-fold coordination. In fact, it was found that partially dissolving an oxalic acid-formed film in its forming acid led to a structure of only 6-fold coordination. This was not related to anion-containing and anion-free regions, but suggested that the whole film had adopted a "hydrated", or more correctly a hydroxylated,"' structure. The higher formation temperature of the chromic acid film may have promoted the observed structure. It was postulated that hydroxyl ion mobility may be an important factor determining the basic structure of porous anodic films. Thompson[64] has suggested that there is probably no distinct interface between the microcrystallites, but an hydrogen bonded intracrystallite material comprising alumina, the acid anion and molecular water.

More recent work using X-ray absorption spectroscopy has confirmed that both barrier-type and porous films have largely 4- and 5-fold coordinated aluminium, with 6-fold coordination being indicative of hydration effects." Electrolyte pH and anion type, for growth at high efficiency, appear to have little effect on the structure, but under conditions where the efficiency is lower, 6-fold coordination is observed as a result of partial hydration. In this context it is worth noting that anodized aluminium gains weight considerably in humid environments particularly above about 70% relative humidity[228] and that film conductance is proportional to moisture content.[229] Heating anodic films causes them to lose ionic conductance, originally attributed to a decrease in aluminium ion,[230] but now believed to be due to structural entities within the film material which may redisperse when conductivity is restored by further ionic movement.[231]

Thompson *et al*[62] suggested that there is a transition from solid to gel-like material in moving from the cell wall towards the pore wall surface. Stabilized negatively charged colloidal particles are held in solution under the influence of acid anions and the low pH of their environment. Under the influence of the field, they are deposited on the relatively pure alumina layer to give an outer layer of fine microcrystallites. Whilst this structure is fairly stable in the pore walls, in the barrier layer region of the film, during growth, the pure alumina layer must be continuously transformed into gel-like, anion incorporated material.

Thompson and Wood[184] considered the local field strengths across the barrier layer regions of films formed in the four types of electrolyte referred to above, and found that, for films formed at 20 V, typical rates of film formation decrease in the order:

sulphuric acid > oxalic acid > phosphoric acid > chromic acid

This represents the observed order of increasing cell boundary band thickness (Fig. 6-50), and suggests that the rate-determining step may be solid state ionic

migration across the relatively pure alumina layer. The passage of ions through the outer anion-incorporated regions of the barrier layer is thought to proceed relatively easily, so the greatest field is across the inner, relatively pure alumina region. The total voltage drop across the barrier layer is similar for all four electrolytes, even though, in the case of the highly anion-contaminated film produced in sulphuric acid, the cell boundary band to contaminated film material ratio approaches zero, and in the anion-free film formed in chromic acid the ratio approaches infinity. The explanation of this is indicated in Fig. 6-55. The voltage drop is greater and linear across the relatively pure alumina region and lower across the outer acid anion contaminated film material where the voltage decreases progressively towards the film/solution interface. Consequently, the highest field is across the least extensive relatively pure alumina region, evident for films formed in sulphuric acid, decreasing for the films formed in oxalic and phosphoric acids respectively, and lowest for the most extensive pure alumina region present in films formed in chromic acid. The rates of formation of the corresponding films decrease in the same order.

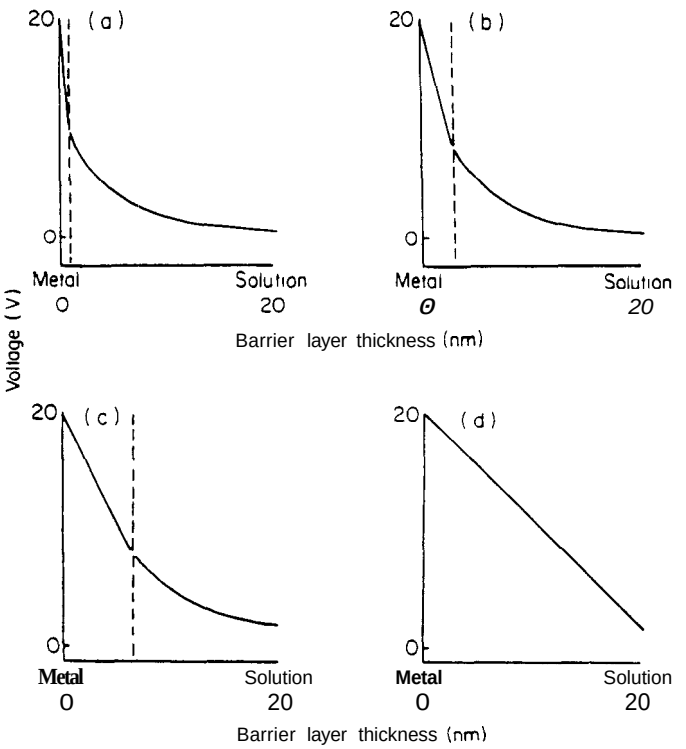


Fig. 6-55. Distribution of the voltage drop and field (slope of the voltage/distance plot) across typical barrier layers of porous anodic Films formed in each of the major anodizing acids: (a) sulphuric; (b) oxalic; (c) phosphoric; (d) chromic.[184]

Thus the steady-state anodizing behaviour of porous anodic films formed in the major anodizing acids can be related to the distribution of the acid anions within the barrier layer and the true field strengths across the relatively pure alumina regions.

Some researchers have attributed the colour of integral-coloured anodic films to the presence of unoxidized aluminium in the anodic films,[232,233,234] although others have questioned their results.[235,236] Saito and coworkers[237] have studied films produced in sulphuric acid using optical and chemical techniques to verify the presence of unoxidized aluminium. Anodic film separated from 99.99% aluminium was pulverized and treated in a bromine-in-methanol solution, which, after filtration, **was** analysed. They reported the presence of ellipsoidal aluminium particles in the film at a concentration from 0.5 to 1.5 ppm depending on current density from 20 to 150 mA/cm^2. They believed that the ellipsoids lie parallel to the pores at cell boundaries and particularly at cell triple points.

The presence of unoxidized aluminium, Al^0, and oxygen-deficient film material, $Al_2O_{3\,x}$, was investigated by measuring the amount of Al^0 in separated anodic films, and measuring the amount of hydrogen evolved by a titration method.[238] Al^0 contents up to about 1250 ppm were reported for films produced under dc conditions in sulphuric acid and under ac in a sulphosalicylic/formic acid mixture. The oxide deficiency, x, in the film material, excluding the contribution from Al^0, was calculated to range from 0.0010 to 0.0720. The Al^0 content increases with film thickness, while the oxygen deficiency decreases. Sulphuric acid anodizing under ac conditions gave both higher Al^0 (−1400 ppm) and oxygen deficiency (x−0.1572).

Defects

Many properties of anodic films are controlled or influenced by local defects or non-uniformities in the barrier layer. Such defects may include stress-induced breaks in the oxide, local regions of crystalline oxide and, on a larger scale, the effects of second phase particles at the metal surface. This section reviews the current knowledge of defects and the implications of their presence.

Crystallization

Barrier-type anodic films suffer dielectric breakdown during formation at a characteristic voltage largely dependent on the acid anion.[239] Early work[240,241,242,243,244,245,246] indicated that the breakdown voltage increases with film thickness, and was attributed to electron avalanching. Electron injection at the cathode following the Fowler-Nordheim mechanism has been described by Forlani and Minnaja,[247] and is influenced by a positive space charge,[248] and takes into account Joule heating.[249] De Wit and others[250] using evaporated gold contacts, found that the breakdown field was independent of thickness and was close to the anodizing field. It was stated that this cannot be explained by avalanching, and it

was suggested that the process is initiated by ionic transport related to the anodizing process.

Zahavi and Metzger[251] suggested that breakdown events at the base of pores may contribute to film growth. They interpreted electronoptical evidence to show that channels arise through the barrier layer, sometimes related to small pits at the metal/oxide interface, which subsequently repair due to further anodic oxidation, thus extending the front of the porous film into the metal.

Anodic films on aluminum exhibit both electroluminescence (EL) or galvanoluminescence (GL) and photoluminescence (PL).[252] GL occurs during anodizing in many electrolytes and probably represents a "pre-breakdown" glow.[253,254] It is normally not observed during anodizing in sulphuric acid, but pore-filling experiments have revealed that this is possible. Ikonopisov and co-workers[255] have explained that the GL centres are probably located in a small thickness of the barrier layer which is thin in sulphuric acid-formed films, and that the light emission may be absorbed by thick porous layers. They confirmed that GL depends on the electrolyte type. It is possible that the initiating current is ensured by a mixed Schottky/Poole-Frenkel mechanism.[256,257]

Mizuki and coworkers[258] observed EL during the electrolytic colouring of porous films formed in sulphuric acid. They used an Al-1%Mn alloy because films on such substrates emit a yellow EL due to the collision excitation of a manganese activator by accelerated electrons in the film. During the ac deposition of copper from solution, the EL intensity was found to be almost proportional to the electronic current, although this was only a small proportion of the total applied current. Maximum EL intensity was found at 100 Hz, while the best frequency for colouring was 1000 Hz. At ac voltages below 8V neither EL nor colouring occurred, from 8 to 17V both EL and colouring took place, but above 17V bright EL spots were observed and spalling took place. These authors proposed that during electrolytic colouring, copper deposition is initiated when protons migrate through the barrier layer during the cathodic half cycle causing hydrogen ions to be generated by reaction with trapped electrons, which causes the pH to rise at the bottoms of the pores permitting Cu^{2+} reduction.

The occurrence of PL has been associated with the incorporation of carboxylate anions into the film,[252] or the suggestion that PL centres are formed by adsorption of water molecules, or OH^- radicals at specific points (defects) in anodic films.[259,260] Jovanic and coworkers[261] compared the excitation maxima of anodic films formed in a number of different acids with predictions using molecular orbital theory, and found good agreement indicating the significance of incorporated anions or anion fragments. It is interesting to note that they postulated structural changes in certain anodic films to explain the existence of two excitation maxima (Table 6-9). Thus, they suggested that S^{2-}, P^{3-} and COO^- exist deeper in oxide layers produced in sulphuric, phosphoric and oxalic acids respectively.

TABLE 6-9

Experimental and calculated PL excitation wavelengths for anodic films formed in various electrolytes[261]

Anodizing Electrolyte	*Incorporated Anion*	*Excitation Wavelength (nm)*	
		Experimental	*Calculated*
Sulphuric acid	SO_4^{2-}	340	338
	S^{2-}	*265*	*265*
Phosphoric acid	PO_4^{3-}	340	337
	P^{3-}	270	279
Chromic acid	CrO_4^{2-}	325	344
Sodium carbonate	CO_3^{2-}	360	379
Formic acid	$COOH^-$	370	313
Oxalic acid	$C_2O_4^{2-}$	250	250
	COO^-	305	305

If aluminium is reacted with hot water to form a surface hydrous oxide film, then subsequently anodized in a neutral electrolyte, it will produce a largely crystalline barrier-type film, attributed partly to the field-assisted dehydration of the hydrous oxide.[262,263,264] The capacitance of the crystalline barrier film is higher than would be the case for an amorphous anodic film formed similarly but on a substrate without a hydrous film. The crystalline composite oxide exhibits an electrical instability which can be corrected by a relaxation or depolarization step, often a hydrothermal treatment, followed by reanodization.

Alwitt and coworkers[265,266] have suggested that this is caused by the presence of closed voids in the largely crystalline anodic film, which are opened to the surface during the hydrothermal treatment. Bernard and Russell[267] found that oxygen was present in the original film at a volume that suggested that it must be under high pressure or in the condensed state. They suggested that the conversion of the relatively low density hydrous oxide to anodic oxide results in a reduction of volume, which produces shrinkage cavities which are filled with electrochemically generated oxygen. Whereas heating at 600°C allowed about 55% of the trapped oxygen to escape, treatment in boiling water effectively opened the sealed cavities.

Alwitt and Dyer[268] identified three classes of void in films formed on 99.99% aluminium; the first two classes have been confirmed by Stevens and Shaffer.[269] Class I are connected voids in the crystalline layer of the film forming long chains or strings. They are 3-4 nm in width, up to 70 nm long with a density of about $10^{10}cm^{-2}$. Unlike class I voids, class II voids are unconnected, not removed by reanodizing, about 3nm in diameter and present at about $10^{12}cm^{-2}$. Class III voids

are present in specific thicker films, but with similar size and population to class II voids. They appear similar to ones reported to constitute breakdown sites.[270]

Hutchins and Chen[271,272] found that annealing aluminium in air at 600°C produced γ-Al_2O_3 crystallites which were substrate orientation dependent (the smallest population density was on (100) grains), and served as nuclei for the growth of less ordered crystals of γ'-Al_2O_3 during anodizing. The number of crystalline sites increased markedly with electrolyte temperature, while their growth rate increased with electrolyte temperature and anodizing voltage, but with lower current density. A transition region of possibly more ordered amorphous oxide was observed surrounding the crystallites as they expanded by converting the amorphous oxide. Ultimately during anodizing, a sheet of crystalline material completely covering the surface was obtained. These authors and Kobayashi and coworkers[273,274,275,276] showed that crystallites can develop on electropolished foil without the use of annealing or a hydrothermal treatment, when anodized in ammonium dihydrogen phosphate at 85°C. Kobayashi showed that the crystallinity depended on how long the electropolished sample was immersed in the anodizing solution before anodizing was commenced. He also found that the transition to γ'-Al_2O_3 may be inhibited in certain anodizing solutions, possibly due to the presenck of acid anion in the amorphous oxide. It was proposed that the voids observed above the γ'-Al_2O_3 crystallites arose during anodizing, due to the migration of oxygen ions across the interface between the amorphous- and γ'-Al_2O_3 causing a loss of excess volume associated with the oxygen ions in the amorphous phase. The crystals nucleated in the centre of the film thickness, which is the location of initial thermal oxide crystallites (possibly too small to be visible), after anodic film formation at the boundary of the layers produced by cation and anion transport.

Shimizu *et al*[270] explained their observations that breakdown starts at flaws in barrier-type anodic films. The incidence of flaws was reported to be dependent on substrate grain orientation. They supported Young's assumption" that breakdown may be triggered by local heating effects caused by conduction through electrolyte-filled fissures and flaws in the film, but believed that electron avalanching may be significant in causing local temperature rises. This may contribute to the overgrowth of film around the flaws (Fig. 6-56) and, in certain cases, cause the thermal instability leading to the formation of conducting channels. Crystalline film material was found at breakdown sites.

It has also been shown that crystalline anodic film material develops on 99.99% aluminium annealed in air at 500°C for 15min.[277] This was related to breakdown during anodizing, and it was shown that the annealing process reduces the breakdown voltage. Voids within the anodic films were observed above the islands of crystalline material. It was suggested that γ-Al_2O_3 crystallites in thermally produced oxide subsequently served as nuclei for the growth of crystalline material during anodizing. More recently[278] using microdiffraction, it has been shown that microcrystalline regions, perhaps a few nm in size, develop during relatively low temperature annealing (450°C for 1 hour) of anodic films formed in an ammonium pentaborate solution. It was proposed that the size of such crystallites is comparable

to the critical size for a stable presence. Structural reordering associated with their dissociation into amorphous oxide was suggested to explain the ion conductivity results of Crevecoeur and de Wit.[279]

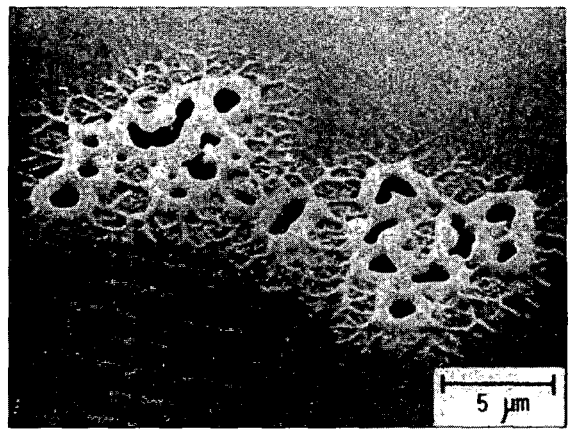


Fig. 6-56. Scanning electron micrograph of the surface of the aluminium specimen anodized at a constant current density of 50 A/m^2 in 0.3 mol/l ammonium borate solution at 298K to 320V, showing the cluster-like appearance of developing breakdown craters.[270]

Dignam[280] showed that after annealing a barrier-type film, reanodizing with an increased voltage produced a pronounced current peak. He showed that the ionic conductivity of the oxide after annealing was very low, but that it could be restored by the application of a high electric field. Subsequent work where films were annealed at 400°C in oxygen, showed that during reanodizing at constant voltage, there was an induction period before the current started to increase.[279] During the period of the current peak, film growth occurred inhomogeneously at nuclei of normal-conductivity material, which expanded parallel to the surface until the complete surface coverage was obtained. A model was developed combining the theory of two-dimensional phase transformation with the exponential relationship between ionic current and field. During this work, neither X-ray nor electron diffraction showed any difference between non-annealed and annealed films.

Shimizu and coworkers[281,282] have shown that regions of crystalline alumina develop surrounding flaws in barrier-type films formed on 99.99% aluminium in aqueous ammonium borate solutions. The population density of flaws varied from 2.4×10^8 cm^{-2} for as-received rolled surfaces to less than 10^5 cm^{-2} for electropolished samples. Thus, they believed that the flaws were associated with

impurity segregates introduced during the rolling process. Evidence was presented of fine channels above the segregates in the growing film, and it was suggested that oxygen evolution occurs at such sites under high local current conditions. The crystalline islands were suggested to arise due to local heating, and became most evident as the anodizing voltage approached 100V, beyond which the islands grew radially. This growth was found to be influenced mainly by electrolyte temperature, and almost unaffected by electrolyte concentration and applied current density. It hindered the local growth of normal barrier film.

Arnott *et al*[283] investigated the role of defects in barrier-type films, attributed to surface preparation of the metal either via impurity segregation or flaws in the natural air-formed film. They reported that during tensile deformation of the anodized metal. the extent of fracture of the anodic film is controlled by the density of defects initially present. For films <30 nm thick, the fracture occurs at slip steps emerging from the underlying metal, provided that the oxide contains debilitating defects in their immediate vicinity. The onset of film rupture was at strain levels of 5×10^{-3} to 10^{-2}. Experiments were performed to show that the same defects control both the mechanical properties and the leakage current, or effective resistivity, of the anodic film.

The presence of iron or copper in high purity aluminium can affect leakage currents and breakdown events.[284] This relates to the topic of the next section where the effect of impurity elements on anodizing is considered in more detail.

Effect of substrate

Much of the fundamental understanding of anodizing has been developed from investigations using high purity aluminium. However, aluminium alloys are generally used in commercial practice. Alloys contain a range of intermetallic compounds which may locally influence the course of the anodizing process and the properties of the film obtained. They also contain varying amounts of different elements in solid solution, which may have a more general effect on both the anodizing process and the film.

Intermetallic compounds

Intuitively, it may be expected that intermetallic compounds with a composition very different from that of the matrix will have a more dramatic influence on the anodic film than solid solution elements. Guminski and others[285] have investigated the reaction rates of binary second-phase constituents during oxalic acid anodizing using optical microscopy and electron probe microanalysis of specially prepared alloys. The results are summarized in Table 6-10. Ramous and Sticchi[286] used X-ray fluorescence to study the incorporation of magnesium, iron, manganese and silicon into porous anodic films as a function of film thickness, current density and electrolyte type.

TABLE 6-10

Reaction rates of constituents during anodizing in oxalic acid compared with the matrix[285]

Constituent	*Reactivity relative to matrix*	*Composition*			
		Element	*Matrix* (%)	*Film above matrix* (%)	*Film above constituent* (%)
Mg_2Si	greater	Mg		trace	trace
		Si		trace	5
$CuAl_2$	greater	Cu	1.5	trace	none
β-AlMg	greater	Mg	5.5	0.5	trace
$CrAl_7$	greater	Cr	0.4	0.1	trace
$FeAl_3$	equal	Fe	none	none	12
Si	less	Si	1	none	
$TiAl_3$	less	Ti	none	none	
$NiAl_3$	less	Ni		none	none
$MnAl_6$	less	Mn	1.2	0.4	

Kobayashi and coworkers[287] have examined the behaviour of Si precipitates during anodizing of an Al-0.5%Si alloy in sulphuric acid. The precipitates were incorporated into the anodic film growing over the matrix surrounding the precipitates. Incorporation proceeds in such a manner that the pores growing over the matrix branch to undercut the aluminium beneath the precipitates (Fig. 6-57).

In contrast, anodizing in phosphoric acid an Al-0.5%Fe alloy caused an Al_3Fe intermetallic particle to be itself anodized during incorporation into the film (Fig. 6-58).[288] The barrier layer produced above the particle was considerably thicker than that of the adjacent matrix. This indicated that a considerably lower field strength was necessary for ionic transport through the barrier layer above the Al_3Fe particle. Microanalysis revealed substantial incorporation of iron into this part of the barrier layer at a level decreasing towards the outer surface of the film, which probably accounted for the different conductivity (Fig. 6-59 & 6-60). However, the extent of phosphate incorporation was less than for the barrier film over the matrix. The concentration of iron in the barrier film adjacent to the substrate (position 8) was significantly less than the ratio of 1.1 within the intermetallic particle (position 9).

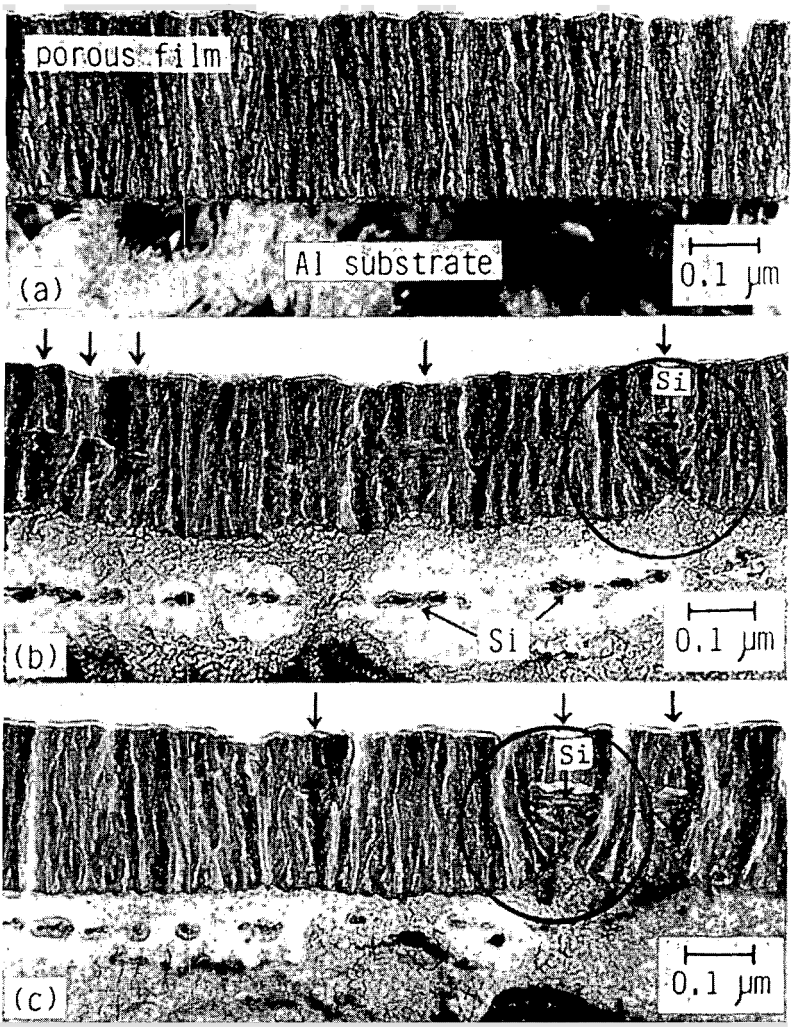


Fig. 6-57. Transmission electron micrographs of cross-sections of the porous anodic film formed on Al-0.5%Si alloy for 2 min. in 2.4 mol/l sulphuric acid solution at 25°C with a constant current density of 5 mA/cm^2. Arrows indicate local regions where Si precipitates are present. At local regions indicated by circles, pore-branching is observed clearly within the porous film grown over the aluminium matrix surrounding the precipitates.[287]

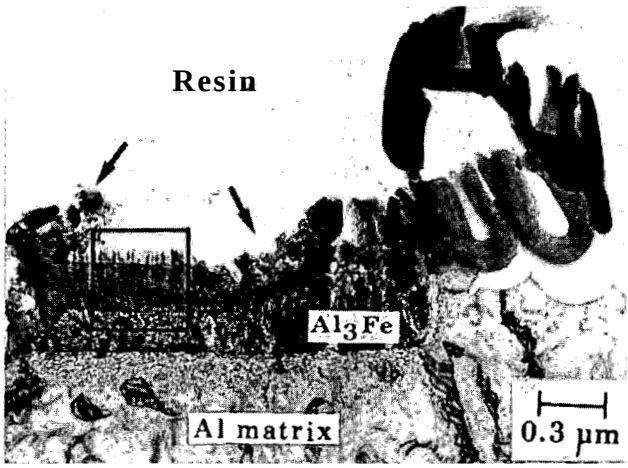


Fig. 6-58. Transmission electron micrograph of an ultramicrotomed section of a Al-0.5%Fe alloy and its anodic film. Anodizing was carried out at a constant current density of 5mA/cm² in 0.4 mol/l phosphoric acid at 25°C for 5 min.[288]

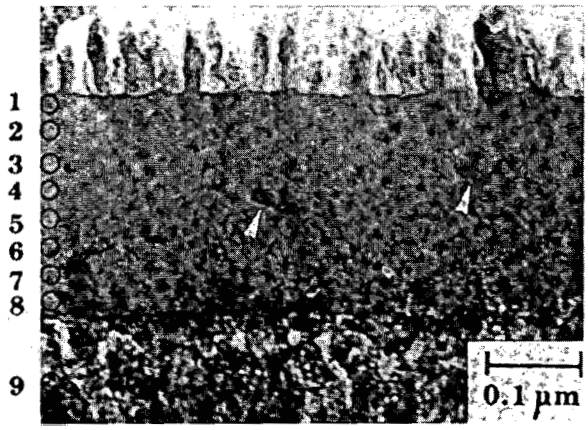


Fig. 6-59. Enlargement of the boxed area shown in Fig. 6-58 showing the approximate probe positions for compositional analysis. The arrows indicate fine debris from the Al_3Fe particle on the barrier oxide layer.[288]

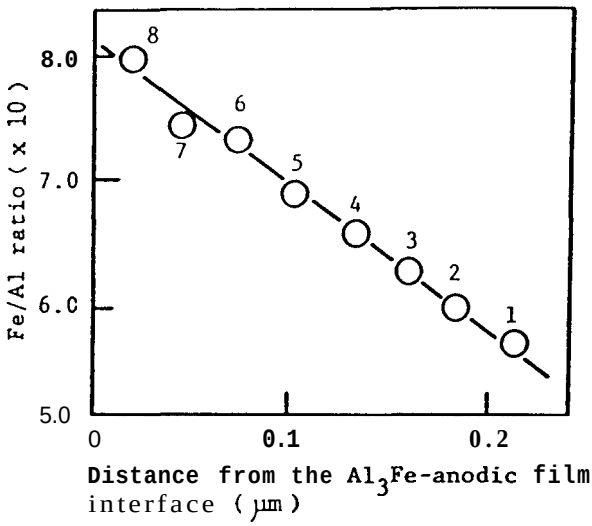


Fig. 6-60. The Fe/Al X-ray count ratio plotted as a function of the distance from the oxide/Al_3Fe interface, showing a compositional variation in the barrier oxide grown on the Al_3Fe phase presented in Fig. 6-59.[288]

Shimizu and coworkers[289] have used ultramicrotomy and transmission electron microscopy to compare further how Al_3Fe and Al_6Fe behave during anodizing in sulphuric acid. They found that Al_6Fe anodized at about 40% of the rate of the surrounding matrix producing an anodic film shown to contain iron by EDX analysis, and an apparently fine pore morphology. Thus, part of the particle became incorporated within the anodic film as pore growth undercut and isolated the particle, and caused an asperity to develop at the metal interface due to current shadowing by the particle (Fig. 6-61). In contrast, Al_3Fe anodized at about the same rate as the matrix (Fig 6-62), but still produced a fine pore structure of iron-containing material. Because of its anodizing characteristics, Al_3Fe could not become incorporated into the anodic film. These observations are important in understanding how second phase particles may affect the reflectance properties of aluminium surfaces used for such applications as lighting reflectors. If exposed to the incident light, the particles can absorb light, reducing the total reflectance, and scatter light, reducing specularity.

Mukhopadhyay and Sharma[290] have investigated the effect of Fe-bearing particles during the hard anodizing of 7075 extrusions . They found that in a conventional sulphuric/oxalic acid electrolyte, $Al_{12}(Fe,Mn)_3Si$ survived the anodizing process, which led to a steep rise in the bath voltage and non-uniform film growth. However, the particles were dissolved, depending on their size, when using a sulphuric/oxalic/hydrochloric acid electrolyte.

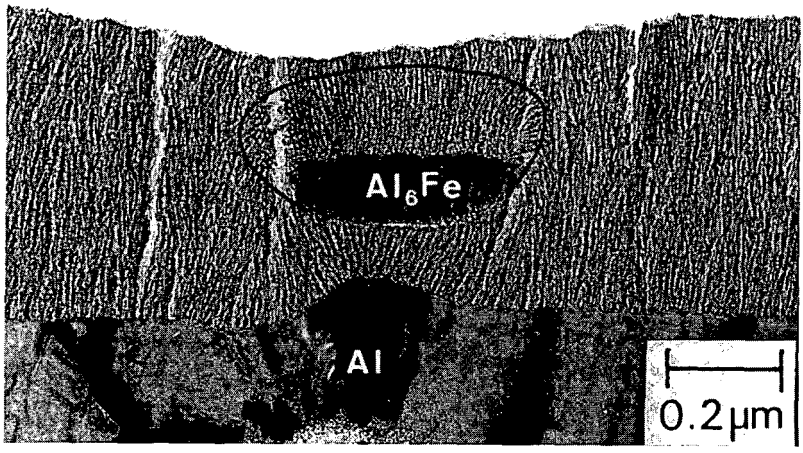


Fig. 6-61. Transmission electron micrograph of a local region of porous anodic film growth resulting from the different oxide growth rates of a Al_6Fe particle and the surrounding matrix region.[289]

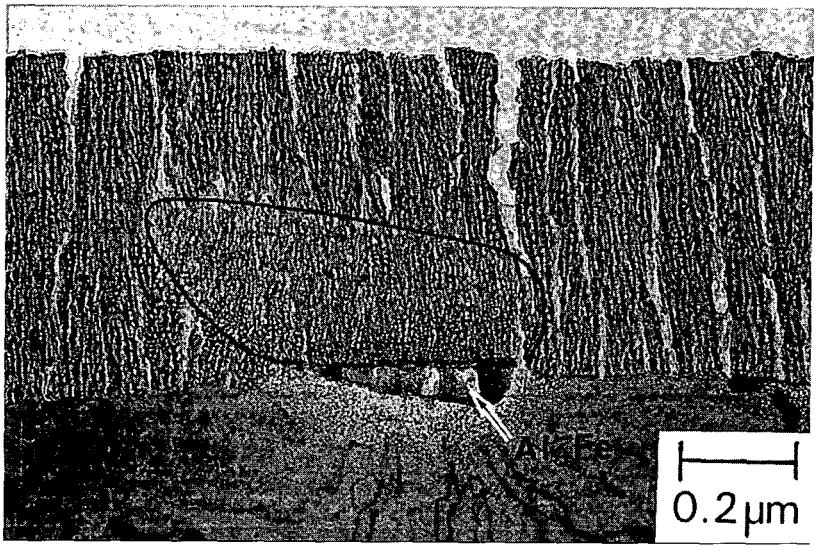


Fig. 6-62. Transmission electron micrograph of a local region of porous anodic film growth over a Al_3Fe particle and the surrounding matrix region.[289]

The presence of an intermetallic particle constituting a flaw by disrupting the anodic film can be significant during cathodic polarization of the aluminium. Thorne *et al*[291] have investigated processes occurring during electrolytic colouring of anodized aluminium. They found that for a specific set of conditions, as the barrier layer thickness increases, then deposition current and thus colouring tend to be channelled to gross flaws with relatively little uniform metal deposition remote from the flaws. The importance of the positive half cycle was confirmed to reduce the activity of gross, persistent flaws by anodic film development above them, and enable uniform metal deposition to take place. These authors also suggested that for the conditions selected, relatively low efficiency, bulk conduction of electrons across barrier layers below 35 nm thick caused metal ion reduction and deposition.

Solid solution elements and superimposed layers

Investigations that may relate to the effects of solid solution species on anodizing have included the use of sputter-deposited or implanted layers of foreign atoms on high purity aluminium surfaces. The Chalk River group[292] found that alkali metals were mobile during anodic oxidation in a manner consistent with their expected ionic charges, and that metals are outwardly mobile if implanted into the air-formed film, but those with higher oxidation potentials than aluminium remain static with respect to the metal/oxide interface if implanted into the aluminium surface.[293] This was interpreted to indicate that the implanted ions have a higher degree of mobility in the aluminium close to the surface due to a high concentration of vacancies in this region. Mobility through the oxide depends on ionic size and charge. Group V and VI elements behave similarly, except selenium which appeared to exhibit both anionic and cationic characteristics.[294] Khalil and Leach[295] have developed the α-spectrometry technique further for studying ionic transport numbers during anodic oxidation.

Panitz and Sharp[296] found that the surface composition of alloys may vary considerably from the bulk composition depending on the surface preparation method used. The time to achieve a given voltage during constant current barrier anodizing of 6061 alloy was greater after cleaning with an organic solvent, or immersion in nitric acid, than after immersion in a nitric acid/ammonium bifluoride etch. These authors suggested that the surface compositions led to flaws in the anodic films, which affected the anodizing characteristics.

Several studies[297,298,299,300,301] have examined the barrier film anodizing behaviour of superimposed layers of valve metals. For tantalum-above-aluminium, ultramicrotomed cross-sections of anodic films revealed a dark band in the outer region of the film consistent with the initial development of anodic tantalum oxide followed by the formation of anodic aluminium oxide.[302] For aluminium-on-tantalum, cross-sections revealed tantalum oxide fingers penetrating the anodic alumina to different extents. This behaviour was ascribed to the higher resistivity of anodic alumina than anodic tantala which led to preferred current pathways

through the fingers. Similar phenomena have been found from anodizing AI-30 at% Mo and A1-30 at% W alloys.[303,304] In these cases, the anodizing was carried out under barrier film forming conditions. During porous anodizing, it is possible that film material containing the heavy metal may contact the electrolyte. It would be interesting to find out how such an occurrence would modify the anodizing process and thus the film properties.

A significant recent finding is that during the oxidation of aluminium, enriched alloy layers may develop immediately beneath the surface oxide.[305] During the anodic oxidation of a A1-1.5 wt% Cu alloy, it was found that a thin layer, about 2nm thick, developed within the alloy at the interface with the oxide film, which was enriched **in** copper to about 40 at%.[306,307] The layer arises because during the early stages of oxidation, only aluminium atoms are oxidized prior to a stage when sufficient enrichment has occurred for the alloying element to be oxidized[308] (Fig. 6-63). The necessary enrichment depends on the alloying element and the alloy composition. The effect is most evident for relatively dilute alloys (less than about 5 at%). More concentrated alloys attain the required level of enrichment much more rapidly, while very dilute alloys may require substantial oxidation before sufficient enrichment is achieved. The level of enrichment has been found to correlate with the Gibbs free energy per equivalent for formation of the alloying element oxide (Fig. 6-64). Significant enrichment is predicted for many alloying and impurity elements in aluminium alloys, particularly copper and iron, but not for magnesium. Enrichment can occur during anodizing, alkali etching, chemical- and electro-polishing. For ternary alloys, each alloying element behaves as it would in a binary. Thus, one of the elements will reach the critical level of enrichment before the other and be oxidized into the surface film (Fig. 6-65). Also, for intermetallic particles present in the alloy, which generally have higher proportions of alloying elements than the matrix, the critical enrichment will be attained very rapidly. Thus for a commercial alloy, different areas of the surface may achieve critical enrichments of different alloying elements after different times of anodizing.

After enrichment, the alloying element enters the oxide film in the approximate alloying proportions. **As** such elements move locally into the anodic film they may alter its properties, such as ionic conductivity and Pilling-Bedworth ratio, such that the barrier film thickness may locally vary. Depending on the mobility of the element cation in the anodic oxide under the field, variously layered films may result. Where the mobility is similar or less than Al^{3+}, then an inner layer of oxide develops containing the cation and with a thickness dependent on mobility. If the element cation is more mobile than Al^{3+}, dependent on the barrier layer thickness, it may reach the solution interface where it may be ejected into the solution or, if it forms a stable oxide under the electrolyte conditions, then an outer layer of relatively pure alloying element oxide may develop. These effects are expected to be essentially similar for porous anodizing but, additions: , there is the influence of field-ejection of cations from the film and field-assisted dissolution.

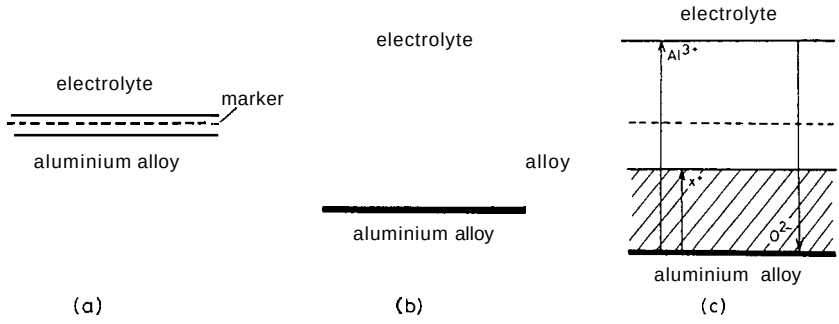


Fig. 6-63. Schematic diagrams illustrating the development of the enriched alloy layer during film growth at high faradaic efficiency on a dilute binary aluminium alloy. (a) Initial condition of the alloy, with a thin oxide film above an alloy substrate with no significant enrichment. (b) Formation of an essentially pure alumina film, neglecting the incorporation of foreign species from the electrolyte. The alloy layer just under the film is enriched progressively in the alloying elements. (c) On achieving sufficient enrichment of the alloy, the alloying element is oxidized at the alloy/film interface and then migrates outwards in the film. The hatched area corresponds to the region of film containing foreign species.[308]

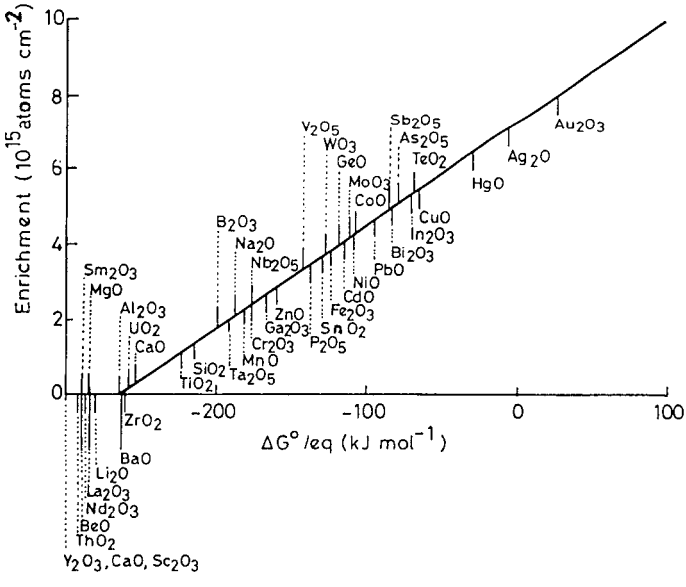


Fig. 6-64. The steady-state enrichments of the alloy predicted for anodizing of binary aluminium alloys, containing about 1-5 at% alloying element. The predictions are obtained using the relationship between enrichment and Gibbs free energy per equivalent for formation of the alloying element oxide derived from experimental results for a limited range of alloys anodized at 50 A/m^2 at 293K.[308]

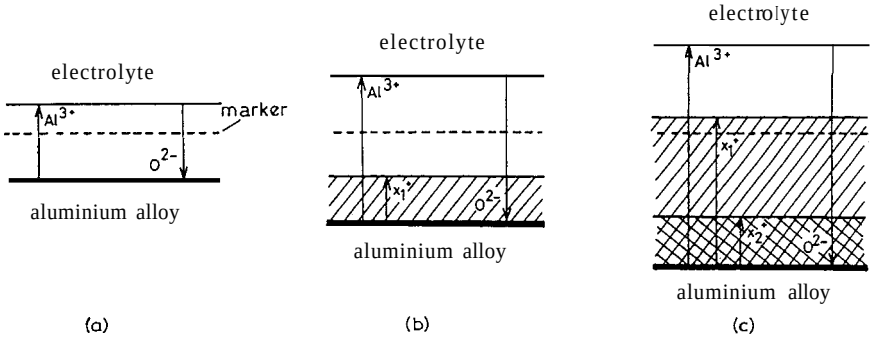


Fig. 6-65. Schematic diagrams illustrating the formation of an anodic film at high faradaic efficiency on a ternary aluminium alloy revealing alloy enrichment.
(a) Initial formation of a relatively pure alumina film, neglecting the incorporation of foreign species from the electrolyte, with progressive accumulation of both alloying elements in a thin alloy layer just under the film.
(b) Oxidation of alloying element 1 at the alloy/film interface following sufficient enrichment of the enriched alloy layer. Enrichment of alloying element 2 continues during the growth of an anodic film containing alloying element 1 species, X^{+}_{1}, which migrate outwards in the film. The hatched area corresponds to the region of film containing alloying element 1 species.
(c) Oxidation of alloying element 2 at the alloy/film interface following sufficient enrichment of the alloy layer. Both alloying elements are now incorporated into the film at the alloy/film interface, in their approximate alloy proportions, and migrate outwards in the film. The cross-hatched area corresponds to the region of film containing species of both alloying element 1 and 2.[308]

As expected, enriched layers are produced by anodizing sputter deposited AI-1.9 at%W alloy.[309] Also, similar to work on superimposed layers, fingers of WO,, developed into the anodic alumina film. It was observed that transient fingers developed from discrete sites, of about 1-2 nm spacing, which were believed to be tungsten-rich clusters of critical size. The fingers were limited in length to about 5 nm probably due to the limited thickness of the enriched layer. Thus tungsten was incorporated discontinuously into the anodic film at local sites, with alternating local depletion of tungsten in the enriched layer by formation of the finger from a tungsten-rich cluster of critical size, and subsequent enrichment of tungsten, to redevelop clusters, by oxidation of aluminium (Fig. 6-66).

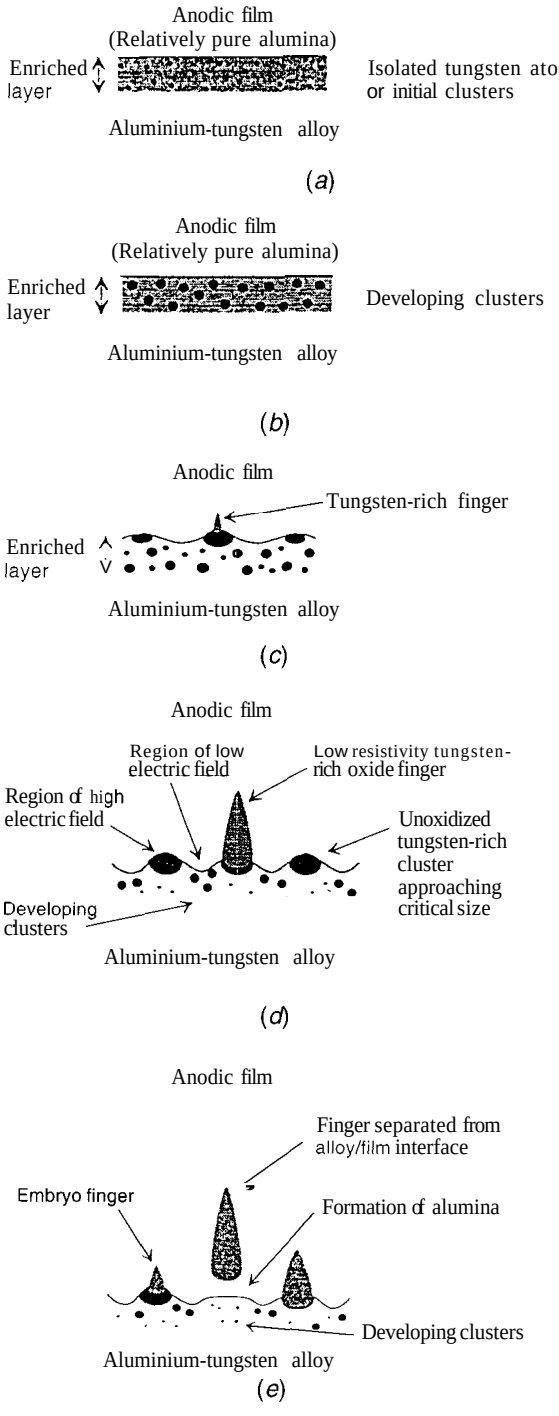


Fig. 6-66. Schematic diagrams illustrating possible mechanisms of formation of fingers at the alloy-film interface during anodic oxidation of Al-1.9 at%W alloy. **(a)** Initial **growth** of relatively pure alumina film; (b) development with further film growth of tungsten-rich clusters beneath a relatively pure alumina film; (c) formation of fingers of tungsten-enriched oxide on reaching the critical cluster size; (d) details of formation of fingers at tungsten-enriched clusters; (e) detachment of fingers from the alloy film interface, and their dispersal in the anodic alumina by the ionic transport processes.[309]

When a solution treated Al-1.5 wt% Cu alloy, chemically polished to produce surface enrichment to the critical level, is anodized in an ammonium pentaborate solution, the resulting anodic film only contains copper at a concentration about 44% of that in the alloy.[306] This is because copper ions are more mobile than aluminium ions through the anodic film under the field, and on reaching the film/electrolyte interface are ejected into the solution. Otherwise, a layer of copper oxide or hydroxide would develop at the outer surface of the alumina film, which has not been observed. Flaws develop in the anodic film, which act as a barrier to copper migration and lead to differential copper concentrations in different parts of the film. It has been found that 50% or less of the copper ions appear to be mobile, which implies that the unimpeded mobility of copper ions is not greater than 3.7 times that of the aluminium ions.

It has been proposed that copper ions migrate into the anodic film from mobile clusters of atoms and vacancies.[310] As they develop further during the oxidation and diffusion of aluminium into the film, they may come to constitute obstacles to aluminium diffusion. These circumstances may promote the oxidation of copper, which produces oxide of lower resistivity than the aluminium oxide. Consequently, this tends to lead to the development of fingers of copper oxide extending into the film, in a similar manner to the situation referred to above for superimposed layers. However, for the copper-containing alloy, the cluster is rapidly consumed so the growth of an individual finger cannot be sustained. Rather, a series of embryo fingers are produced from different sites as clusters are generated and oxidized.

A further effect occurs with certain alloying elements. For copper and chromium, oxidation after enrichment is also associated with oxygen gas generation within the anodic film.[307,311] It is believed that this is related to the semi-conducting properties of the alloying element oxide. Thus, oxygen gas accummulates at relatively high pressures in voids, and can cause local rupture of the barrier type films. Similar effects occur for certain precipitates, eg the θ phase in Al-Cu alloys, which leads to the cracking of porous films with subsequent electrolyte access to the precipitate, dissolution and eventual reanodizing. Consequently, many alloys with strengthening phases have anodic films with extra porosity above that normally expected for porous anodizing.

Other alloying elements can lead to other effects. The presence of magnesium, zinc, gold or gallium can lead to the loss of the anodic film from the anodized binary alloy surface.[311,312] This is related to the development of voidage at the alloy/film interface, with or without enrichment of the alloying element, where the alloying element may be associated with low Pilling Bedworth ratio and cation mobility. Whereas magnesium is not enriched at the surface because its oxide has a lower Gibbs free energy per equivalent for formation than aluminium oxide, zinc is enriched to at least 7.8 at% over a layer thickness of about 10 nm.[313]

Considerable detailed scientific understanding of the effects of second phase and solid solution composition on anodizing is currently being generated.

Interestingly, much of this is also relevant to etching and brightening processes as well as reactive pretreatment systems. Clearly, we still await the full integration of these concepts. Then, a full understanding of the events taking place during the treatment of complex commercial alloys and the arising surface properties can be attempted. One recent publication includes an analysis of the roles of the elements present in a two-phase, high-strength aluminium alloy containing $Al_{13}(Fe,V)_3Si$ dispersoids, where the concepts of enrichment, mobility and oxygen evolution are invoked.[314]

Surfaces

O'Sullivan, Hockey and Wood"'" used infra-red spectroscopy and deuterium exchange to investigate the water and/or hydroxyl content of porous films produced in sulphuric acid. They showed that the crystallites of which the film was composed were anhydrous, but with hydroxyl groups adsorbed onto their surfaces. They described the film as composed of a relatively open array of amorphous, largely anhydrous alumina crystallites which carry hydroxyl groups or ions, and are permeated by molecular water and probably acid anion.

Imai and Nishio[316] have estimated the number of active surface hydroxyl groups on treated aluminium surfaces by analysing their interaction with zinc ions and epoxy polymers. They found the highest levels, 330-680 OH^-/nm^2, for phosphoric acid anodized surfaces.

The surface electrochemistry of anodic films formed in phosphoric and oxalic acids, and separated from their substrates to produce hydraulically permeable membranes,[125] has been determined using electro-osmosis techniques, hydrogen-ion titration, and modelled based on electrical double-layer theory.[317] The surfaces of the pores were described as comprising a three-dimensional array (gel) of charged groups where counter-ions may penetrate to a depth of about lnm. Results are given in Table 6-1I. These show that there is a higher density of ionizable phosphate than oxalate groups on the surfaces, and the total number of ionizable sites is much less than determined by Imai and Nishio.[316] The pH_{iep} is the iso-electric point, the pH where the ζ potential is zero. The experimentally determined pK values were ascribed as follows: pH7 to incorporated phosphate, pH6.5 to aluminium oxide surface groups, and pH4 to oxide surface groups and to incorporated oxalic acid.

Ludwig and Hönicke[318] have found the iso-electric points of anodic films grown in sulphuric, oxalic and phosphoric acids to be at pH 6.1, 6.8 and 6.9 respectively.

Cordier and Olliver[319] have used X-ray photoelectron spectroscopy to compare chromic- and phosphoric-acid anodized films and several pretreatment films. Residual energy shifts between the spectra were observed, which could be attributed to differences in the Fermi energy values between the treated aluminum surfaces. They proposed, based on this parameter, a classification of the relative Lewis

acid-base characteristics. On this basis the chromic-acid anodized film had slightly lower Lewis acidity, while the acidity of both types fell due to ageing or hydrothermal treatment.

TABLE 6-11

Surface properties of porous anodic films

Parumeter	*H_3PO_4-Film*	*$(COOH)_2$-Film*
Counterion penetration depth*(nm)	1.1	0.7
No. of ionizable surface sites*(nm^{-2})	2.5	1.0
Ratio of no. of ionizable-oxide to -acid anion sites*	2.0	2.6
pH_{iep} (10^{-2}mol/l solution)†	3.05	3.75
pH_{iep} (10^{-3}mol/l solution)†	4.51	4.03
ζ potential at pH 7 (mV)	–100 to –200	–10 to –15
pK_1^*	4.1 (4†)	4.0 (4†)
pK_2^*	5.0	*5.0 (6.5')*
pK_3^*	6.9 (7†)	3.6

* Data from the model

† Experimental data

Mullins and Averbach[320] used bias-reference X-ray photoelectron spectroscopy and determined the Fermi energy levels of etched and anodized aluminium alloy surfaces (AA6061 and AA5052) relative to those of bulk oxide crystals. Using a previous correlation between point of zero charge (pzc) and Fermi energy levels in aluminium oxide powders, they determined the pzc values of the surface oxides, i.e. the pH at which there is no net surface charge. Results for anodized surfaces are given in Table 6-12. They described the significance of their results in terms of adhesive bonding of aluminium. The high Lewis acidity can increase the reactivity of surfaces with common hydroxyl-functional polymeric systems, which explains the applicability of such surfaces as preparations for painting or adhesive bonding. The increased reactivity of the surfaces makes them more susceptible to the wetting and spreading by organic coating formulations. However, they will also tend to react with any water in the environment to form stable stoichiometric oxides and hydroxides. This explains why paints and adhesives bond well initially but tend to lose strength on exposure to water. The exception is phosphoric acid-anodized surfaces which are protected from reaction with water by the presence of phosphate groups.

TABLE 6-12

Fermi energy levels and values of the point of zero charge (pzc) of anodized surfaces

Alloy	*Surface*	*Fermi Level (eV)*	*PZC*
AA6061	as-received	4.5	7.8
	chromic acid anodized	4.8	4.2
AA5052	phosphoric acid anodized	5.0	3.6
	chromic acid anodized	4.2	5.9
	phosphoric acid anodized	4.7	4.2

Fermi levels were computed from Al2p shifts using sapphire as a standard with E_F=3.6 eV

Lopez *et al*[227] cross-compared a range of techniques to investigate hydration/hydroxylation and acid/base properties. Their findings were relative. They found that phosphoric acid anodized films are slightly hydroxylated and hydrated but are very basic. In contrast, boehmite films which would represent a hydrothermally sealed surface, were highly hydroxylated, only slightly hydrated but again very basic. Using a simple peel test, they found that either of these surfaces is good for adhesion.

Bemstein and White[321] have reported that a wet porous anodic film on aluminium acts as a transducer for ultrasonic waves (piezoelectric-like behaviour). In response to an acoustic wave, there is movement of charged liquid within a Debye length of the pore walls, which creates an electrical current and externally measurable alternating voltage. Although the authors did not give values for surface charge density on the pore walls, they were able to use results to calculate the pore diameter, 9.4 nm, of films formed in 10% sulphuric acid at 20°C with 160 A/m^2.

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CHAPTER 7

Decorative and Protective Anodizing

1. INTRODUCTION

Anodizing has been known since the 1920's but it was not until after the war that the process really developed in commercial importance. The first process to be introduced was the Bengough-Stuart' chromic acid process developed in 1923 for the protection of Duralumin seaplanes. The process is still used in Britain, including the complicated voltage cycle made mandatory by Defence specifications, although there is no technical reason why the voltage should not be raised to its maximum value in the shortest possible time. In America it was replaced to some extent by an accelerated process which used a more concentrated solution and operated at a constant voltage, thus facilitating the use of automatic plant. A further modification of this process was developed in America by Battelle,[2] in which a 5-10% chromic acid solution was renewed with sulphuric acid.

The most widely used processes are those based on sulphuric acid, and the first of these was patented by Gower and O'Brien[3] in 1927 in the U.K., though the industrial development of these processes first took place in the U.S.A. Other early developments included the use of oxalic acid by Japanese workers and the widespread use of this process in Germany! In much more recent times phosphoric acid anodizing has found significant commercial importance particularly as a replacement for chromic acid anodizing in the aerospace industry and as a pretreatment for organic coatings.

A very large number of anodizing electrolytes appear in the patent literature, but most of those practically used are based on the four acids just described. Table 7-1 summarises the most common conditions used with these electrolytes. It must be remembered however that operating conditions may vary within wide ranges, and those given are typical procedures used for commercial purity aluminium.

TABLE 7-1

Some anodizing processes in use for decorative and protective applications

Type of process	*Name or Description*	*Electrolyte composition (weight %)*	*Current (A/dm²)***	*Voltage*	*Temp (°C)*	*Treatment time (min)*	*Colour*	*Film thickness*		*Applications*
								(μm)	*(mil)*	
Chromic acid	Bengough-Stuart*	CrO_3 2.5-3%	d.c. 0.1-0.5	0 → 40 40 40 →5 0 50	40	10 20 5 40' 5	Opaque grey	2-15	0.1-0.6	For protection, more rarely for decoration Not far allays containing more than 5% heavy metals
	Accelerated chromic acid	CrO_3 5-10%	d.c.0.15-0.30	40	35	30	Opaque grey	2-3	0.08-0 12	Coatings not sealed
Sulphuric acid	Alumilite, Eloxal GS	H_2SO_4 15-20%	d.c 1-2†	14-22	18-25	10-60†	Transparent colourless	3-35	0 1-1.2†	Hard, protective coatings, good base for dyes. Sealed for max. corrosion resistance. Not used an work with joints.
	Hard Anodizing (see also Chapter 8)	H_2SO_4 7%	d c 2-5	23-120	-5 –+5	Up to 240	Greyish	Up to 250	Up to 10	Max wear resistance and absorptive capacity, i.e., for lubricants
Oxalic acid	British and American practice	$(COOH)_2$ 5-10%	d.c. 1-2	50-65	30	10-30	Semi-transparent	15	0.6	
	Eloxal GX	$(COOH)_2$ 3-5%	d.c. 1-2	40-60	18-20	40-60	Yellow	10-65	0.4-2.5	Both protective and decorative. Now largely supplanted by sulphuric acid
	Eloxal GXh	$(COOH)_2$ 3-5%	d.c. 1-2	30-35	35	20-30	Almost colourless			
	Eloxal WX	$(COOH)_2$ 3-5%	a c. 2-3	40-60	25-35	40-60	Yellowish			
	Eloxal WGZ	$(COOH)_2$ 3-5% (1)	d c 2-3 d c. 1-2	30-60 40-60	20-30	15-30	Yellowish			
	Thick films	(2) $(COOH)_2$ 3-5%	d.c. 1-2	40-60	3-5		Yellow	Up to 625	Up to 25	As thick H_2SO_4 films
	Ematal	$(COOH)_2$ + Ti, Zr or Tl	d.c. 0 2-0.3 until voltage is 120 V, then voltage is kept constant		50-70	20-40	Opaque porcelain or enamel tone	10-20	0.4-0 7	Protective or decorative, particularly for non-metallic appearance.
Phosphoric acid	Boeing process	H_3PO_4 10%	d.c.	10-12	23-25	20-30	Colourless	1-2	< 0 1	Thin films for adhesive bonding purposes
Boric acid	Condenser processes	H_3BO_3 9-15% Borax 0-0 25%	d.c. d.c	50-500 230-250	90-95		Iridescent	0.25-7 5	0.01-0.3	Thin dielectric films for electrolytic condensers

* The original Bengough-Stuart patent recommends a slightly longer voltage-time cycle lasting 60 rnin. The cycle given is the one in common practice at the present time.

** 1 A/dm^2 = 10 amp/sq. ft.

† Various concentrations and conditions are used for different applications, for each of which, however, operating conditions are often critical.

2 THE BASIS METAL

Alloy behaviour

In general pure aluminium anodizes better than its alloys, and an appreciable difference is to be detected between the appearance of coatings produced on the various grades of aluminium. The difference between commercial-quality material (99%) and super-purity aluminium (99.99%) is particularly noticeable. The appearance or performance in service of anodized alloys is closely connected with the whole metallurgical history of the alloy production, which determines whether the additions or impurities are in homogeneous solid solution, as intermetallic compounds within the grains, or as precipitates at the grain boundaries. The size and shape of the intermetallic compounds and their composition also affect behaviour, and the anodic response depends on whether they are oxidized, dissolved or remain inert during treatment. This will be discussed later.

Tables 7-2 and 7-3 give general guidance on alloy behaviour with respect to those suitable for protective anodizing, decorative and colour anodizing, bright anodizing and hard anodizing. Most aluminium alloys can be provided with an anodic oxide coating which is moderate to good, provided that the appearance is of no great concern and that protection is the objective. Also, for general decorative work, the majority of these will be satisfactory provided that they do not become excessively dark or patchy. However, where brightness is the primary requirement there are few alloys to choose from, as the table indicates, only metal of high purity being classed **as** excellent. In the case of hard anodizing characteristics the comments are based on the ability to produce a satisfactory 50 micron anodic coating.'

In general, wrought alloys are superior to cast alloys for anodizing due to their greater homogeneity, the smaller particle size of impurities, lesser porosity, as well as the fact that the chemical composition of cast alloys, especially those containing high silicon, makes them less suitable for anodizing purposes.

Among the wrought alloys the Al-Mg alloys (5000 series), and the Al-Mg-Si alloys (6000 series) with or without small additions of manganese, produce the best decorative and protective coatings, and Al-Zn-Mg alloys (7000 series) are also good.[6] Alloys containing appreciable amounts of copper and other heavy metals, e.g., Duralumin (2000 series) alloys, usually produce coatings of inferior colour, and lower protection.

The role of intermetallics

The effect of intermetallic compounds in the metal matrix depends on the extent to which they can be taken into solid solution, because up to this point a solution heat treatment may produce a complete dispersion of the second phase, and by rapid cooling this uniformity may be sustained without the growth of

TABLE 7-2

Guide to selection of finishes for wrought alloys

Material Designaiion (BS 1470-75)		*Nominal Composition*	*Suitabilityjor*				
			Protective anodizing	*Anodizing and dyeing*	*Bright anodizing*	*Hard anodizing*	*Electro-plaiing*
	(1)	99.99%Al	E	E	E	E	–
1080 A	(1A)	99.8%Al	E	E	E	E	–
1050 A	(1B)	99.5%Al	E	VG	VG	E	VG
I200	(1C)	99.0%Al	VG	VG	VG	E	VG
2011	(FCI)	Al-5.5%Cu, 0.4%Pb, 0.4%Bi	M-G	M-G*	U	G	–
2014A	(H15)	Al-4.25%Cu, 0.75%Si, 0.75%Mn, 0.5%Mg	M	M*	U	G	VG
2031	(H12)	Al-2%Cu, 1%Ni, 0.9%Mg, 0.8%Si	M	M*	U	G	VG
3103	(N3)	Al-1.25%Mn	G	G	M	G	G
3105	(N31)	Al-0.6%Mn, 0.5%Mg	G	G	M	G	–
4043A	(N21)	Al-5%Si	G	M*	U	G	t
5005	(N41)	Al-1%Mg	E	VG	G	E	–
5056A	(N6)	Al-5%Mg	G	G	M	E	t
5083	(N8)	Al-4.5%Mg, 0.7%Mn, 0.15%Cr	G	G	M	G	t
5154A	(N5)	Al-3.5%Mg, 0.3%Mn	VG	VG	G	E	†
5251	(N4)	Al-2.25%Mg	VG	VG	G	E	†
5454	(N51)	Al-2.7%Mg, 0.75%Mn	VG	VG	G	E	–

6061	(H20)	Al-1%Mg, 0.6%Si, 0.2%Cr	VG	G	M	VG	†
6063	(H9)	Al-0.75%Mg, 0.4%Si	E	VG	G	E	†
6082	(H30)	Al-1%Mg, 1%Si, 0.7%Mn	G	G	M	G	†
6463		99.8%Al-0.75%Mg, 0.4%Si	VG	VG	VG	VG	–
7020	(H17)	Al-4.5%Zn, 1%Mg	G	G	M	G	–

E Excellent; VG Very Good; G Good; M Moderate; U Unsuitable

* Only suitable for dark colours

† A modified etching technique prior to plating is essential and some initial difficulties may occur

TABLE 7-3

Guide to selection of finishes for cast alloys

Material Designation (BS 1490)	*Nominal Composition*	*Suitability for*			
		Protective anodizing	*Anodizing and dyeing*	*Bright anodizing*	*Electro-plating*
LMO	99.5%Al	VG	VG	VG	VG
LM2	Al-10%Si, 2%Cu	M	U	U	M‡
LM4	Al-5%Si, 3%Cu	G	M*	U	M
LM5	Al-5%Mg	VG	VG	G	M§
LM6	Al-12%Si	M	U	U	M‡
LM9	Al-12%Si, 0.4%Mg	M	U	U	M‡
LM10	Al-10%Mg	VG	M†	U	U
LM12	Al-10%Cu, 2.5%Si	M	M*	U	G
LM13	Al-11%Si, 1%Cu, 1%Mg, 1.5%Ni	M	U	U	M‡
LM16	Al-5%Si, 1%Cu, 0.5%Mg	G	M*	U	M‡
LM18	Al-5%Si	G	M*	U	M‡
LM20	Al-12%Si, 1%Fe, 0.5%Mn	G	M*	U	G‡
LM21	Al-6%Si, 4%Cu, 2%Zn	M	U	U	M‡
LM22	Al-5%Si, 3%Cu, 0.5%Mn	G	M	U	G
LM24	Al-8%Si, 3%Cu, 1.3%Fe	M	M*	U	M‡
LM25	Al-7%Si, 0.5%Mg	G	M*	U	M‡
LM26	Al-10%Si, 3%Cu, 1%Mg	M	U	U	M‡
LM27	Al-7%Si, 2%Cu, 0.5%Mn	G	M*	U	G‡
LM28	Al-19%Si, 1.5%Cu, 1%Mg, 1%Ni	U	U	U	M‡
LM29	Al-23%Si, 1%Cu, 1%Mg, 1%Ni	U	U	U	M‡
LM30	Al-17%Si, 4.5%Cu, 0.5%Mg	U	U	U	M‡

E Excellent; VG Very Good; G Good; M Moderate; U Unsuitable
† Anodizing conditions must be carefully controlled for good results
‡ These alloys containing silicon require a modified treatment to get good adhesion

* Only suitable for dark colours
§ Can be plated satisfactorily but not recommended

coarse precipitates. Much depends on how readily these precipitates form, at what temperatures, and whether the necessary metallurgical operations can be performed without detriment. Table 7-4[7] shows the solubilities of the principal impurities and alloying additions at three temperatures; it is quite clear from these why iron is in a class of its own by remaining almost completely insoluble up to 600°C. This is the reason why, when alloy purities are referred to in connection with bright anodizing, it is usually the iron content which is implied, i.e. 99.8% base purity will have an iron content of less than 0.08% but several other elements may also be present.

TABLE 7-4

Solid solubility of alloy constituents and impurities in aluminium'

Element	*Wt.% soluble in the matrix at* 20°C	300°C	500°C	*Eutectic temp.*	*Eutectic Temperature "C*
Fe	*0.005*	0.005	0.006	0.05	655
Si	0.01	0.1	0.8	1.65	577
Cu	0.1	0.45	4.05	5.7	548
Mg	1.9	6.7	–	17	450
Mn	–	–	0.35	1.4	658
Cr	–	0.015	0.19	0.72	660
Ti	–	–	0.08	0.12	660
Zn	*2*	37	–	**82**	382
Ag	0.5	3.2	28	55.6	566
Mg_2Si	0.3	0.3	1.0	1.8	595
$MgZn_2$	0.5	4.5	–	17	475

The anodic coating on 99.99% purity aluminium will be clear and transparent when formed in sulphuric acid, but with iron at 0.08% it is slightly less clear and becomes increasingly cloudy as the film thickness is increased, while when iron is at 0.3%, a typical level for 99.5% purity metals, the coating becomes quite grey in comparison. It may be a uniform light grey colour, or striated or mottled according to the distribution of the iron-containing constituent in the primary cast structure.

A large number of intermetallic compounds may be formed in aluminium alloys, the following representing the principal binary, ternary and quaternary compounds (silicon out of solution in high silicon alloys is normally present as elementary particles of the metal).

$FeAl_3$ Mg_5Al_8	$(Mn,Cu)Al_6$
Mg_2Si $(Fe,Mn)Al_3$	$(Mn,Fe,Cr)Al_6$
$CuAl_2$ $(Fe,Cr)Al_3$	α-AlFeSi
$MnAl_6$ $(Fe,Cu)Al_3$	*a*-AlFeCuSi
	β-AlFeSi
$CrAl_7$ $(Fe,Mn,Cr)Al_3$	α-AlFeMnSi
$TiAl_3$ $(Mn,Fe)Al_6$	*a*-AlFeCrSi
$NiAl_3$ $(Cr,Mn)_2Al_1$,	

Keller and Edwards,[8] who conducted a series of experiments on the effect of impurities, found that silicon was not oxidized or dissolved during treatment, while intermetallic compounds such as $CuAl_2$ and the β-Al-Mg phase (which occurs in certain aluminium-magnesium alloys) were oxidized or dissolved much more rapidly than aluminium, with the result that the coatings produced were thin, rough and porous. Intermediate between the two extremes were constituents such as $FeAl_3$, the a-Al-Fe-Si phase, and $MnAl_6$ of which part was dissolved and part remained in the coating, and which affected the colour, transparency and continuity of the film to varying degrees.

Fischer, Budiloff and Koch[9] anodized intermetallic compounds separately. Among those which took oxide films were Al_6Mg, $FeAl_3$, $CuAl_2$ and silicon. Others, e.g., Al_3Zn_2 and Pb, were partly dissolved and partly anodized, while Mg_2Si, $Al_3Mg_2Zn_3$ were dissolved.

Work by Lacombe in France[10] has shown that silicon and silicon-rich phases as well as Al_6Mg are oxidized much more slowly than aluminium and thus remain dispersed in the anodic coating with loss of transparency, while Al_3Mg_2 and $CuAl_2$ oxidize at a faster rate and may leave gaps in the oxide film.

Guminski, Sheasby and Lamb[11] have studied the common intermetallics in considerable detail to assess the effects of caustic soda etching, chemical brightening in a phosphoric acid type brightener, and anodizing in oxalic acid on the intermetallic as compared with the aluminium matrix, and these useful results are summarised in Table 7-5. Sheasby and Short have extended this work to cover more complex constituents[12] but at the time of writing only the effects of caustic soda etching have been published. Cote *et al.* have also published the results of similar studies.[13]

More fundamental work on model binary alloys by workers at UMIST[14,15] have shown that enrichment of the alloying elements occurs in a layer 1-5nm in thickness just beneath the anodic film. This is a direct consequence of the formation of the anodic film, but has also been found to occur with other processes such as chemical polishing and alkaline etching. A very elegant piece of work by Shimizu *et al.*[16,17] showed by means of ultramicrotomy, the effects occuring during the anodizing of an AI-Fe alloy with $FeAl_3$ and $FeAl_6$ particles present.

More recently Forsyth[18,19] has studied the effect of aluminium microstructure and the role of intermetallics during hard anodizing. He found similar results on intermetallics to other workers, but he saw that coarse intermetallic particles that entered the oxide film unchanged produced a dimpling at the aluminium / oxide interface. This is similar to the effects seen by Cooke[20] and referred to in Chapter 3 (fig. 3-30). However Forsyth saw that the dimples were accompanied by shallow cracks in the oxide, and these were thought to indicate high stresses in the oxide resulting from the uneven growth rate in the vicinity of the particles.

Perhaps the most extreme cases of included second-phase particles are the metal matrix composites in which SiC is added for strengthening purposes. Anodizing of such material appears to present a problem, but Shahid[21] has shown that, after sulphuric acid anodizing, although the anodic film thickness was not uniform, it afforded adequate corrosion resistance to cope with hostile environments. He found that the silicon carbide particles were occluded within the film, forming an integral part of it.

TABLE 7-5

The reaction rate of constituents"

Treatment	*constituents more reactive than matrix*	*Constituents equally reactive with matrix*	*Constituents less reactive than matrix*
Etching in 10% sodium hydroxide solution	Mg_2Si, $MnAl_6$, $CuAl_2$ *	$FeAl_3$, $NiAl_3$	Si, $TiAl_3$, β-AlMg, $CrAl_7$
Anodizing in oxalic acid electrolyte	Mg_2Si, $CuAl_2$, β-AlMg, $CrAl_7$	$FeAl_3$	Si, $TiAl_3$, $NiAl_3$, $MnAl_6$
Chemical brightening	Mg_2Si	$FeAl_3$, $NiAl_3$, β-AlMg, $MnAl_6$, $CuAl_2$	Si, $TiAl_3$, $CrAl_7$

* Only marginally more reactive than the matrix

Appearance of anodized alloys

The effects of the various alloying elements in the commercially marketed aluminium alloys may be briefly summarised thus:

Iron – is the principal impurity which detracts from the specular brightness of the high purity bright anodizing alloys, even in quite small amounts. Iron additions to 99.99% aluminium lead to dark grey or black streaks, and these occur in ordinary pure metal when iron:silicon ratios are very high, e.g., 7:1.

Silicon – leads to cloudiness when out of solution, but about 0.8% can remain dispersed. It is beneficial with the iron impurity. In magnesium alloys silicon goes more readily into solution. At the 5% level, alloys anodizing to dark grey or black are obtainable.

Titanium – detracts from brightness in the same way as iron, but is added to produce fine grain. Along with boron it also promotes nucleation helping to get a fine uniform structure.

Magnesium alloys – can give clear colourless coatings for magnesium up to 3%, probably because magnesium oxide has **a** refractive index (1.736) very near to **that** of aluminium oxide (1.69).

Copper – up to 2% can give alloys with a clear protective coating in the solution treated condition. At higher copper levels the coating is more discoloured, anodizing becomes more difficult and the coating is softer with less protective value.

Manganese alloys – up to 1% Mn, may anodize to clear silver, grey, brown or mottled according to production history and particle size of the constituent. With the thicker anodic films manganese contents of 0.3-0.5% give quite brown anodic oxide coatings on all of the alloys where the metal is present.

Zinc alloys – form good protective coatings with zinc up to 5%. These may be colourless when homogeneous or quite brown or marbled in appearance when second phase precipitates are present.

Chromium – at *0.3%* leads to coatings which are yellow in colour.

The above brief summary is a general statement of what might be expected to happen but would require a great deal of qualifying to describe the situation in full.

Anodizing quality aluminium

Wrought products

The production of anodizing quality aluminium is not merely, or even mainly, a matter of the composition. The metal producer will certainly note in detail the chemical analysis of the primary cast rolling blocks or extrusion billets, but he will also see to it that the liquid metal is suitably degassed, cleaned or filtered, and cast in such a manner that entrained oxide is excluded and heat extraction proceeds in a steady predetermined manner to promote a fine grained and uniform metallurgical structure.[22,23,24,25,26,27,28,29,30,31,32]

To this end suitable nucleants containing titanium and boron may be added.'' After this the cast metal may be subjected to a prolonged high temperature soak at only a few degrees below the solidus temperature to dissolve or disperse the constituents, and from then on the production procedure will be designed to prevent the formation of precipitates of coarse intermetallic particles. This tends to occur at the intermediate temperatures used for artificial ageing of heat-treatable alloys, but fortunately the alloys in common use for anodizing will normally develop their maximum properties before the precipitates have grown to a point where the metal begins to darken after anodizing.

In addition to the above, the production schedule will also be designed to avoid damage or excessive die lines in extruded profiles, and in the case of rolled sheet meterials, to minimise rolling lines, reticulation or rolled-over damage. The designation 'Anodizing Quality' refers, therefore, more to a production schedule than to a metal composition.

The metal surface may be host to a whole catalogue of effects which will relate to either the basic metallurgical structure of the primary cast material; to gas or non-metallics associated with the liquid metal; to mechanical tearing or scoring; to adhesion between the metal and rolls giving roll-coating effects; to fine transverse fracturing (reticulation); or many other causes. Herenguel and his co-workers[33,34,35] have described some of these effects and have also described a 'Hyper hot working process' as a method for producing controlled surfaces on extruded metal. Insufficient homogenising may result in bands of metal structure which follow the direction of rolling. Lacombe has shown that bands of Al_3Mg_2 may lead to striations of a dark colour after anodizing.'" The work of Sendorek and Thomas'' has shown how structural effects coming from the primary casting operation can affect the structure of extruded products, but it is in the case of the highly specular finishes produced by bright anodizing high purity materials that the need for uniformity is most great. Tuebler[30] has described the production techniques used to produce these products with sufficient uniformity, indicating the importance of the method of casting and showing the various types of structural variation that can arise. Lelong, Sabetay and Tigeot[31] have also pursued the same theme in France. Cooke and Spooner[36] have investigated the effect of alloying and impurity elements on the bright anodizing characteristics of AI-1% Mg sheet alloys. The beneficial brightening effect of copper, either in the alloy or in the brightening solution was noted, and alloys containing second-phase constituents generally showed a reduction in bright anodizing quality. They concluded that, to produce an alloy with good bright anodizing characteristics, the alloys employed should be completely single-phase, or essentially single-phase, with any second-phases dispersed sub-microscopically. Alloying elements such as copper, magnesium and zinc have the required high solubilities, and additions of combinations of these are frequently used for bright trim materials.

The reasons why second-phase particles can have such a marked effect on the brightness of bright anodized materials has been described by Cooke[20] and has

already been discussed in Chapter 3. However it is important to understand the formation of the 'conical asperities' which he describes (Fig. 3-30), and to realise that the degree of roughness produced is dependent on the anodizing voltage used.

The effect of grain size on anodizing quality varies with the alloy in question and the particular surface treatment applied. In general the anodizing process may reveal patterns related to the distribution of intermetallic constituents, which tend to survive recrystallization procedures, but the grains of the metal are not necessarily brought into evidence. However, a preliminary etching treatment may well reveal the grain structure, and a non-uniform rate of reaction in electro- or chemical polishing processes can also do the same thing. **Also,** mechanical deformation or bending of metal with coarse grain can produce an appearance of orange peel. For these reasons, therefore, a fine grain size is sought with diameters below 100μm. The growth of large grains may take place during annealing to an extent which is critically dependent on the treatment prior to annealing, and high purity metal is particularly prone to this, while alloys containing manganese or chromium are much easier to produce with consistently fine grain.

The annealing treatment can also be accompanied by the formation of precipitates which detract from the brightness or image clarity of the anodized material so that soft temper materials may often be inferior to the metal in the hard condition, but this is not necessarily so. Intermediate tempers in the case of rolled sheet or strip may be produced either by temper-rolling of the recrystallized product with sufficient cold work to produce the desired hardness, or by rolling in hard temper to the final gauge and then softening by partial annealing or 'temper-letting-down'. It has been stated that the latter procedure produces material of better anodizing quality[37,38] and is often used for bright-anodizing qualities, but production schedules for the multifarious products are vastly complicated and the metal producer will select the route best suited to the circumstances, knowing the effect of each step on the final product. Scharf[28] and also di Russo[29] have discussed the importance of avoiding Mg_2Si precipitates in Al-Mg-Si alloys for anodizing. Workers at Pechiney[39] have described both compositional and fabrication procedures affecting the properties of anodized surfaces. They again highlight the importance of second-phase particles and indicate their effect in both bright and matt anodizing.

Franz[40] has studied metallurgical factors affecting the etching and anodizing characteristics of 6063 alloy extrusions and concludes that, in terms of composition, iron content has the most significant effect, the higher iron contents (> 0.20%) favouring development of a more matt surface. Ingot homogenisation and extrusion practices affect caustic etching response to a lesser degree, with more diffuse surfaces favoured by lower billet pretreat temperatures. Artificial ageing practice had the most significant effect on final etched and anodized appearance, with material aged to peak hardness (T6) giving the most pleasing satin appearance; overaged material (T52) and naturally aged material (T4)

gave the most specular appearance. Defects such as 'soft spots' or 'hot spots' caused by localised cooling and reheating and consequent coarse Mg_2Si precipitation[41] (Fig. 7-1), spangling or galvanizing (Fig. 4-12), and streaking are also discussed. **A** paper by Hauge and Karhausen[42] looks at a whole range of extrusion parameters that affect the anodizing quality of 6000 series alloys, and they point out that many extrusion processing defects are only detected at the etching and anodizing stage. This means that good communication between the extruder and the anodizer is essential.

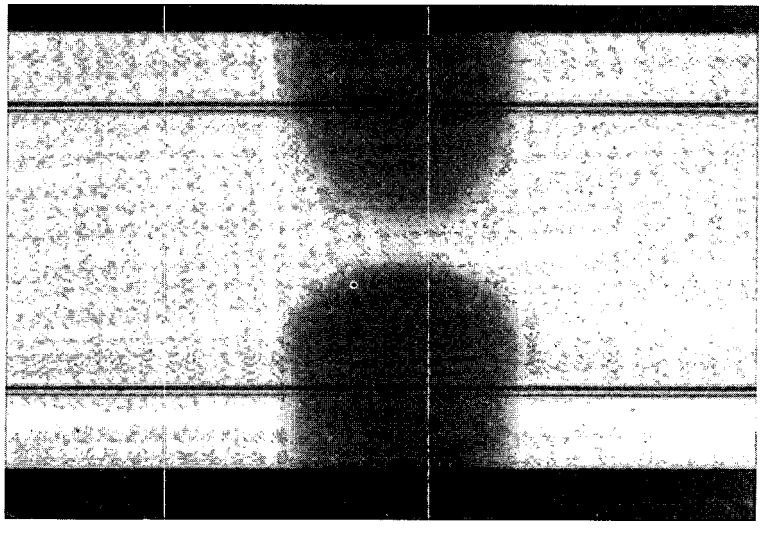


Fig. 7-1. 'Hot spot' on etched and anodized 6063 extrusion

Such metallurgical defects are discussed very usefully by Short and Bryant,[43] who describe and illustrate both metallurgical and processing defects. The origin of the defects concerned and the stage at which they become visible in the anodizing process is detailed. Surface defects on extrusions have also been studied by Wyman,[44] and Brace has published a book on anodizing defects.[45]

Castings

Castings, in the nature of things, are not amenable to the treatments that can be given to wrought products, and what can be done to improve quality and response to anodizing is much more limited. Gravity die-castings are more suitable for anodizing than sand castings, the latter requiring most pretreatment. Schenk[6] lists

Al-Mg-Si (Si 2.5% max.), Al-Mg and Al-Zn-Mg type casting alloys as being the most suitable for decorative anodizing. According to Smith[46] sand-castings do not dye satisfactorily owing to blow-holes and porosity, while pressure die-castings produce a dark and patchy coating. Among gravity die-castings the binary Al-Mg and Al-Cu alloys containing more than 95% aluminium are satisfactory, while ternary and quaternary alloys, e.g., LM4, are of restricted value for decorative anodizing due to uneven segregation effects which can, however, be overcome to some extent by solution heat-treatment. Low pressure castings will usually produce better anodizing results than high pressure die-castings. Keskulla and Edwards[47] have produced light, attractive and corrosion resistant coatings on die-casting alloys containing 8% magnesium, and on alloys containing 2% copper and 2% nickel. The Al-8% Mg alloy, however, suffers from the disadvantage of producing a considerable amount of dross and tends to entrap mould lubricants in the surface.[48]

Castings which are anodized for motor trim in the U.S.A. include pure aluminium and aluminium-4% zinc-1% iron alloy. In Britain an aluminium-3% magnesium-1% manganese alloy has been found suitable for anodizing, and considerable quantities of low pressure die-castings in aluminium-2% copper-1% manganese have been anodized. The high silicon containing alloys give very dark anodic coatings.

In general the main problem with castings is to obtain a sound structure free from porosity, entrained oxide and segregational effects. The type of alloys which are easiest to cast, i.e., high silicon and high copper alloys, are least suitable for anodizing, and those that are most likely to give porosity problems, e.g., the high magnesium alloys, give the best anodizing response. Nevertheless many castings are anodized for both decorative and functional applications and careful casting and anodizing procedures can give very satisfactory results.

Anodizing process characteristics of alloys

The aim in anodizing is usually to operate at a particular current density rather than voltage because it is only in this way that the rate of coating formation can be known and controlled. The various alloys require different voltages for the same current density, a point which Kissin, Deal and Paulson[49] have demonstrated well in Fig. 7-2 which gives the voltage-time curves for a number of alloys anodized at 1.3 A/dm^2 (12 A/sq ft) in 15% (wt) sulphuric acid. It is interesting to note that pure-aluminium comes in the middle of this series, some alloys requiring a higher voltage and some a lower voltage to maintain the anodizing current.

The current required per unit film thickness depends on the effect of the alloying constituents on the conductivity of the coating. Thus alloys containing magnesium and zinc increase the conductivity of the coating and hence give thicker films per unit of electricity than copper-containing alloys where segregated $CuAl_2$, for instance, increases the ohmic resistance. Experiments carried out by Fischer, Budiloff and Koch[9] have also shown the relationship between voltage and anodizing time and other properties with different alloys.

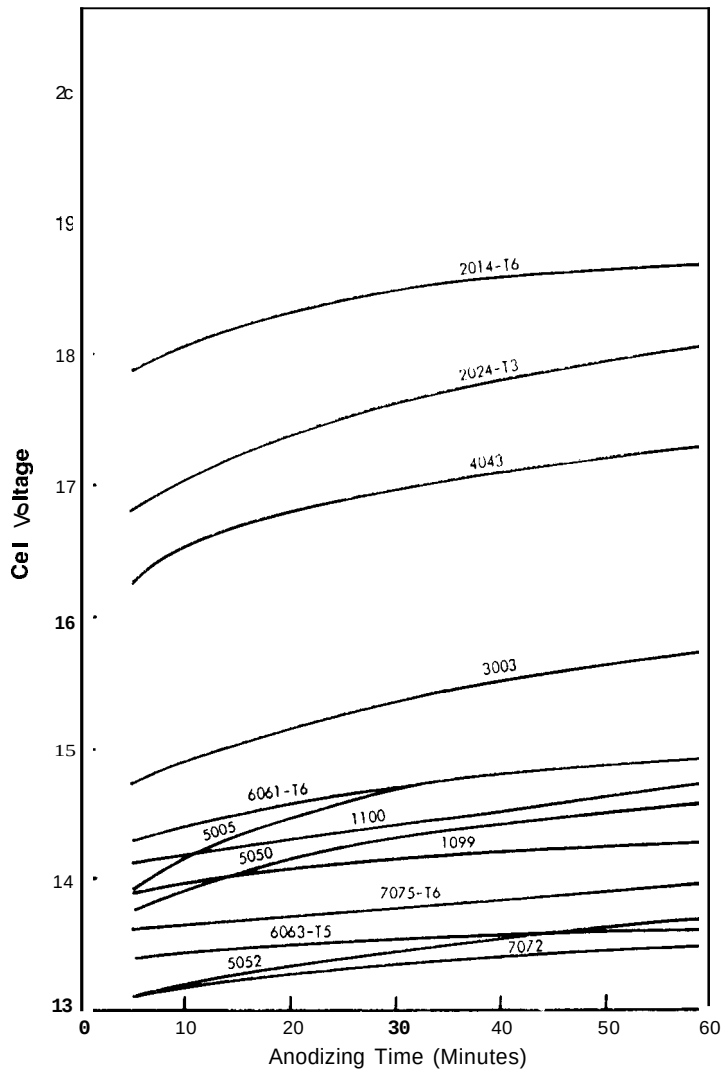


Fig. 7-2. Voltage required to maintain a current density of 12 amp/sq ft (1.3 A/dm^2) for various aluminium alloys anodized in 15% H_2SO_4 at 25°C[49]

The most important factor was found to be the homogeneity of the alloy. Increase in heterogeneous constituents had the greatest influence on the reflectivity, and the colour of the coating was not affected until substantial amounts of segregated constituents were present.

The voltage required for anodizing can vary with the condition of the alloy, i.e. whether it is homogeneous or heterogeneous. Thus copper alloys in the cast condition will anodize at a low voltage of about 14, but when solution heat-treated the voltage to maintain the same current may be 20-22. Other alloys can behave in the opposite manner. Thus two groups of alloys have been distinguished:[9]

Group 1.	Heterogeneous; low voltage Homogeneous; high voltage	Examples:	Al-Cu Al-Cu-Mg
Group 2.	Heterogeneous; high voltage Homogeneous; low voltage	Examples:	Al-Mg Al-Mg-Si Al-Zn-Mg

The differences in behaviour are attributed to the effect of the constituent on the resistance of the coating. For example, in the heterogeneous condition selective attack on the precipitated constituent causes the formation of sparingly-soluble basic salts in the pores, while the increase of voltage in the case of silicon alloys in Group 2 is explained by the relatively high oxidation potential of the metal itself. In the homogeneous condition the alloys still behave differently from high purity aluminium. Thus, compared with the latter, the presence of copper in solid solution, and also manganese and silicon, increase the voltage, probably by producing a denser coating, while the opposite effect is observed in Group 1 alloys.

It can be seen from the above comments that at any particular anodizing voltage, different alloys will give a different rate of anodizing. Whilst the rate of anodizing can be adjusted, when dealing with a complete load of one alloy, by applying the appropriate voltage, the jobbing anodizer has a major problem when he needs to anodize more than one alloy at the same time. Whenever possible alloys should be segregated such that this does not occur, but alloys with very different anodizing characteristics, such as the Al-Mg alloys (5000 series) and the Al-Cu alloys (2000 series), should never be anodized together. The AI-Cu alloys, in particular, present problems if not anodized separately, as a voltage of above 20 V will normally be required to maintain a reasonable anodizing rate. Jackson and Thomas[50] have examined this problem with bright trim alloys. They conclude that it is fairly safe to process small quantities of other bright trim alloys with 5252, bearing in mind that the film thickness on these alloys will be a little below the desired level, but that it is more hazardous to include small quantities of 5252 with other bright trim materials, because of the risk of obtaining a high current density and hence too thick an anodic film on the 5252 (see Fig. 3-31).

The maximum film thickness depends upon the alloy's composition. Fig. 7-3 shows the behaviour of a number of alloys in sulphuric acid anodizing. The thickest coatings are obtained with pure aluminium, the thinnest with the heat-treatable heavy-metal-containing alloys, while the quantity of electricity required to reach this maximum is naturally less in the latter group. In some cases, notably

with some AI-Mg alloys and some heavy-metal-containing alloys, the film thickness may decrease again after the critical value is reached.

The effect of magnesium content on the anodic coating thickness is well demonstrated in Fig. 7-4. Here it is seen that increasing magnesium content substantially increases the rate of oxidation at a fixed voltage, at least initially, though as already stated the coating may decrease in thickness after a certain time. According to Lacombe[10] the formation of a coating of uniform thickness is best assured with a perfectly homogeneous alloy. If variations in the composition of the solid solution exist, they are revealed after oxidation in the form of undulations. This has been shown, for example, by Herenguel and Segond[51] in the case of an aluminium-3% magnesium alloy after anodizing at 1.5 A/dm^2 for 30 minutes (see Fig. 7-5), and is particularly likely to occur when alloys are prepared from high purity metal. Harris and Scott[52] have shown that this effect can be avoided by reducing the current density to 1.0 A/dm^2 or by raising the anodizing temperature, and have recommended conditions suitable for bright anodizing magnesium alloys.

The size of second phase constituent particles is also of importance. On general physical principles the maximum light scattering effect of dispersed particles is to be expected when their size is in the range of 0.3-0.5 microns, that is about the same as the wave length of visible light. Thus the colour of 5% silicon alloys when anodized in sulphuric acid is affected by the casting procedure, and becomes very dark grey when the alloy is modified to give silicon particles in a very fine dispersed form. Iron aluminides can have the same effect. Magnesium silicide precipitates formed by overageing of the Al-Mg-Si alloys can lead to a darkly coloured anodic coating,[28,29,37] and tnanganese constituents can yield various colours.

Heterogeneity of the basis metal not only leads to darker, more opaque or structured coatings which affect the appearance, but may also adversely affect the corrosion resistance. To some extent the last disadvantage can be counteracted by providing a thicker anodic coating, when there is a tendency to eliminate weak spots by growth of oxide around unoxidized constituents.

Apart from their importance in anodizing, impurities have a considerable influence on electropolishing, as in the Brytal and Alzak processes, where high purity metal must be employed to obtain maximum reflectivity because the polishing action depends on the formation of a solid uniform oxide film on the metal during polishing. Etching behaviour can also be affected particularly in acid etchants; the Erftwerk brightening bath is notably intolerant of any impurities in the metal. Short and Sheasby have reported the behaviour of a number of segregated intermetallic phases in caustic soda solutions.[12] Their conclusions are as follows.

The $(Fe,Mn)Al_3$, $(Fe,Cr)Al_3$, $(Fe,Mn,Cr)Al_3$ and $(Fe,Cu)Al_3$ constituents all react at a slower rate than the matrix: this is in contrast to $FeAl_3$, which reacts at approximately the same rate as the matrix. The slowed rate of reaction of the $FeAl_3$ complexes is particularly detrimental to surface finish.

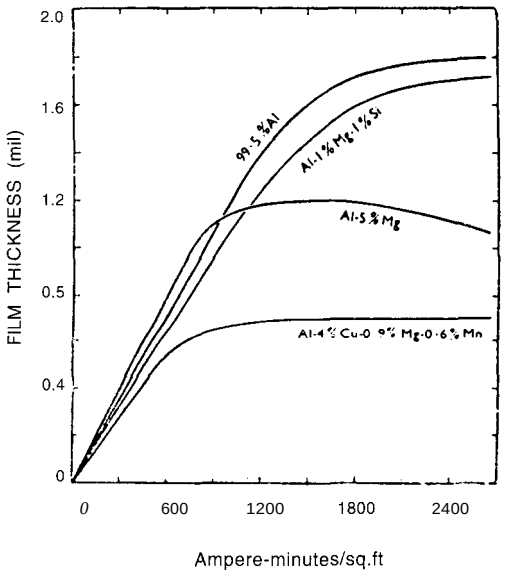


Fig. 7-3. Anodizing behaviour of some commercial aluminium alloys in sulphuric acid (after Elssner[53])
1 mil = 25.4 μm
10 amp-minutes/sq ft = 1 amp-minute/dm^2

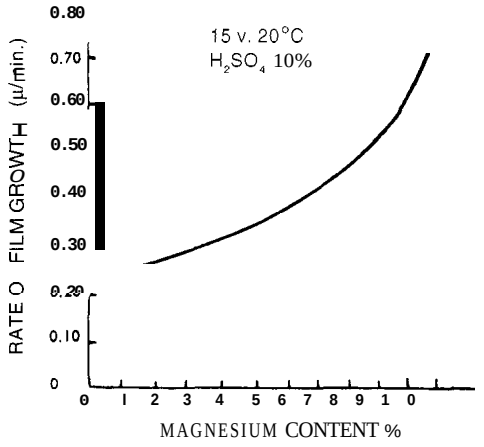


Fig. 7-4. Effect of magnesium content of high-purity-base aluminium-magnesium alloy on the rate of film growth in anodizing in 10% (vol) sulphuric acid at 15 volts, 20°C



Fig. 7-5. Differences in level from grain to grain, caused by differences in oxidation rate, in an aluminium-3% magnesium alloy made from pure metals (15 amp/sq ft, (1.5 A/dm^2) 30 minutes).[51] The surface carries an alumina film. Oblique illumination

The $(Cr,Mn)_2Al_{11}$.$(Mn,Fe,Cr)Al_6$ and $(Mn,Cu)Al_6$ constituents are attacked at a slower rate than-the matrix, whereas $(Mn,Fe)Al_6$ reacts at approximately the same rate as the matrix. Slight roughening of the surface adjacent to the constituent occurs with all four intermetallics. This behaviour is entirely different from that demonstrated by the $MnAl_6$ constituent which reacts at a much faster rate than the matrix.

The α-AlFeCuSi and α-AlFeMnSi constituents both react marginally more slowly than the matrix, whereas the α-AlFeCrSi constituent reacts fractionally faster than the matrix. The α-AlFeSi phase reacts at a slower rate than the matrix and quite heavy pitting occurs on the constituent. In the case of these substitutions there are two distinct changes; firstly the differential between etch rates of constituent and matrix **is** reduced, and secondly, the pitting associated with the a-phase is reduced by the addition of copper to the phase and is non-existent on the manganese- and chromium-bearing phases.

The authors also confirmed that the use of alkaline etches modified with nitrates, nitrites or fluorides did not significantly alter the etching characteristics of the constituent as compared with the matrix, but they noted that the pitting associated with $FeAl_3$ etched in sodium hydroxide was somewhat reduced in the more complex etches, and the reaction rate of $MnAl_6$ constituent was slowed down considerably in the etches containing sodium nitrate and sodium nitrite.

Selection of alloys for anodizing

The relationship between alloy composition, its production history and its response to anodizing is complex and needs to be understood if optimum results are to be achieved. Useful guidance is provided in the general anodizing standard BS 1615:1987, where it states that most alloys in the general engineering series described in BS 1470-1475, BS 1490 and BS 4300/7 can be anodized. However alloys containing a high proportion of copper, zinc or silicon are likely to require modified anodizing techniques and advice should be sought from the manufacturer or anodizer.

Special grades and alloys of aluminium are available as anodizing quality materials to give specific properties. For example BS 4300/4 specifies alloys for bright trim or reflectors. Other alloys, not necessarily covered by British Standard specifications, have been developed for integral colour anodizing processes, and other special applications.

After anodizing, some variation in appearance and colour, maximum coating thickness, reflectivity, abrasion resistance, corrosion resistance and electrical breakdown voltage can be expected from different batches of the same material and different forms of the same material, e.g. castings, extrusions, forgings and rolled sheet. Additionally, anodic treatment may reveal some lack of homogeneity in the aluminium. These variations can be kept within acceptable limits by cooperation between the material supplier, the anodizer and the purchaser. Similar advice is provided in the new European Standard, EN 12373: Part 1, that will soon replace BS 1615. Both these standards list the information that needs to be supplied by the purchaser to the anodizer before the process begins, and this is equally important for the metal supplier on many occasions. Special anodizing or processing may be required to achieve the desired properties, for example high reflectivity or high abrasion resistance, and it is essential that everyone involved is aware of the product requirements.

3. PRETREATMENT; JIGGING; EQUIPMENT

Pretreatment for anodizing

Pretreatment of the aluminium before anodizing is essential in all cases, though it may be needed for a variety of reasons. In the simplest case the material may only need to be cleaned or degreased, but in others it may require more complicated treatments to remove the air-formed oxide film or modify the surface appearance. Such surface oxides may be formed during casting or heat-treatment and can be removed by etching in alkaline or acid solutions. Alloys containing magnesium, during high temperature heat treatment or during storage in slightly humid conditions, tend to build up a layer of magnesium oxide on the surface which is insoluble in alkaline solutions, and attempts to etch in caustic soda may lead to a very rough and patchy surface as the etch acts selectively in removing the oxide skin by undercutting. This oxide is readily removable in nitric or sulphuric acid and it is always a wise precaution to institute an acid dip before alkaline etching of magnesium alloys.[54] However in most cases the pretreatment will establish the required appearance for the application involved. Pretreatment processes have been described in detail in the previous Chapters, but again the standards provide useful guidelines.

EN 12373 : Part 1 indicates in its guidance that different surface textures can be obtained by a variety of processes. Usually the work, either polished or

unpolished, is subjected to a chemical etching procedure to provide a range of textures from light satin with varying degrees of gloss to full matt, according to the type of etch used. Surface variations such as corrosion, which has occured before treatment, or different material characteristics, can become visible after etching. Alternatively, the texture can be produced mechanically by brush, abrasive belts or wheels to give a range of matt finishes which are lined or directional, in contrast to the essentially non-directional etched finishes. Mechanical finishes have good reproducibility and are less dependent on metal structure and composition than chemical pretreatments. Surface irregularities, if not too deep, can be removed by mechanical means.

Aluminium can also be mechanically polished to obtain a smooth or bright surface, and chemical or electrochemical brightening can be employed with special alloys to give a highly reflective surface. The Standard warns that very rough surfaces, either chemically or mechanically produced, are best avoided in external applications as they tend to hold dirt and have an adverse effect on the durability of anodic coatings. Heavy etching can also cause problems with some of the high strength alloys as they may become more susceptible to stress-corrosion.

A surface preparation designation system is suggested in this Standard, and this is shown in Table 7-6.

Jigging for anodizing

The objective in jigging is, first to form a positive contact with the work, and, second, to make handling as easy as possible without running the risk of deforming the work in jigging or unjigging or by movement between loose points of contact, etc. Points of contact should be chosen with care, preferably, of course, in positions which are hidden from the eye, as no film is formed at such points. Three or more points of contact may be necessary in order to avoid movement of the part within the jig (Fig. 7-6[55]). Each contact point should not be allowed to carry more than 10-20 amperes, though this is to some degree dependent on the gauge of metal of which the article is made.

Jigs for anodizing are often referred to as racks. Ideally, when made from aluminium, the jig material should be of the same or a similar alloy type to the material being anodized, or at least from a material that does not tend to rob the work of current by consuming more than its share. In practice this situation is normally met by using the Al-Mg-Si alloys 6063 or 6082 which have suitable anodizing characteristics for most purposes and which, in the fully heat-treated condition, have the mechanical strength and rigidity to provide a good spring contact with positive pressure. The 2000 series AI-Cu alloys should not be used because of their high current consumption and rapid deterioration. Care is also needed when anodizing materials like silicon alloys which have a rising voltage characteristic, because the 6063 type jigs will take a progressively increasing

current at the expense of the load, which makes calculations of film thickness difficult, and when it comes to hard anodizing the jig may fail by breakdown and arcing.

TABLE 7-6

Surface preparation designation system

Symbol	***Type of pretreatment***	***Notes***
EO	Degreased and deoxidized only	Surface preparation before anodizing in which the surface is degreased and deoxidized without further pretreatment. Mechanical marks such as scoring and scratching will remain visible. Corrosion effects, which could barely be seen before treatment, can become visible after processing.
E1	Linished only	Linishing produces a comparatively uniform appearance with a somewhat dull appearance. Any surface defects present are largely eliminated but, depending on the coarseness of the abrasive, Linishing grooves may be visible.
E2	Brushed only	Mechanical brushing results in a uniform bright surface with visible brush marks. Surface defects are only partially removed.
E3	Polished only	Mechanical polishing **results** in a shiny, polished surface but surface defects are removed only to a limited extent.
E4	Linished and brushed	Linishing and brushing gives a uniform bright surface with mechanical surface defects eliminated. Corrosion effects, which may become visible as a **result** of EO or E6 treatments, are eliminated.
E5	Linished and polished	Linishing and polishing gives a smooth, shiny appearance with mechanical surface defects eliminated. Corrosion effects, which may become visible as a result of EO or **E6** treatments, are eliminated.
E6	Chemically etched	After degreasing the surface is given a satin or matt finish by treatment in special alkaline etching solutions. Mechanical surface defects are smoothed out but not entirely eliminated. Any corrosion effects on the metal surface may become visible as a result of this treatment. Mechanical pretreatment before etching can eliminate these effects, but it is preferable to handle and store the metal correctly to avoid corrosion.
E7	Chemically or electrochemically brightened	After degreasing the surface in a vapour degreaser or non-etching cleaner, the surface is given a very bright finish by treatment in special chemical or electro-chemical brightening solutions. Surface defects are removed to only a limited extent and corrosion effects may become visible.
E8	Polished and chemically	Grinding and polishing followed by chemical or electrochemically brightening. This gives a very smooth bright appearance and mechanical surface defects and incipient corrosion are normally eliminated.

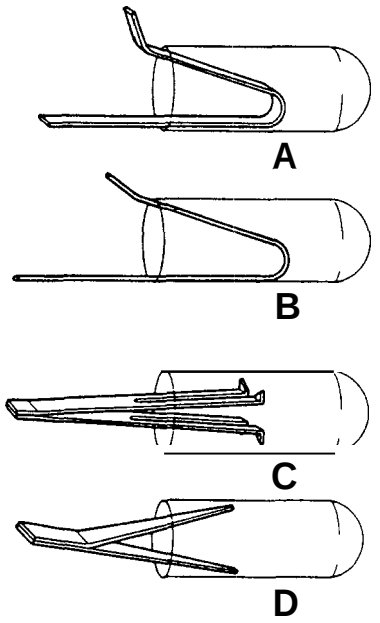


Fig. 7-6. Good rack design can manage placement of rack marks. **(A)** Sheet metal U-bend clip leaves marks over a large area. (B) Wire U-bend clip leaves two thin line marks. **(C)** Split finger clip leaves four small marks and reduces part rocking. (D) Pointed tip leaves two very small marks, but may allow rocking and cause burning.[55]

The type of jig and jig coating to be used for a bright anodizing sequence consisting of chemical brightening, anodizing and dyeing presents special problems. Table 7-7 gives physical and mechanical properties of four alternative materials. Most difficult, however, are the chemical problems involved. None of the first three metals in Table 7-7 is entirely satisfactory without a jig coating. Titanium is inert in most of the solutions of the sequence and, although it has a fairly high corrosion rate in dilute sulphuric acid solution at 21°C in the absence of current, during anodizing itself it is protected by anodic passivation. Titanium is thus satisfactory provided jigs enter and leave the solution while the current is on.

Fig. 7-7 shows an insulated copper or aluminium anodizing jig, with removable titanium tip. The joint between the removable tip and the jig coating is sealed in the manner shown in Fig. 7-8. The initial expense of titanium-tipped jigs is soon justified by their longer life, as compared with other materials. Commercially pure titanium, 0.06-0.08 inch (1.5-2 mm) gauge and 0.75-0.62 inch (19-16 mm) wide, is suitable and a further increase in jig life is obtained by applying a plastisol coating to leave approximately 25 mm of titanium exposed. Parts must be of an adequate cross-section to carry the current. The current-carrying capacity of titanium has been variously quoted at 52 A/cm^2 (335 A/in^2) by Reynolds,[57] 93 A/cm^2 (600 A/in^2) by Tonks[58] and 80 A/cm^2 (500 A/in^2) by Survila.[59] However these are the current-carrying capacity in air, and all agree that much higher currents, up to 460 A/cm^2 (3000 A/in^2), can be carried below solution level. Practical designs for clips, tips and clamps to carry various currents (Fig. 7-9) are included in a good summary of jigging procedures by Leopold.[55]

TABLE 7-7

Physical and mechanical properties of jig metals[56]

	Aluminium	***Copper***	***Phosphor-bronze***	*Titanium*
Machineability	Good	Good	Fair	Difficult and costly
Formability	Special annealing and hardening required	Good	Fair	Poor
Tensile strength	Fair	Good	Excellent	Good
Weight	Tends to be too light	Good	Fair	Good
Spring temper	Spring tension softens	Good	Poor	Excellent
Electrical conductivity	Fair	Excellent	Poor	Good

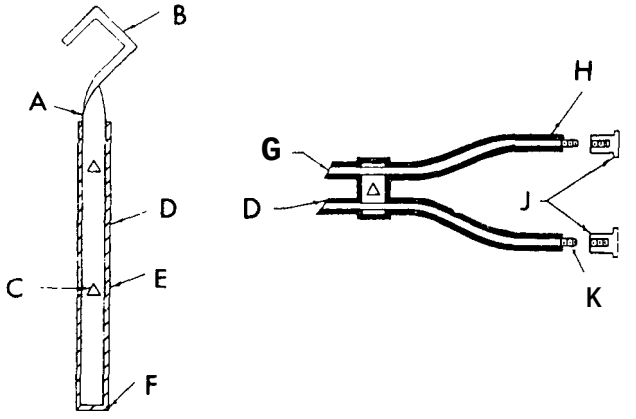


Fig. 7-7. Insulated anodizing **jig** with removable titanium tip.[56]

(Left) Jig spline or major structural member. Cross-section shown
(Right) Removable tension-holding adaptor, coated. Cross-section shown

A Copper or aluminium
B Hook. Either a continuation of the spline metal or elsereplaceable mass
C Stud hole used for attaching adaptor
D Coating 3 mm thick
E Moulded synthetic blended elastomer coating vulcanized to rack metal
F Greatest thickness on corners and edges
G Phosphor-bronze spring
H Moulded synthetic elastomer coating vulcanized to adaptor metals
J Removable titanium or aluminium tips
K Threaded ends

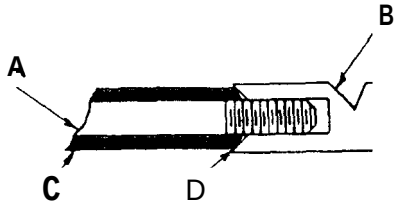


Fig. 7-8. Showing how the removable tip of the jig in Fig. 7-7 is sealed against the jig coating[Sh]

A Threaded spring holding member
B Expendable titanium tip is threaded to facilitate replacement
C Coating
D Joint to be sealed

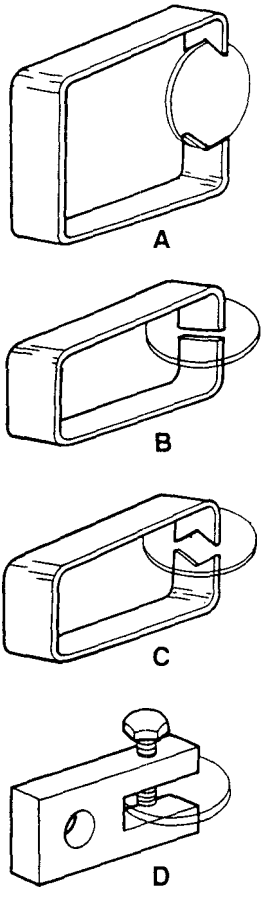


Fig. 7-9. Design clips, tips and clamps to carry ample current.

(A) 8A (Ti)/25A (AI) for each of two point contacts.

(B) 8A (Ti)/25A **(AI)** for each of four point contacts.

(C) 15A (Ti)/45A (Al) for each of two line contacts.

(D) 60A (Ti)/180A (AI) for a clamp contact.[55]

The non-titanium part of an anodizing jig must be insulated if of copper. Many jig coatings, including natural and synthetic rubber, PVC and polythene, will stand up to sulphuric acid anodizing solutions. PVC and polythene are alsn satisfactory for chromic acid anodizing. The jigging problem for chemical polishing solutions is difficult, however, and only a fair life can be obtained by the use of synthetic thermosetting elastomers, the other coatings mentioned being readily attacked.

The life of an aluminium jig with titanium contact tips and springs is in practice limited only by the life of the plastic jig coating, and in sulphuric acid anodizing a life of 1,000 process cycles can be expected. However, in one such plant an average of 2,500 cycles was achieved,[60] despite the fact that a hydrofluoric acid dip used in the sequence attacked titanium at the rate of 0.001 inch in 200 cycles.

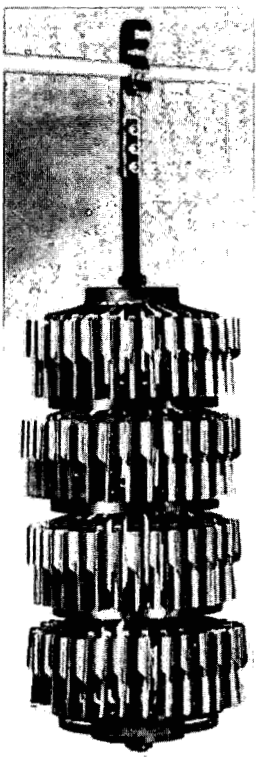
Very frequently today the jig frame and splines of all-titanium jigs are constructed from rod or sections while the contacts are made either from wire, which is caulked into position, or from sheet or strip which is spot welded to the frame.

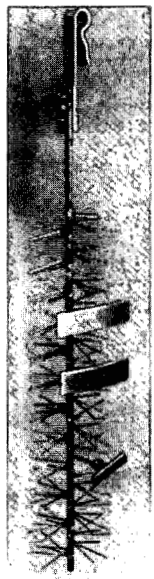
Another development is the use of a solid aluminium rod spline with a titanium coating, the object being to obtain a higher conductivity than is possible with a titanium spline. Also used are movable jigging fixtures which allow one spline to handle different types and sizes of work. These are very common for handling small parts and typical titanium racks are shown in Figs. 7-10 and 7-11. A large variety of such titanium designs has been described by Tonks[58] and Brace.[61] Local burning of the workpiece can sometimes occur with this type of jig when high current densities are used, and Alcan[62] claim that this can be overcome by using an aluminium contact surface which is protected with a compressible outer sleeve of non-conductive material such as silicone rubber.

Compared with all-titanium, jigs constructed of aluminium with titanium tips have a shorter life, although the tips themselves may be re-used when the frame is expended. In practice, the tips are fitted by caulking and the joints are retightened when the plastic coating is renewed every 2-4 months.[63]

The comparative cost of all-titanium and titanium-tipped jigs depends to a large extent on the number of parts to be processed. Thus, in one example in which a long run of components was to be bright anodized, Polfreman found that the cost of using titanium jigs was only 8-20% of that of aluminium jigs,[64] although where a jig was made for a short run, titanium-tipped aluminium jigs might have the advantage. The all-titanium jig, although more expensive, dispenses with the need for a jig coating and can be used with greater confidence in sequences which include vapour degreasing and chemical polishing. Titanium jigs have sometimes caused localised pitting problems, particularly with dyed work and with thin anodic coatings.[43] This is a galvanic effect which has been described in detail by Henschel[65] and he recommends the use of sacrificial magnesium anodes to prevent the problem. The cleaned anodes are clamped onto the work bar, either side of the titanium racks being used, before the work enters the dye bath and they are kept in position for the dyeing and sealing operations. Galvanic effects can also arise

from contact with the stainless steel dye or seal tanks, and the flight bar needs to be insulated from the tank.





Figs. 7-10 & 7-11. Titanium jigs for holding small parts
[courtesy of Norman Radcliffe Ltd.]

In chromic acid anodizing, the use of unprotected titanium is not always to be recommended as at the higher voltages used in the Bengough-Stuart process, the oxide film on the titanium may break down. Thus the material should normally be insulated.[66]

'Matrix' jigs in which flat pieces are inserted into a diamond-shaped opening to obtain four-point contact, and 'window-frame' jigs for tubular or circular parts are described by Engle,[67] and several other specific jig designs have been patented.[68,69,70]

After the anodizing operation aluminium jigs need to be stripped before re-use. This is normally done by immersing them in the caustic etching solution until the oxide has been removed, but inevitably this means significant loss of aluminium from the jigs and hence eventual replacement. This is the main limitation in the use

of aluminium jigs and for this reason they are sometimes coated with organic materials to minimise the attack of the aluminium. Contact is then made by removing the protective coating at the contact points. In some cases mechanical stripping of the contact surfaces can be arranged, and chemical stripping of the whole jig is not necessary (see Fig. 7-12).

If possible jigs should be designed to allow reasonable spacing between articles and to hold them parallel to the cathodes, as although the throwing power of most anodizing electrolytes is good, significant variations in anodic film thickness will occur if work is too densely packed or is at very different distances from the cathodes.

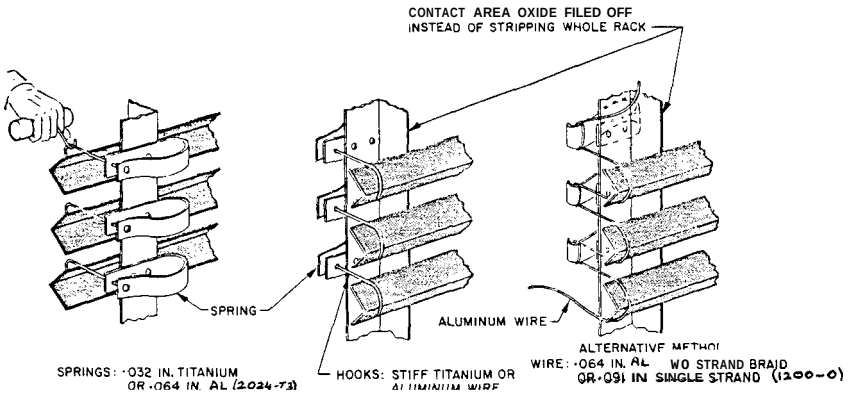


Fig. 7-12. Jigging systems suitable for light extruded shapes

Although spring clips with exterior or interior contact represent the normal mode of operation for miscellaneous small or medium sized articles there are many variations, and effort and imagination applied to jigging can often spell the difference between profit and loss. When components are large with convenient threaded holes a rod screwed into one of these provides an excellent contact, and in the case of large thin gauge sheets there is often no good alternative to clamping contacts onto the surface near one edge although the area can be kept quite small on the significant face. Because both the work and jig form an insulating coating the pressure between them needs to be more positive than it does for electroplating. There is also a tendency for the thicker films to separate the jig from the work, a tendency which becomes aggravated if there is a temperature rise in the vicinity, and, as they cut out, an extra load is thrown onto the other contacts until arcing or

burning occurs at one of them, or the current flow ceases altogether: the point is often missed here that the visible defects are remote from the original faulty contact. Many operators have experienced difficulties in forming 25 μm coatings when using titanium clips because of contact failures at about the 15 μm mark, and hard anodizing is often uncertain with spring clips unless the pressure is made very high, but in either case there is no problem with contacts that are bolted onto the work.

Bolted or clamped contacts are very much the standard form of jigging for the long lengths of extrusion used in architectural applications, though wiring onto a vertical spline is still used in some plants. However clamps made in plastics materials are increasingly replacing the aluminium or titanium clamps formerly used for this purpose.[71] The plastics used must be resistant to all the processes involved in the anodizing operation, so they are not usually used for chemical brightening operations. Design of the clamp is also important, in order to ensure that they have the mechanical strength required, as well as the necessary chemical resistance. Examples of jig designs for architectural work are given in Figs. 7-12 to 7-14. The stacker jig, illustrated in Fig. 7-14, is widely used in North America,[72] and several rows of work are placed side by side at each level, but this type of jig is not usually suitable for producing thick anodic coatings in European plants, as the film thickness spread from the outside to the centre of the load is too great. Other commonly used jigs are described by Spencer[73] (Fig. 7-15). A comparison of racking costs in architectural anodizing has been reported by Burlingham,[74] and this clearly shows the benefit of the use of plastic clamps.

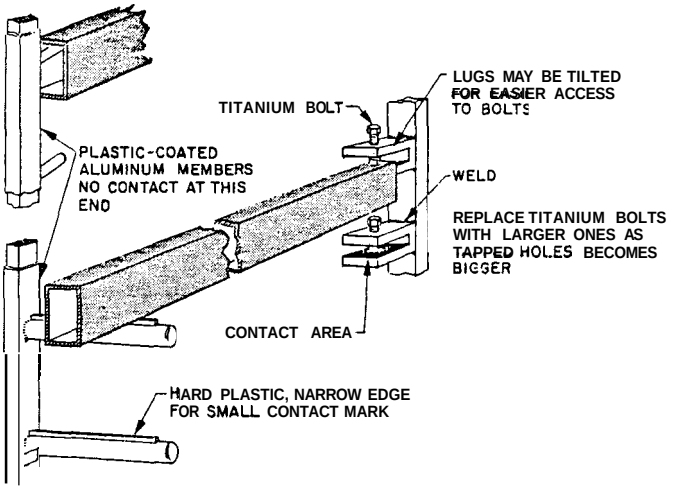


Fig. 7-13. Jigging systems suitable for long lengths of hollow extrusions

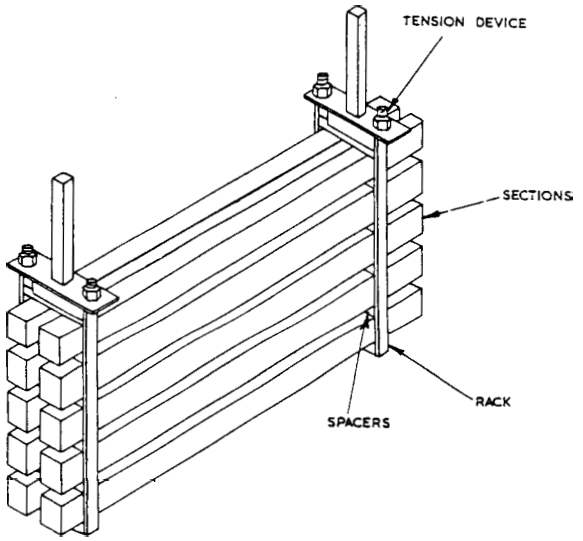


Fig. 7-14. Principle of stacker jig for extruded sections

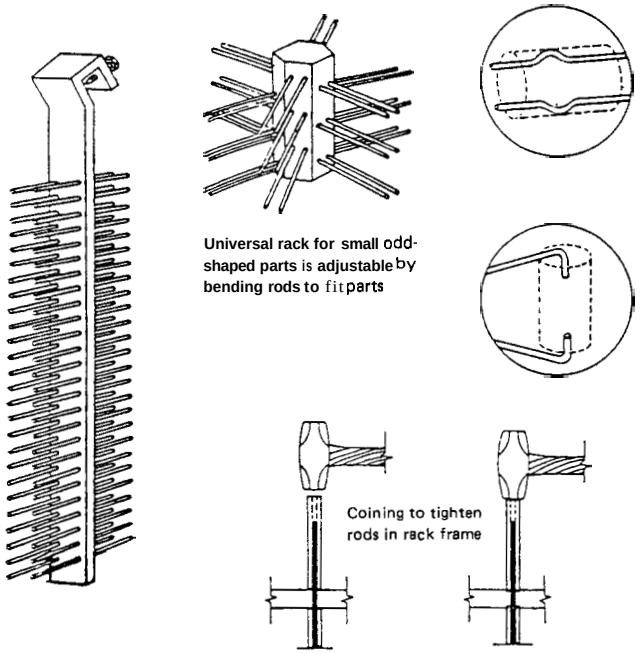


Fig. 7-15. Wire and bar racks produced from readily available stock. Lower right shows method of tightening elements in frame by upsetting frame around rods or wire[73]

Throwing power and auxiliary electrodes

Compared with most electroplating solutions, the throwing power of anodizing solutions is good due to the high electrical resistance of the Al_2O_3 film in relation to that of the electrolyte. The high anodic polarization in anodizing is also responsible for the high covering power. initial polarization at high current density areas divert!; the current to the areas receiving a lower current density than that expected according to the primary current distribution. Nevertheless, differences in coating thickness are found over complicated shapes and over large complex loads. For example, film thickness variation of 4-8 microns (0.16-0.32 mil) is commonly found within a load of architectural sections anodized to a nominal thickness of 20 microns.

McDougall[75] reports the following thickness variations over different anodized motor trim parts:

High	*Low*
0.40 mil	0.30 mil
0.57	0.41
0.45	0.35
0.47	0.40

Aluminium sheet suspended close to, and parallel with, a single cathode will be coated on both sides,[76] film formation beginning on the further side as soon as the resistance of the electrolyte between the cathode and the near side added to the resistance of the coating already formed on the near side is equal to the resistance of the solution between the cathode and the further side.

Few quantitative tests have been carried out on either covering or throwing power. The good throwing power obtained in anodizing is illustrated in Fig. 7-16[77] which shows the depth to which the anodic coating grows in 0.2 and 0.3-1 mm (0.008 and 0.012-0.040 inch) spaces between packed aluminium sheets. It is seen that the throwing power is better using d.c. than a.c. Rohrig found that at a ratio depth : width of 60:1, coatings of 3 and 15 μm (0.12 and 0.6 mil) were obtained with d.c. and superimposed a.c. on d.c. respectively. The use of auxiliary cathodes is necessary, however, where hollow bodies with small openings are to be treated (Fig. 7-17), the resistance of the electrolyte being proportional to the cross-sectional area of the opening. Where the inside of tubes is to be treated, the problem becomes more difficult, and for long, narrow and bent tubes, anodizing is often replaced by chemical treatment.

The throwing power of anodizing solutions can be determined without difficulty by using Pan's method[78] as adapted by Herwig and Leigh." An aluminium box, constructed in two pieces, is used. The sides and ends are faced off and one side of each piece is lapped. The lapped sides are bolted together and placed against a backing plate into which different sized holes are drilled. Visual inspection shows the depth to which the solution will throw. If colourless coatings are investigated,

the whole structure is immersed in a black dye when depth of colour will be proportional to the film thickness. After opening, the coating may be further subjected to salt-spray in order to test for corrosion resistance.

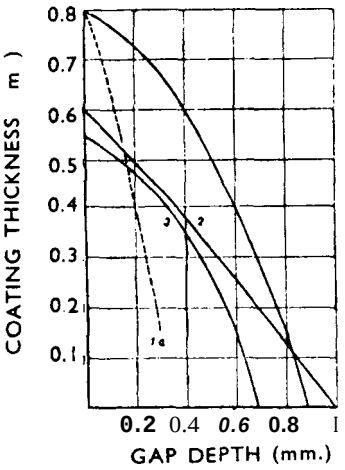


Fig. 7-16. Relation between coating thickness and gap depth."
(1) and (1a) 6 g/l oxalic acid,
50 amp-minutes/dm² (500/sq ft) a.c. and 40 amp-minutes/dm² d.c., 25°C
(2) 150 ml/l sulphuric acid,
40 amp-minutes/dm² d.c., 25°C
(3) 60 g/l oxalic acid,
120 amp-minutes/dm² a.c., 25°C
Gap width (1), (2) and (3): 0.3-1 mm; (1a): 0.2 mm

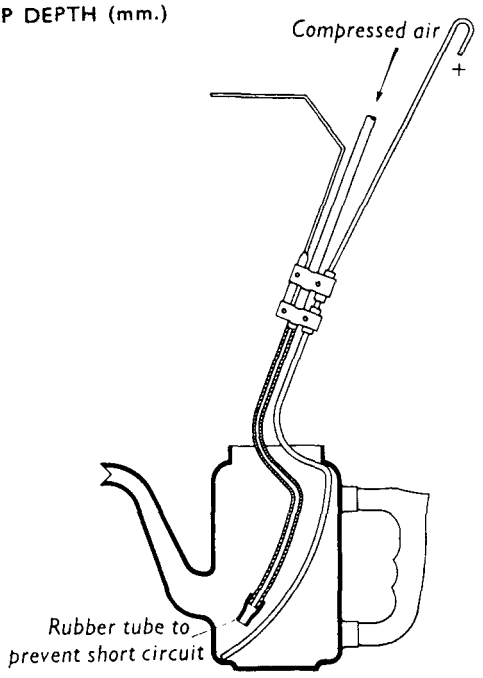


Fig. 7-17. **An** arrangement for anodizing the interior of a coffee pot with internal cathode and compressed air pipe. The end of the cathode is covered with a rubber hose to prevent short circuiting[80]

Hollow extrusions

One would normally expect the whole surface of a quite complicated article to be anodized, but a special situation frequently arises in practice in connection with architectural anodizing of hollow extruded sections or tubes which may be 10 or 12 metres (33 to 40 ft) long. The current requirements for forming a coating of known thickness are calculated from the surface area, and the problem is knowing what allowance to make for the interior surfaces when the coating thickness must be precisely controlled. There is no exact method for doing this but operators have evolved a rule of thumb procedure where approximately one third of the internal surface area is added to the external area in order to arrive at the effective area of the whole load. This meets the situation over quite a range of shapes and sizes, but the fraction may be made one quarter for smaller hollows in long lengths, while it can reach a half or more as the throwing power is good enough for any interior surface to constitute an appreciable fraction of the load.

Unfortunately, the throwing power is not good enough to obtain a coating of uniform thickness on a tube bore, and when this is required it is necessary to employ interior cathodes and forced electrolyte circulation.

Anodizing equipment

Tanks

Anodizing tanks are usually constructed in mild steel, lined with suitable acid-resistant materials such as polypropylene, PVC, or rubbers such as neoprene. Lead-lined tanks, with the lead lining acting as the cathode, have also frequently been used. In the latter case chemically pure lead is used, and it will usually be necessary to shield off the bottom and ends of the tanks with plastic shields to avoid uneven current distribution to the load. The remaining tanks in the anodizing line are normally mild steel for alkaline cleaning and etching tanks, acid resistant stainless steel for chemical brightening tanks, plastic or rubber lined mild steel for rinse tanks and electrolytic colouring tanks, and stainless steel for desmutting, dyeing and seal tanks. In recent times large architectural anodizing lines have often been built with lined concrete tanks, but care and experience is needed in the casting and lining of these tanks, and special attention must be paid to the finish on the concrete and adequate time allowed for complete setting. Reinforced resin-bonded fibreglass is usually used to line such tanks, with further inner metal linings where necessary. Tanks must be easily drainable and should slope towards the outlet to facilitate draining and cleaning. Filtration is sometimes provided.

Refrigeration and temperature control

The control of temperature in the anodizing electrolyte is of fundamental importance in almost all processes, and temperature control to within ±1°C, or even ±0.5°C, of the desired temperature is often necessary. This frequently requires a refrigeration system, as not only does the electrical energy input to the tank have to be removed, but the formation of aluminium oxide from aluminium is itself an exothermic process. The heat of formation of the oxide coatings is approximately 70 J/dm²/micron of coating (14 Btu/ft²/0.1 mil).

The cooling capacity required, for example in a normal sulphuric acid anodizing process, has been indicated by Survila[81] and he suggests that:

$$\text{Refrigeration capacity required} = \frac{\text{electrical load in watts} \times 3.42}{12{,}000} \text{ tons}$$

The motive power is then approximately 1.2 hp per ton of refrigeration. For example an anodizing bath with a capacity of 6000 **A** at 20 V requires

$$\frac{6{,}000 \times 20 \times 3.42}{12{,}000} = 34.2 \text{ tons of refrigeration}$$

Cooling can be achieved either by means of cooling coils in the anodizing tank, or by pumping the electrolyte through an external heat exchanger. With large capacity plants the second method is nearly always used, and the two main types of system are indicated in Fig. 7-18.[82]

The first is a direct system involving a single heat exchanger with refrigerant circulating through one side of the exchanger and the anodizing electrolyte through the other. This requires a specialised heat exchanger material and lead-coated copper tubes are often used, but great care is necessary in the construction of the exchanger, as. if the tubes fail, acid can be carried directly to the compressor. The acid is pumped continuously through the heat exchanger and the compressor is switched on and off as necessary to control the electrolyte temperature.

The second system is an indirect method involving two heat exchange stages. It is inevitably the more elaborate and often the more expensive method but is capable of very good control. With this system the electrolyte is pumped continuously through a stainless steel or carbon block heat exchanger, the other side of the heat exchanger being fed with cooled water from a reservoir, which in turn is cooled by cooling coils through which the refrigerant is pumped. Temperature control is achieved by controlling the flow of chilled water through the exchanger by means of a 3-way valve, which can allow partial or complete by-passing of the heat exchanger.

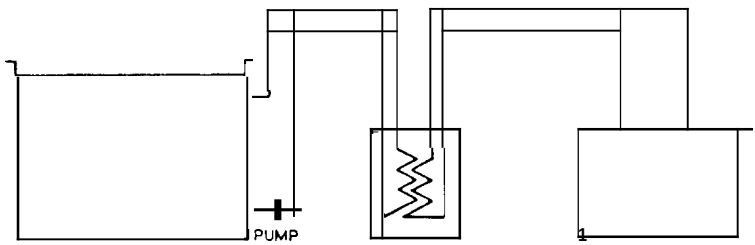
In smaller facilities cooling coils placed around the sides of the anodizing tank may give sufficient cooling capacity. They are usually constructed of either lead or titanium. Whilst titanium is the more expensive material the cost of the coils themselves may not be higher, as, for example, Tope[83] found that titanium coil

replaced lead coil 5 times its length and twice its diameter for cooling anodizing solutions. To ensure corrosion resistance, a titanium coil should be made anodic both during anodizing and also during the times the tank is not in operation. The use of a battery charger and a lead cathode has proved effective for this purpose.

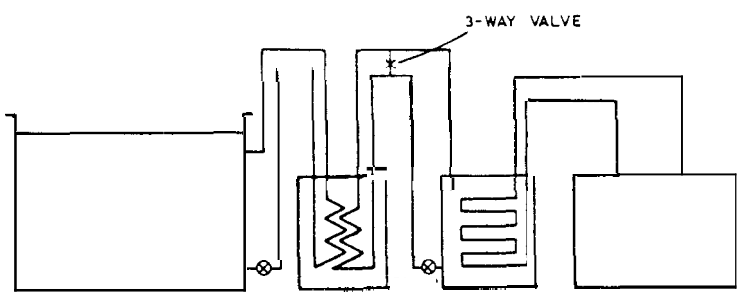
The area of cooling coil required, in the case of lead coils, is indicated in an early Qualanod Specification.[84] This suggests that the area of cooling surface in m^2

$$= \frac{12 \times \text{applied current in amps}}{250(21 - \frac{18 + \text{water temp. in °C})}{2}}$$

In other words a 1000 amp anodizing bath using water at 10°C for cooling requires a surface area of coil of 6.9 m^2.



DIRECT SYSTEM WITH ACID CIRCULATION



INDIRECT SYSTEM WITH ACID CIRCULATION

Fig. 7-18. Refrigeration systems using acid circulation"

Again there is a possibility of either a direct or indirect system and these are illustrated in Fig. 7-19.[82] With the direct system the refrigerant is circulating directly in the coils in the anodizing tank, and, if a coil becomes accidentally damaged the refrigerant will leak into the electrolyte. For this reason many anodizers use an indirect system using a chilled water, water-glycerine or water-glycol coolant. The refrigeration system then consists of a primary direct-expansion system which cools a reservoir of suitable liquid by means of cooling coils. The cooled liquid is then pumped through the cooling coils in the anodizing tank, the circulating pump being activated by a thermostat in the anodizing tank.

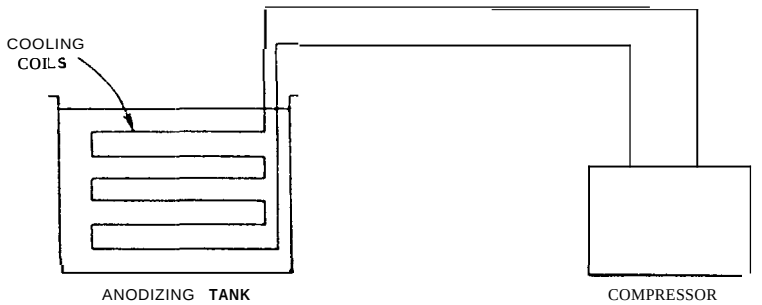
Baths may also be heated in a similar manner, i.e., by hot water or steam carried in coils through the bath, or by water-jacket. Wherever possible, it is advisable to use thermostatic control. Plastic balls or 'croffles' are frequently used to reduce heat losses from the surface of solutions operating at high temperatures. They are usually made of polypropylene, and reduction of heat consumption by 70% or more is claimed.[85,86] In anodizing they are most effectively used in the sealing baths, and many different sizes and shapes of croffles have been developed in order to give effective surface cover without them being caught up in the work as it leaves the bath.

Agitation and exhaust system

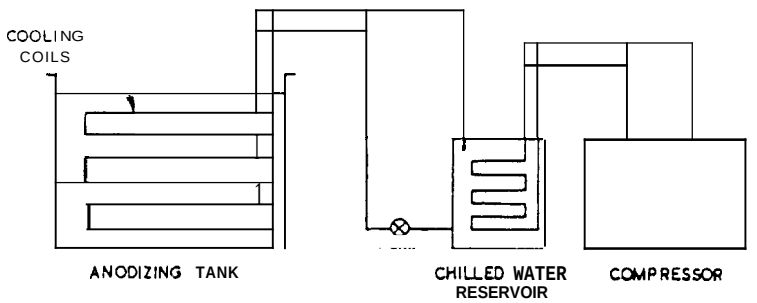
Agitation of the electrolyte is also an essential requirement for successful anodizing, mainly to ensure that heat is taken away from the surface of the film and that the electrolyte temperature is uniform. The most common method of agitation is by means of air which must be clean and free from oil. This is fed from a blower or compressor to perforated PVC or polypropylene pipes which are held along the bottom of the anodizing tank. Air blowers are usually of the positive displacement or centrifugal type, and are favoured in larger plants as they produce the required large volume of low pressure air. Compressors are more likely to give variable agitation along the length of the bath, and must have oil traps fitted to prevent contamination of the electrolyte. The amount of air required has been little discussed but Turner[87] suggests a level of 0.22-0.45 m^3 of air per m^2 of tank surface in anodizing tanks, and Qualanod[88] in their specifications recommend 12 $m^3/hr/m^2$ of tank surface. For general purpose anodizing Satoh[89] has described the benefits of what he calls 'micro-explosive' air agitation, produced from a porous ceramic pipe. He claims many advantages including increased production rates as a result of the ability to use higher current densities, better film thickness uniformity, and better corrosion resistance of the products. In a quite different direction Japanese workers[90] have found the benefit of ultrasonic waves.

In special cases anode work bar movement or a mechanical paddle may provide adequate agitation.

All anodizing baths should be fitted with fume extraction systems, as the hydrogen evolved at the cathodes carries with it a fine mist of the acid electrolyte.



DIRECT SYSTEM WITH COOLING COILS IN TANK



INDIRECT SYSTEM WITH COOLING COILS **IN TANK**

Fig. 7-19. Refrigeration systems using internal cooling coils in the anodizing tank"

Push-pull extraction systems are usually used on wide anodizing tanks, but twin-lip-extraction systems are often used. In most cases the fumes will require scrubbing before discharge into the atmosphere. In some cases wetting agents are added to the anodizing electrolyte to provide a thin foam blanket and reduce the necessity for fume extraction but care must be taken to ensure that these additives do not interfere with subsequent colouring or sealing operations. **A** perfluoroalkane sulphonic acid has been used in this way in sulphuric, phosphoric or oxalic acid electrolytes.[91]

Power supply

Both rectifiers and motor generators have been used for anodizing, but the developments in rectifier technology and the general use of silicon rectifiers has meant that generators are little used today. For normal sulphuric acid anodizing a 24 V rectifier is suitable, but for chromic acid anodizing or anodizing in organic acid based electrolytes, voltages up to 60 or 70 V are needed. Even higher voltages may be used in the case of hard anodizing and for the production of barrier-type films.

As the required operating voltage increases, and also the amperage output, silicon rectifiers come into their own in terms of installed cost, operating efficiency and reliability. They are very compact and are usually air cooled, but some water cooled units are available with large capacity units. Most are thyristor controlled, but care must be taken that adequate smoothing circuits are used, or a very distorted wave form may be produced, particularly with small loads. A small voltage ripple can be beneficial in some circumstances as Colombini[92] has shown. He has deliberately superimposed an artificial ripple and has shown benefit with both normal and hard anodizing. The importance of rectifier efficiency has also been highlighted by Comombini,[93] who demonstrates that efficiency decreases with increasing rectifier voltage, so it is desirable to use the rectifier at as low a voltage as possible to achieve the desired anodic coating.

In recent times anodizing using pulsed power supplies is being increasingly recommended.[94] These power supplies are particularly effective in situations where high anodizing current densities are required, or where difficult alloys are being processed, such as those with high copper contents. Both improved corrosion resistance and increased abrasion resistance are claimed for coatings produced by pulsed current anodizing.[94,95,96]. In practice these rectifiers allow anodizing at higher rates than normal[97] without the danger of 'burning' of the anodic coating. Burning is an uncontrolled breakdown and dissolution of the coating caused by locally high electrolyte temperature and current flow (Fig. 7-20), and it can be a serious problem in processes such as hard anodizing. Much work has been carried out on this subject in Japan,[98,99,100] and it has been established that burning takes place at sites where localised heating is possible. It begins when the cell voltage reaches a critical value and this value is dependent on electrolyte type and composition and on bath temperature. The threshold film thickness and anodizing time at which burning can take place are lower the higher the anodizing current density used. Burning is not usually a problem with normal sulphuric acid anodizing, but the high anodizing rates possible with pulsed current anodizing can be beneficial. Limiting film thicknesses for both sulphuric acid and oxalic acid anodizing have been studied by Japanese workers,[101] and they showed values of over 200 microns for oxalic acid anodizing, and more than 150 microns for sulphuric acid anodizing. However, as can be seen from Fig. 7-21, very high current densities of 10-20 A/dm^2 were used.

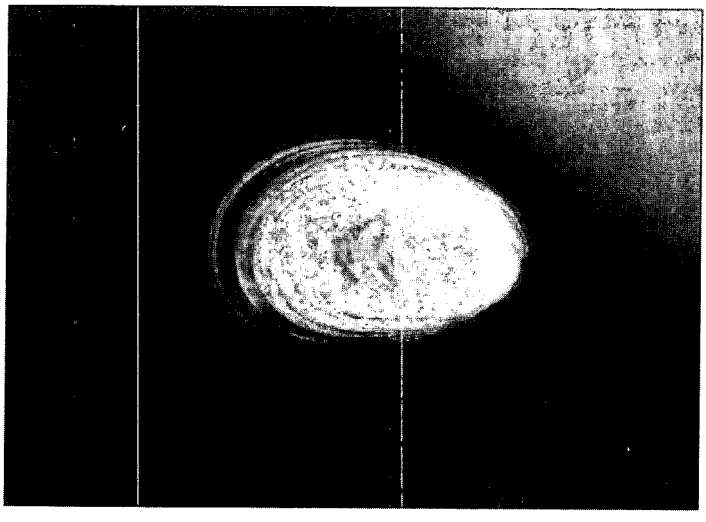


Fig. 7-20. Burning on anodized **AI-Mg** sheet alloy

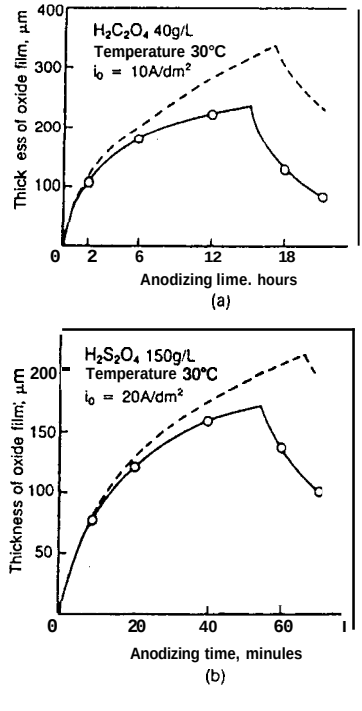


Fig. 7-21. Critical thickness of anodic oxide films formed by the high speed anodizing process in (a) oxalic acid and (b) sulphuric acid.""

The control of rectifier output is the most important factor in determining the effective current density on the work and hence the rate of growth of the anodic film. The rule-of-thumb method of controlling by voltage can give problems, but for many anodizers it is still the most practical form of anodizing control. Provided that it is realised that the relationship between voltage and current density is controlled by the resistivity of the anodizing electrolyte, and in some circumstances the load size also, good control can be obtained. The main factors affecting solution resistivity are the electrolyte concentration and the electrolyte temperature, and these must be controlled within very close limits if good reproducibility is to be achieved. If these are controlled the relationship between the voltage applied and the current density produced is essentially constant, and, as the current density controls rate of film growth, the build-up of oxide can be predicted under any particular conditions.

The alternative to voltage control is some form of current or current density control, but, whilst this is nearly always used in laboratory experiments, there are practical problems when it comes to a production plant. The simplest method is to calculate the surface area of the load concerned and, using the current density desired, work out the current to be applied to the load. This current is then applied and maintained during the anodizing period either manually or automatically. The problems are that it may be difficult to calculate the area of complex loads and it is also difficult to assess how the current will be distributed over the load, especially in the case of hollow sections. Nevertheless many anodizers use this method of control. Alternatively, an aluminium control electrode of accurately known area can be placed in parallel to the load, and a known current density applied to this, assuming that the current density on the rest of the load is similar. However the placing of this electrode in relation to the rest of the load is critical, and it must be of the same alloy and surface texture as the load. In one such system a small tantalum probe has been used.[102]

Many power supplies are now computer controlled and one, described by Colombini,[103] can, after suitable calibration, calculate the effective area of the load, and hence the current that needs to be applied, to achieve any particular current density.

Cathodes

Whilst with lead-lined tanks the tank walls can be used as cathodes, in most cases it is normal to employ separate cathodes. This gives greater flexibility in terms of materials, and allows appropriate arrangement of the cathodes along the length of the tank. In some cases, such as chromic acid anodizing, anode-cathode area ratio is important, and this can be controlled more readily with separate cathodes.

Cathode materials used include lead, stainless steel, aluminium and graphite, and sheet, rods, bars and shaped electrodes are all used. In the case of sulphuric

acid anodizing, aluminium is the normal electrode material, usually in the form of 1050 or 1200 alloy plates or 6063 extrusions. The benefit of these over lead has been described by Grubbs,[104] who found reduced energy costs with aluminium and improved efficiency. He stresses the importance of correct cathode positioning and indicates a minimum anode-cathode distance of 25 cm. It is also important to minimise excess current effects by not extending the cathodes below the bottom workpiece on the load, and shielding the cathodes at the solution surface. An adjustable shield for rod electrodes has been described by Boeing.[105] Cathodes placed along the length of the tank should not exceed the length of the longest material being anodized. An anode:cathode ratio of 3:1 is normal. Welding of the cathodes to the aluminium busbar is recommended in preference to bolting, as the latter system makes contacts difficult to maintain. The only limitation of aluminium electrodes is that they are slowly dissolved, but one user reports a cathode thickness loss of only 1 mm/year.[104]

Stainless steel cathodes are used for chromic acid anodizing and for some integral colour anodizing processes and graphite is used in many continuous anodizing processes. Lead is still used, and lead-covered aluminium cathodes have solved many of the problems of supporting pure lead electrodes.

Control of solutions

In general, the following factors are to be taken into account in the routine control of an anodizing solution:

(1) Evaporation losses
(2) Spray losses
(3) Drag-out
(4) Losses due to neutralization of the solution by dissolved aluminium and impurities
(5) Losses caused by electrolytic reaction, both cathodic and anodic, as well as chemical secondary reactions, e.g., by dirt, carried over from cleaning solutions, etc.

Bath control is thus similar to that in electroplating, and includes restoring evaporation losses by working to a given bath level, pH measurement or volumetric determination of the acid content, determination of aluminium content and of impurities such as chloride, organic impurities, etc. In addition to control of the solution, physical and mechanical tests may be carried out on the anodized work which include control of film thickness, porosity, corrosion and wear resistance, flexibility, reflectivity, etc. Such tests, as well as methods of analysis of anodizing solutions, are described later and are often supplementary to each other, as specific properties required may depend more or less critically on the balance of bath constituents and operating conditions.

Barrel or basket anodizing

Barrel anodizing is not carried out in slowly-rotating barrels as is barrel plating, since any movement of the work would make it impossible to re-establish electrical contact through the insulating anodic coating. The process has been applied in Great Britain on a limited scale to zip fasteners and similar components using a barrel rotating at **a** sufficient speed to hold the work against the peripheral anode by centrifugal force.

In general, however, it employs a basket of the type shown in Fig. 7-22.[106]

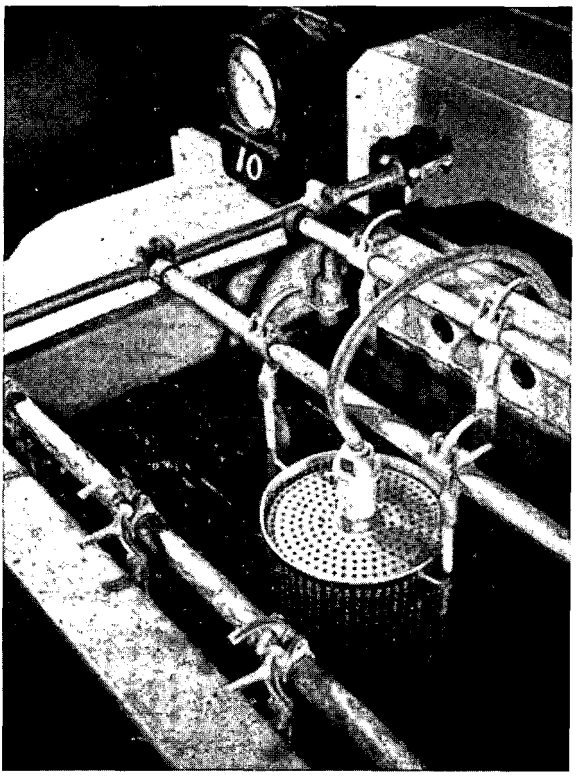


Fig. 7-22. Anodizing tank showing a cylindrical basket being lowered into the electrolyte, with tube attached for circulating cooled electrolyte through the work

The work is packed into the baskets, which are normally of perforated aluminium sheet stopped-off on the outside by a chemically-resistant plastic coating. The work is held tightly in place by the basket lid. The basket fits into the normal anodizing tank and,

unless refrigeration is employed, the tank volume should not be less than 4.5 litres per ampere passed. Cooling of the solution is probably best carried out by the circulation of solution from a storage tank, as shown in Fig. 7-23. Normal solution agitation is supplemented by slow movement of the basket along the length of the anode bar over a period of 5-10 minutes. Anodizing itself is carried out for 30-45 minutes below 23°C with 12-14% (vol) sulphuric acid electrolyte using a current density of 1 A/dm^2 (10 amp/sq ft) for a dense load, or 1.5-2 A/dm^2 (15-20 amp/sq ft) for larger work.

The usual cleaning techniques are used and, if a bright finish is required, the work may be chemically polished before anodizing. Normal sealing or dyeing may be carried out if desired after the process is complete. Efficient rinsing is essential to remove traces of acid, particularly for work which is to be dyed, and it is best to transfer the work to a larger basket before the final rinse.

Applications of basket anodizing are stated to be fittings, parts of tongs, awning rings, clasps, crochet hooks, curtain rings, hooks and runners, pencil sharpeners, knobs, handles, pen caps, umbrella ferrules, dress clasps, zip fastener ends, press studs, buttons, buckles, and costume jewellery. The method has been also introduced for basket anodizing aluminium castings and architectural parts. the surface being impregnated with plastic to reduce the effect of porosity.[107]

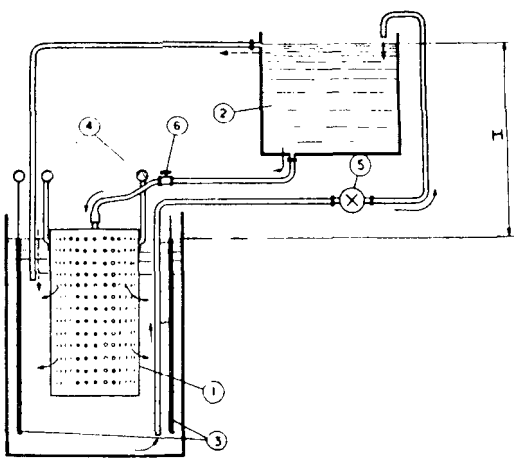


Fig. 7-23. Diagram of the equipment used for basket anodizing using external cooling of the electrolyte

Key:
1. Basket
2. Electrolytic reservoir
3. Cathodes
4. Anodes
5. Pump
6. Control valve

- - - ● = overflow
H = height of pressure head
——● = (direction of circulation of electrolyte

4. SULPHURIC ACID PROCESSES

The first sulphuric acid process was patented in England in 1927, though it was first extensively used and developed in the U.S.A. Since then the use of sulphuric acid for anodizing has spread all over the world, and many variations of the process have been patented.

Early solutions contained approximately 25% (wt) sulphuric acid; in later years the acid concentration has been reduced to 10-20% (wt) according to the film properties required, while several addition agents are in use. **All** the industrial processes employ direct current. In the standard processes, current densities are normally of the order of 1-2 A/dm^2 (10-19 A/ft^2) requiring 10-22 volts, and the bath is worked at temperatures between 15 and 24°C for anodizing times of up to about 60 minutes. After anodizing (and colouring if required) the work is normally sealed in boiling water or steam (see Chapter 11).

On most aluminium alloys a colourless, transparent anodic coating is produced, but alloys containing high manganese and silicon levels, or those in a heterogeneous condition, tend to give greyish or brownish coloured coatings. In almost all cases the transparency of the coating decreases as the film thickness increases.

The particular operating conditions chosen will depend on the application envisaged and the film properties desired, but, particularly with sulphuric acid anodizing, small changes in operating conditions, especially electrolyte temperature, can affect film properties considerably, so they must be closely controlled. The use of dilute solutions and lower temperatures favours harder coatings, while more concentrated solutions and increased temperatures and operating times, i.e., those factors which favour the dissolution of the coating in the electrolyte, may produce coatings which are soft at the surface, and in the extreme, may be powdery or spongy and easily rubbed off. For this reason also, the hardness and wear-resistance of a coating are not uniform throughout the film but are lower nearer the top surface.

Thus there is always a balance between oxide film formation and its redissolution in the sulphuric acid electrolyte, and this controls the upper limit of thickness which can be produced under any particular operating conditions as well as the film properties. The way in which the anodizing parameters are altered in practice for typical cases of bright, architectural and hard anodizing is shown in Table 7-8.

The difference between bright anodizing and protective anodizing conditions in Table 7-8 arises from the influence of anodizing voltage on the roughness of the metal/oxide interface (see Fig. 3-30), the higher voltages leading to a rougher metal/oxide interface and hence a reduced specular reflectivity.

In considering operating conditions in anodizing, it cannot be too strongly emphasised that a change in one parameter cannot be effected without corresponding changes in others, and the relationships will vary with different alloys. The voltage required to obtain the same current density may vary considerably between one alloy and another, a factor which must be considered by the practical anodizer when working to specifications, and which frequently makes it undesirable to anodize different alloys at the same time (see page 442).

TABLE 7-8

Variation in sulphuric acid anodizing conditions according to product applications

Product	*Electrolyte concentration* (% by wt of H_2SO_4)	*Electrolyte temperature* (°C)	*Current density* (A/dm^2)	*Typical voltage* (V)	*Approximate limiting film thickness* (microns)
Bright trim	18-24	22-24	1.0-1.2	14-15	30-35
Architectural	15-18	18-22	1.4-1.8	17-20	40-50
Hard anodizing	15-16	0-5	2.0-3.0	25-50	80+

Process details

For architectural anodizing a publication by the British Anodizing Association[""] gives recommendations for good sulphuric acid anodizing practice as follows:

Electrolyte temperatures: 18-20°C controlled to within ± 1°C of nominal. (High temperatures are particularly damaging since **they** lead to excessive film attack and anodizing should not be conducted at temperatures higher than 21 "C. Temperatures below 17°C will not lead to film quality problems, but high anodizing voltages and cooling capacity will normally be required.)

Electrolyte concentration: 160-185 g/l (8.5-10% by vol) H_2SO_4 controlled to within ± 10 g/l of nominal. (High electrolyte concentrations lead to increased film attack, particularly in combination with high electrolyte temperatures. Low electrolyte concentrations will not usually give film quality problems but will necessitate the use of high anodizing voltages.)

Anodizing current density: 1.4-2.0 A/dm^2 (13-19 A/ft^2). (Low anodizing current densities mean a slow rate of film formation, hence increased attack on the film. Use of low current densities is particularly dangerous when producing films more than 15 microns (0.6 mil) in thickness. High current densities mean fast rates of film formation, but film thickness variation over a load is increased and contact problems may be experienced.)

Electrolyte agitation: Even and effective. (Agitation of the anodizing electrolyte is essential in order to take heat away from the surface of the anodic coating. Agitation should be even and effective and should be sufficient to give uniform temperature distribution throughout the anodizing electrolyte.)

Anodizing voltage: in range of 17-21 V as required. (A rectifier supply capacity of up to 24 V is normally necessary.)

These recommendations are made in order to avoid film quality problems when producing thick architectural coatings (25 microns (1 mil)).

In the case of aerospace and defence work the sulphuric acid process is detailed in DEF STAN 03-25/3.[109] It stipulates a solution containing 90-400 g/l of sulphuric acid which shall be maintained within 10% of the normal by additions of acid as necessary. The chloride in the electrolyte shall not exceed the equivalent of 0.2 g NaCl per litre, and aluminium content shall be less than 25 g/l for minimum concentration and **less** than 12 g/l for maximum concentration of sulphuric acid. The electrolyte temperature shall be 20 ± 2°C.

The electrolyte shall be agitated by air or mechanical means sufficient to maintain a uniform temperature throughout the vat, and it shall be kept clean and free from suspended matter by filtration or other means.

The cathode material shall be lead or antimonial lead. The treatment is preferably controlled by current density (normally 100-200 A/m^2 of anode surface) but may be controlled by voltage.

After anodizing the work is washed thoroughly in clean cold running water, and any dyeing should be done immediately without allowing the parts to dry. Sealing is effected in a dichromate solution except in the cases of dyed work, work required in natural colour or where chromate is inadmissible for some other reason (e.g. contact with concentrated hydrogen peroxide), when demineralised water at over 96°C is used.

If the unsealed parts are dried this should be done at a temperature of not more than 110°C except for parts to be bonded or painted where the temperature must not exceed 60°C, or for flaw detection where they are allowed to dry naturally.

The sulphuric acid process is not suitable, according to the specification, for parts containing riveted, lap or folded joints in which retained traces of acid may cause corrosion. Neither must it be used on alloys containing more than 7% copper.

The equivalent American specification,''' MIL-A-8625F (1993), does not specify anodizing conditions for a Type II (sulphuric acid) coating, but the performance requirements are similar.

In practice sulphuric acid anodizing is now almost universally used for general decorative and protective purposes, and other electrolytes are only used when special properties are required. In America and Britain the sulphuric acid process is sometimes known by its original trade name 'Alumilite', while in Germany and other European countries the sulphuric acid process goes under the name Eloxal GS.

Effect of varying the operating conditions

Any discussion of the effect of operating conditions on the properties of the anodic coating is complicated by the interdependence of most of the variables.

Several of the basic properties are associated intimately with the rate of growth and the solvent action of the electrolyte, which not only determine the thickness of the coating but also its porosity, its mechanical properties and its chemical composition. Acid concentration, temperature, current density, agitation, voltage and the type of current will influence these properties. Sheasby[111] has recently reviewed the way in which anodizing conditions are varied for a whole range of applications. In addition the alloy being anodized has a major influence on the anodizing conditions required (see for example Fig. 7-2), and this must always be taken into account, particularly in the case of bright anodizing where reflectivity and image clarity are of importance (see Vol. 2, Chapter 12, pp. 1086-92, 'Factors affecting reflectivity'). In this case anodizing voltage is also critical and decrease in voltage tends to improve image clarity, especially on annealed material.[112] Cooke[20] examined the effect of electrolyte temperature and anodizing current density on a range of film properties, and showed that if higher current densities were used as the electrolyte temperature increased, essentially similar film properties could be produced (Fig. 7-24). An interesting development by Alcoa[113] in the bright anodizing field is a process that produces high reflectance material without using a chemical or electrochemical brightening treatment. In this process bright rolled aluminium is dc anodized in a 26% (wt) sulphuric acid electrolyte at a current density of at least 1.9 A/dm^2 and a temperature of 15-28°C. Anodizing is carried out for 0.5-10 min to give films of about 1-4 microns.

The film thickness produced depends on the alloy used and the operating conditions, and Kissin *et al.*[49] investigated the build-up of anodic coating thickness with time using a wide range of alloys, and their results are shown in Fig. 7-25. They used a 165 g/l sulphuric acid electrolyte at temperatures of 20 and 25°C and a current density of 1.3 A/dm^2 (12 A/ft^2). The much lower limiting film thickness achieved with 2000 series alloys (AI-Cu), particularly at 25°C, can clearly be seen. The thickness of the anodic film is a function of the product of current density and time, electrolyte concentration and temperature being constant. Thus to obtain a thickness of 25 microns (1 mil) requires a minimum of about 85 ampere-minutes per square decimetre of surface (800 A-min/ft^2) in a time not exceeding 75 minutes, assuming an acid concentration of 15% (wt) and a temperature of 20°C. For a thickness of 15 microns (0.6 mil), about 55 A-min/dm^2 (500 A-min/ft^2) in a time not exceeding 45 minutes are required.

In investigating the effect of current density and temperature on the thickness of the coating. Herenguel and Segond[51] obtained the results plotted in Fig. 7-26 for 99.5% aluminium and in Fig. 7-27 for an aluminium-6.5% magnesium alloy. The expected increase in coating thickness with increasing current density and drop in temperature is seen after 45 minutes in 10% (vol) sulphuric acid, being rather more pronounced in the case of the AI-Mg alloy. The vertical hatching shows the thickness of a soft outer layer which is obtained if the current density is too high at elevated temperatures. This soft layer not only adversely affects the

wear resistance of the coating but also reduces its transparency. Acceptable conditions for anodic oxidation are indicated in Fig. 7-28.[10] Above the curve AB the film is too dense and has a tendency to crack.

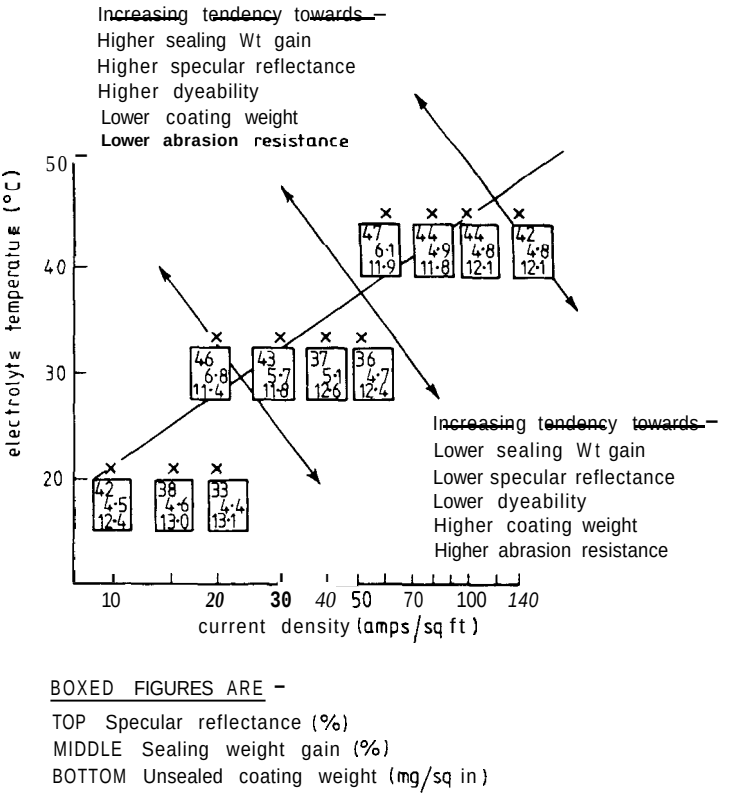


Fig. 7-24. Influence of current density and temperature of 15% (wt) H_2SO_4 electrolyte on the film characteristics of bright anodized 6063 extrusions

On the right of CD soft superficial layers are formed. It should be explained that the full lines are for unalloyed aluminium and the dotted lines are for an Al-Cu-Mg-Mn alloy. The ranges for other alloys will vary with their composition. The softer surface layer is a typical case of film breakdown due to excessive temperature on a heavy-metal-containing alloy.

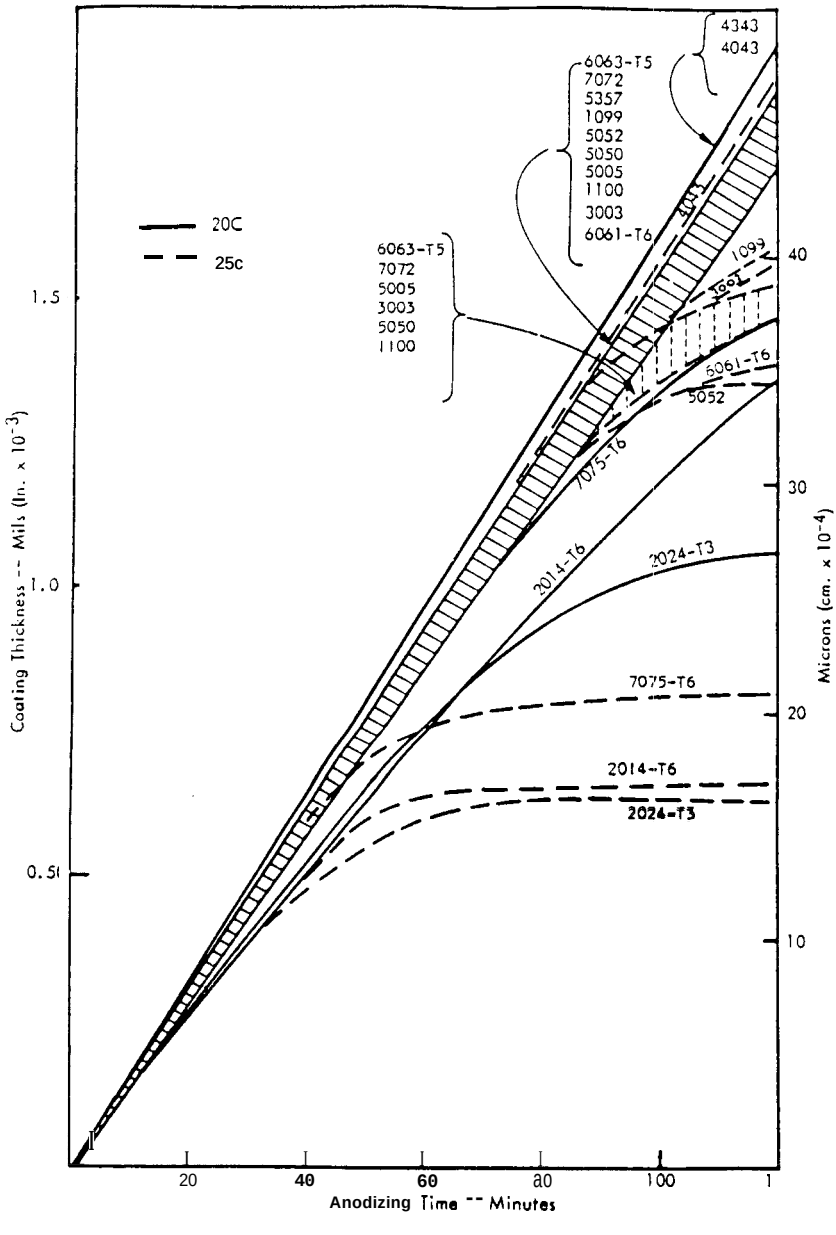


Fig. 7-25. Anodic coating thicknesses of aluminium alloys (15% H_2SO_4, 12 amp/ft^2, 0-120 minutes)?'

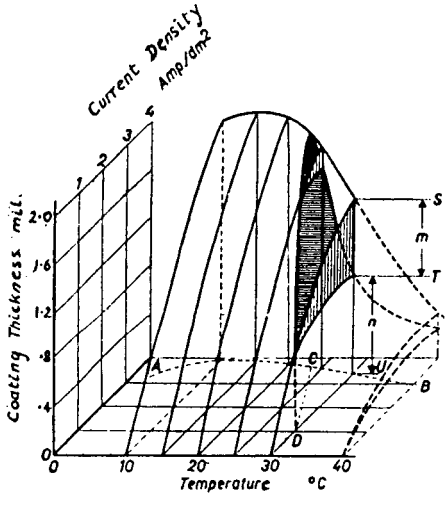


Fig. 7-26. Anodic coating thickness produced on aluminium (99.5%) in 10% sulphuric acid after 45 minutes. Vertical hatching shows soft outer layer.[51]
m = thickness of soft layer.
n = thickness of hard layer. m+n total thickness of coating

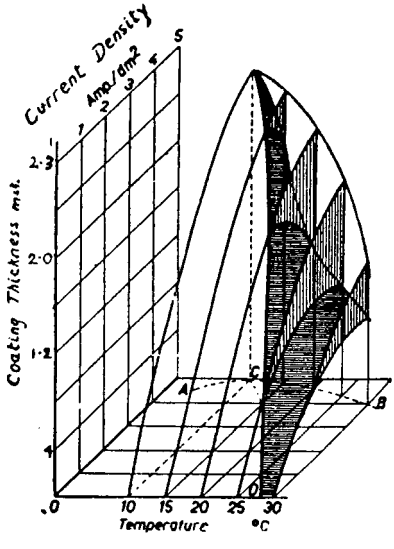
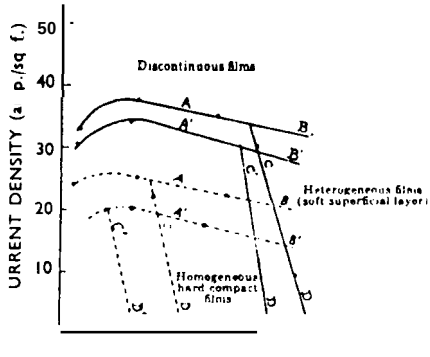


Fig. 7-27. Anodic coating thickness produced on an aluminium-magnesium alloy (6.5% Mg) under identical conditions to Fig. 7-26.
1 mil = 25.4 μm



The softening effect of high electrolyte temperatures on the outer layers of thick anodic coatings has been demonstrated very effectively by Thomas.[114] He measured the abrasion resistance of 25 micron (1 mil) anodic coatings on 5005 alloy. The coatings were produced at electrolyte temperatures of 18-28°C in 180 g/l H_2SO_4 using a current density of 1.5 A/dm^2 (14 A/ft^2). In measuring the abrasion resistance Thomas used both an abrasive jet test (BS 6161: Part 10: 1987) and an abrasive wheel test (BS 6161: Part 9: 1987). The abrasive jet method measures the weight of abrasive required to penetrate the total thickness of anodic coating, and so gives an average abrasion resistance of the coating. On the other hand the abrasive wheel test can be used to remove a particular thickness of film and so can indicate differences in abrasion resistance from the outer to the inner layers. Thomas measured the number of abrasive movements (double-strokes) needed to remove 6 microns (0.24 mil) and 10 microns (0.4 mil) from the film surface and compared them with the average values obtained from the jet test. In each case he gave the result obtained at 18°C a value of 100, and compared other values with it in percentage terms. Results are shown in Table 7-9.

TABLE 7-9

Effect of temperature on abrasion resistance of 5005 alloy using various criteria for measurement[114]

Temperature in °C	Abrasive jet test	Abrasive wheel test	
		Abrasion to remove 10 μ	Abrasion to remove 6 μ
18	100	100	100
20	92	84	80
23	77	41	31
25	67	25	23
28	51	21	13
Ratio of 18" to 28"	2.0	4.0	7.7

It can be seen from Table 7-9 that, in terms of average abrasion resistance, a film produced at 28°C is only half as abrasion resistant as one produced at 18°C. However, from the abrasive wheel test, the outer 6 microns of the film produced at 28°C can be considered to have only one eighth the abrasion resistance of the 18°C film. This is clearly very significant and highlights the problem of producing thick films at high electrolyte temperatures.

Even so other workers have used high electrolyte temperatures and concentrations and Prati, Sacchi and Paolini,[115] who conducted a detailed investigation into the effect of operating variables on the resistance to corrosion and abrasion as well as on other properties of anodic oxide coatings produced in sulphuric acid, came to the conclusion that the best results are obtained with a 15%(wt) sulphuric electrolyte at 25°C and with a 25% electrolyte at 18°C. In the 15% (wt) solution, Spooner[116] has also observed that raising the temperature from 15 to 25°C results in a significant reduction in the number of corrosion pits caused by outdoor exposure. However these conditions are unlikely to be suitable for producing thick films for architectural purposes.

The effect of electrolyte impurities on film properties has been examined by Israeli workers."' They particularly studied the effect of nitrate ions and concluded that up to about 1000mg/l of nitrate in a 20% (wt) sulphuric acid electrolyte improved anodizing efficiency. Above this level there was no further benefit.

A very damaging contaminant in a sulphuric acid electrolyte is chloride, and at levels above 200 mg/l it can lead to pitting during the anodizing process (Fig. 7-29). Heavy metal ions are also claimed to give problems, particularly when anodizing brightened material, and Fe at above 50 mg/l,[82] Cu at above 125mg/l[82] and Pb at above 50 mg/l[6] are said to be detrimental.

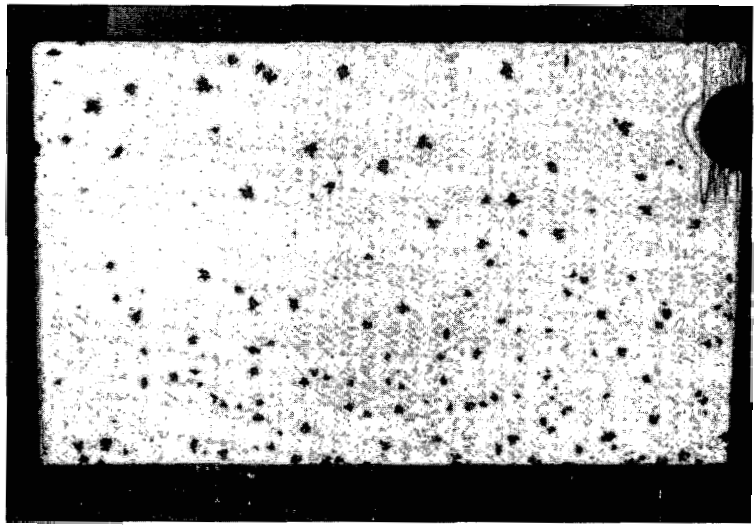


Fig. 7-29. Pitting on 6063 extrusion caused by chloride in the anodizing electrolyte

The contaminant that is always present in anodizing electrolytes is aluminium, and it is generally felt that a minimum level of about 5 g/l is beneficial rather than

detrimental. The rate of aluminium build-up in the anodizing electrolyte will vary with the conditions used, but typically about 10 g of aluminium is dissolved per m^2 of surface anodized (20 micron film). The upper limit permissible has been the subject of much debate and maximum levels of 15-20 g/l are usually quoted. On the other hand DEF STAN 03-25/3[109] allows a varying level of aluminium, according to the sulphuric acid concentration used, whilst for architectural anodizing the current Qualanod Specification[118] limits the aluminium content to 20 g/l in a 200 g/l (max) sulphuric acid electrolyte. In general, however, high aluminium contents do not lead to film quality problems, but they may cause precipitation of aluminium sulphate in heat exchangers and cooling coils and consequent problems with acid circulation. In most plants a proportion of the anodizing electrolyte is dumped when the aluminium content reaches the maximum acceptable level, but ion-exchange systems for regenerating spent sulphuric acid electrolytes are available and are increasingly being used. Alternatively the aluminium may be precipitated as ammonium alum by adding ammonium sulphate and cooling, or the sulphate of an alkali metal could be added to prolong the life of the electrolyte by keeping the aluminium in solution.

Apart from ionic contaminants, care must be taken to ensure that oil or grease are not present in the anodizing electrolyte. The most usual source of such contamination is the air used for agitation and efficient oil traps are essential on all air lines, particularly when using a compressor. Any oil present in the anodizing baths will readily be taken up on the coating surface and will prevent colouring and cause staining. Grease or oil present on the work before anodizing may inhibit film formation completely.

Electrolyte agitation is universally recognised as being an important factor in efficient anodizing, but little quantitative work has been carried out on this subject. Spooner[119] worked with a 1250 litre (275 gallon) bath containing a 15% (wt) sulphuric acid electrolyte at 21°C, and using a voltage of 18 volts he noted the current densities obtained with varying degrees of agitation. His results are shown in Table 7-10.

TABLE 7-10

Effect of agitation on anodizing current density[119] (1050 alloy)

Agitation	*Air flow (cu.ft/min/gal)*	*Current density (A/ft^2)*
None	0	23.2
Light	0.07	19.6
Moderate	0.14	14.0
Vigorous	0.19	14.0

It is obviously desirable to work under conditions where slight variations in air flow will not affect the current density achieved, so the degree of agitation should at least correspond to that described as 'Moderate' in Table 7-10.

Agitation is also important in controlling the film thickness obtained, in that it affects the degree of re-dissolution of the coating during anodizing. This is again demonstrated by Spooner[119] in work carried out at a constant current density of 1.6 A/dm^2 (15 A/ft^2) and shown in Table 7-11.

TABLE 7-11

Effect of air agitation on bath voltage and anodic oxide film thickness[119] (1050 clad alloy)

Agitation	*Bath voltage required (V)*	*Film thickness produced (microns)*
None	16.6	16.2
Light	16.9	17.5
Moderate	18.3	18.7

Prati, Sacchi and Paolini have done similar work[115] with essentially the same results.

The coating ratio

A useful concept in determining the course of anodic oxidation is the 'coating ratio'. This term was proposed by Mason and Fowle[120] and represents the weight of the coating divided by the weight of aluminium reacting (the last being the combined weight of metal converted into oxide plus that going into solution).

Assuming that the coating is composed entirely of Al_2O_3, the coating ratio has a theoretical maximum of 1.89. In practice the anodic coatings nearly always contain some of the solution anion. In the case of sulphuric acid anodizing on 99.95% aluminium, approximately 12-14% SO, (calculated from sulphate determination) is found in the coating which gives a maximum coating ratio of approximately 2.2.

From the foregoing discussion on the effect of the operating variables, it follows that, other conditions being constant, the coating ratio will decrease with time and can be increased by reducing the bath temperature and acid concentration or by increasing the current density and voltage. It can also be increased by certain additions such as oxalic acid.

The way the coating ratio is influenced by some of these variable has been shown in a detailed investigation by Mason and Fowle, one of whose graphs is reproduced in Fig. 7-30. Decrease of coating ratio is approximately linear with time at constant current density. The voltage rises as the coating thickness increases, and this reflects increasing dissolution of the coating during its growth, associated both with a larger active surface area with progressive dissolution in the pores, and increase in the local temperature due to the higher voltage required as the coating grows in thickness.

The effect of increasing the current density is to speed up the rate of growth. This effect of current density will last the whole course of normal anodizing and becomes even more pronounced in time if the bath temperature has a very pronounced effect on increasing the coating ratio. Thus, at 10°C, which is a temperature commonly used in hard anodizing, the effect of anodizing time in reducing the coating ratio is negligible at current densities as low as 24 amp/sq ft (2.5 A/dm^2), while at current densities above 48 amp/sq ft prolonging the treatment causes a progressively steep rise in the coating ratio. This rise can be explained as being due to a decrease in solution rate within the pore channel due to build-up of solution product.

The excess of dissolution products may be pictured as due to the rapid dissolution at the high temperatures obtaining at the pore base (estimated at 125°C), which cannot be dealt with by the diffusion rate further up the pore in the cooler solution. For the same reason, it is noteworthy that increase in coating ratio with time at low temperatures and high current densities is inevitably associated with a steeply rising voltage, and in practice these conditions therefore present serious disadvantages.

Another indication of anodizing efficiency which is related to the coating ratio is a measurement of the anodic coating weight produced under standard conditions. This is clearly dependent on the anodic film thickness produced and is strongly influenced by the alloy being anodized as well as by the anodizing conditions. Kissin *et al.*[49] report work of this type, and results obtained using a 165 g/l sulphuric acid electrolyte at 1.3 A/dm^2 (12 A/ft^2) and temperatures of 20 and 25°C are shown in Fig. 7-31.

Even under the most favourable conditions, the weight of anodic coating produced is only about 61% of the theoretical weight of Al_2O_3 calculated from Faraday's Law. Since most alloys show high anode consumption efficiency, direct electrochemical dissolution of some aluminium must be involved in the reactions taking place. Beyond a 30 minute anodizing time, some of the less efficient anodizing alloys (e.g., the 2000 series) show a fall-off in the rate of oxide production due to dissolution of the coating. This also occurs when the anodic film thickness produced is measured (Fig. 7-25), but the greater effect on the coating weight is a strong indication that much of the dissolution of the coating takes place within the pores.

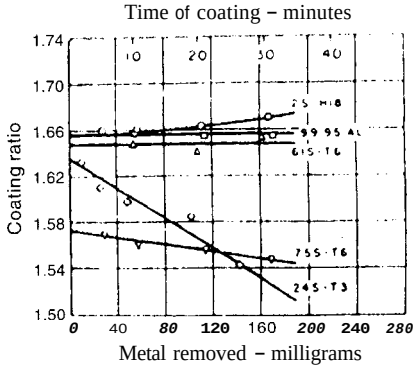


Fig. 7-30. Coating ratios for various alloys anodically treated in 15% H_2SO_4 at 1.1°C with a current density of 24 amp/sq ft (2.5 A/dm^2)

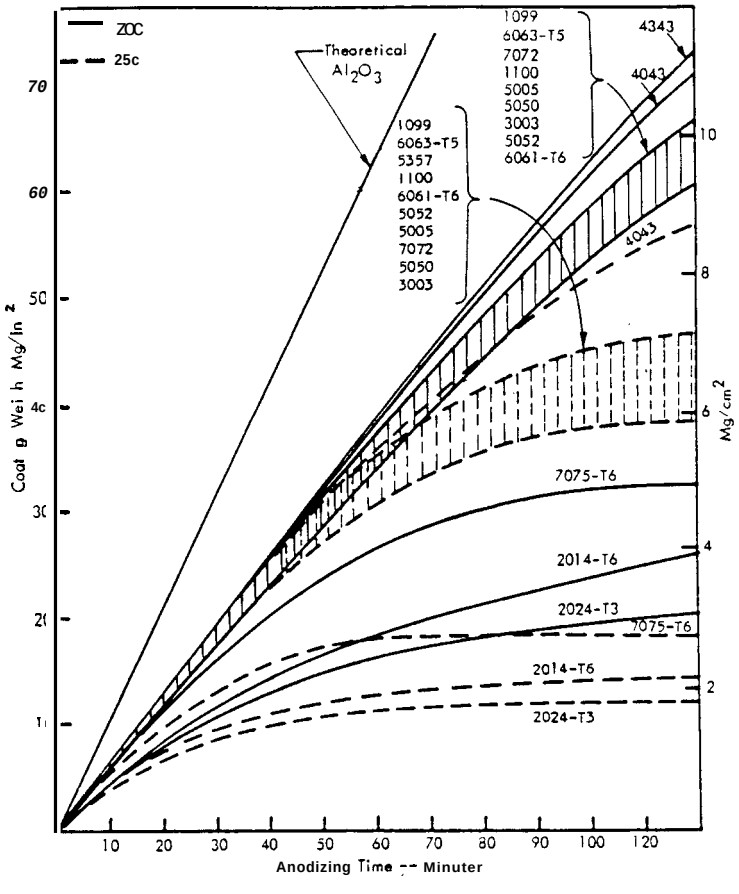


Fig. 7-31. Anodic coating weights of aluminium alloys (15% H_2SO_4, 12 amp/ft^2, 0-120 minutes)[49]

Both coating ratio and coating weight have been used as a control method for evaluating the efficiency of the anodizing process, and, particularly in the U.S.A., minimum coating weights or coating ratios have been used in anodizing specifications.

Anodizing with alternating current

The sulphuric acid electrolyte, in common with oxalic acid, is one which can be used for anodizing with alternating current, although in point of fact there has been scarcely any industrial usage of this fact other than for the treatment of wire. It was described by Jenny in 1937[76] and it is widely believed to provide coatings which are more flexible and more clear. To a large extent such views depend on the fact that when direct current is compared with alternating at the same rms value the latter is only anodizing for half the time so that the effective current density is only half as great arid the final coating thickness very much less. Sacchi and Paolini[121] have made quite a detailed comparison of the a.c. and d.c. processes for strictly equivalent operating conditions, that is when the positive current is the same in each case, investigating the effects on coating ratio, sealing, structure, barrier thickness, colour, reflectivity, dye absorption, corrosion and abrasion resistance. They suminarised their conclusion\ thus:

1. The general opinion that a.c. films are more transparent has been partly confirmed and partly disproved: a.c. does produce clearer films on some alloys, but inuch of the apparent advantage is due to the lower thickness of a.c. films in comparison with d.c. films obtained at the same (effective) current density or total cell voltage.

2. The general opinion that a.c. films can be dyed more deeply and more uniformly has also been partly confirmed. Most of the advantages of the a.c. process could also be obtained by d.c. anodizing at lower voltages, for the same reasons as above. However, on some cast materials, more uniform dyeing can be obtained by the a.c. process because of the very efficient degreasing action of a.c.

3. The general opinion that a.c. anodizing is cheaper has not been confirmed: a.c. anodizing requires higher voltages and about 50% more effective current than d.c. anodizing, and this in the long run should nullify the advantage of using a cheaper current source.

4. No sound films thicker than about 12 μm could be obtained with a.c. and therefore this process should not be suitable when a high degree of resistance to pitting corrosion is required, as is the case of architectural films in severe atmospheres.

5. The pore number of a.c. films is slightly higher than for equivalent d.c. films, but a.c. films have a tendency to hydrate in sealing to a much greater extent than would be accounted for by their presumed real surface.

6. The barrier layer thickness of a.c. films is in the regular range of 1 - 1.1 nm/V if the maximum voltage of the a.c. wave is taken as the forming voltage.

7. Under normal anodizing conditions the rectifying effect of the aluminium electrode is about 15% only; the anodic voltage drop at a current density of 1.5 A/dm^2 **in normal bath conditions is about 6-7 V, that is,** markedly lower than with the d.c. process.

8. The natural colour of a.c. films is yellowish; the depth of colour is a function of film thickness only and not of other anodizing conditions; the colour is greatly diminished by boiling water sealing and is greatly intensified by Cu or Fe ions in the anodizing bath.

9. Abrasion and corrosion resistance of a.c. films are much lower than those of equivalent d.c. films when the comparison is made between films thicker than 6 μm produced at low temperatures, high current densities; the comparison becomes more and more favourable to a.c. films when the range of conditions considered includes thin, soft, and clear films produced at high temperatures, low current densities.

More recently a.c. anodizing in sulphuric acid electrolytes has received more attention and Kape[122] was a particular advocate of this method. He emphasised the cathodic reduction of sulphuric acid that occurs during a.c. anodizing, with the production of hydrogen sulphide in the film, and coatings produced in this way actually smell of hydrogen sulphide on withdrawal from the anodizing electrolyte. Films produced on commercial purity aluminium alloys at 15-20 microns thickness have a pronounced greyish-yellow opacity, whilst those produced on copper containing alloys are opaque light grey; those on silicon containing alloys are dark grey.

These natural colours change considerably on sealing in boiling water. The colour of the coating on commercially pure alloys appears to fade, whilst alloys containing copper turn green owing to the formation of copper sulphide in the film. Brownish shades are produced when anodized alloys containing manganese or nickel are sealed. These colours are very difficult to control and match, but the sulphur content of the film may be combined with heavy metals to produce coloured sulphides which are said to be fast to u.v. light. The range of colours which can be produced is considerable and some are shown in Table 7-12. Japanese workers[123] have also noted the effect of sulphide colouring.

TABLE 7-12

Showing colours produced (before sealing) when a.c. sulphuric acid anodized 1100 or 6063 (15 pm-25 pm) is dipped into salts[122]

1100(SIC) or 6063TF(HE9)

Salt solution	*Basic colour produced*
Antimony potassium tartrate (Sb^{3+})	Orange
Sodium arsenate (As^{3+})	Yellow
Bismuth ammonium citrate (Bi^{3+})	Yellow-brown
Copper sulphate (Cu^{2+})	Yellow-brown*
Cobalt acetate (Co^{2+})	Black
Cadmium acetate (Cd^{2+})	Canary yellow
Gold chloride (Au^{3+})	Violet (purple of Cassius)
Lead acetate (Pb^{2+})	Mahogany
Ferric ammonium oxalate (Fe^{3+})	Black
Sodium molybdate (Mo^{3+})	Orange
Nickel ammonium sulphate (Ni^{2+})	Bronze
Sodium selenate (Se^{3+})	Reddish brown
Silver nitrate (Ag^{+})	Grey-brown
Stannic ammonium chloride (Sn^{4+})	Dull yellow
Stannous ammonium chloride (Sn^{2+})	Brown
Uranium acetate	Brown

**Goes green on sealing*

Most colours are stable on sealing in boiling water.
Nickel acetate sealing causes a brown-black colour

Whilst the sulphide produced can be utilised for colouring, it is detrimental if a clear anodic film is required, and Kape suggested incorporating an oxidizing agent such as ferric ammonium sulphate or potassium permanganate in the anodizing electrolyte to oxidize the sulphides formed.'?![24] Under these conditions he found that a.c. anodizing can be carried out at high current densities, and clear films up to 90 microns in thickness can be obtained. In his final work on this subject Kape[125] compared a.c. and d.c. sulphuric acid based processes. He used an addition of 17.5 g/l of Fe, added as ferric sulphate, in a 167 g/l sulphuric acid electrolyte for the a.c. anodizing, and showed that, in terms of abrasion resistance, sealing quality and corrosion resistance, the films were equivalent *to* those produced under d.c. conditions. **A** slight yellowing of the coating was seen with thick films (25 microns), but an attractive florentine bronze colour was obtained on the Al-Li-Cu alloy, 8090. The latter he found to be much more suitable for anodizing than 2014A or 7075.

Further work on oxidizing additives has been reported by Eyre and Gabe.[126] In later work Gabe[127,128] reported on the role of modifying additives, and showed that they could both increase the film thickness obtained and improve appearance. Ferrous oxalate had the greatest beneficial effect on film thickness, followed by ferric chloride and ferric citrate. Results of film thickness against time are shown for an unmodified solution in Fig. 7-32, and for a solution containing 1, 2 or 3 g/l ferrous oxalate in Fig. 7-33.[129]

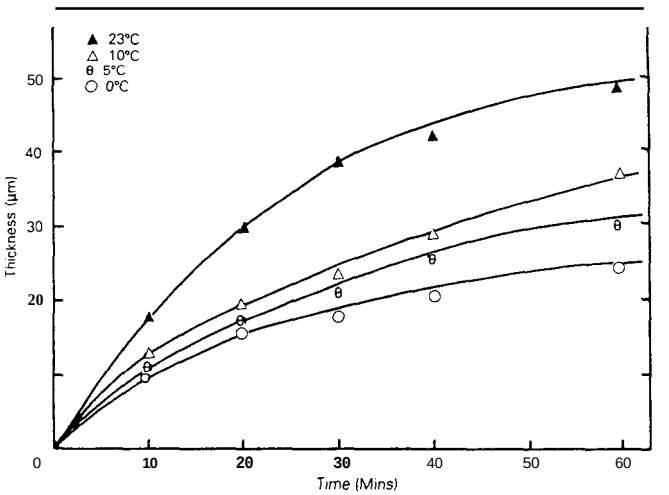


Fig. 7-32. Film thickness against time after a.c. anodizing at 35V and 0°, 5°, 10° and 23°C, in unmodified solutions.[129]

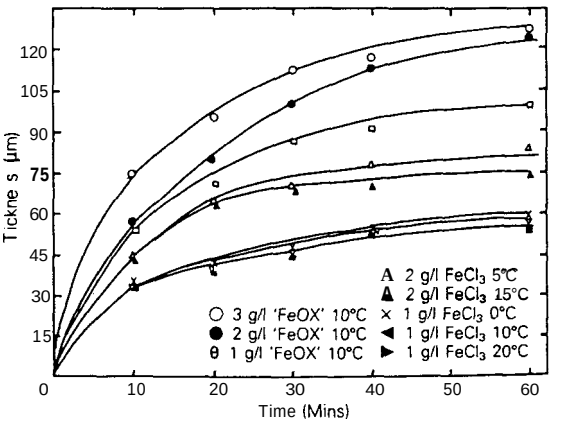


Fig. 7-33. Film thickness against time for solution containing 1, 2 and 3 g/l ferrous oxalate at 10°C and 35V.[129]

Cooke[130] carried out a study of a.c. anodizing in 15% and 38% sulphuric acid electrolytes at temperatures of 0-40°C, current densities of 3.0-12.0 **A**/dm^2 and times of 0.5-30 min, and measured the properties of the coatings produced. He concluded that anodizing efficiency was improved by the use of high current densities and that films with good general properties could then be produced. He again pointed to the presence of sulphide in the film, and found that 60% of the sulphur in the film was in the form of sulphide rather than sulphate.

The incorporation of intermetallic particles during a.c. anodizing has been investigated by workers in Israel"' and more fundamental work has been carried out at U.M.I.S.T,[132] and by Barbosa *et al.*[133]

One of the few significant industrial uses of a.c. anodizing has been described by Harris,[134] who details use by ITT Cannon on both wrought and cast hardware.

Effect of current form

In somewhat similar studies in Japan, Tajima, Satoh, Baba and Fukushima[135] examined the influence of current wave form in the sulphuric and oxalic acid processes, in which they used not only d.c. and a.c. but also a number of combinations of d.c. with single-phase and three-phase a.c. as indicated in Fig. 7-34. The effects were studied of current form on X-ray diffraction patterns, appearance, coating ratio, density, abrasion resistance and hardness and some results are reproduced in Table 7-13. The real difference which these authors noted was when the treatment conditions included periodic interruptions of the current.

The anodizing coating ratio has its maximum value for the rectified single phase half wave current, and the value becomes smaller in the following order: 3-phase non-reversed interrupted current; d.c.; a.c. + d.c.; imperfectly rectified current; a.c. (the smallest). In the imperfectly rectified current the value is larger for 1-phase than for 3-phase current, and decreases with increase of the negative component. In the same manner the interrupted currents also give coatings of the greatest density, thickness, hardness and abrasion resistance.

They conclude that with alternating current the discharge of the hydrogen ion tends to destroy mechanically the oxide structure in the micropores, or promotes the chemical dissolution of the film, so that the properties are inferior. However with interrupted current such as single phase half wave, and 3-phase non-reversed interrupted currents, a current larger than the mean value indicated by the ammeter passes through a rapid discharge followed by a pause. Therefore a good quality film is produced just as in the case of anodizing with a higher current density. They conclude that anodizing with interrupted current gives, in general, oxide films of the best quality as compared with other possible wave form, including direct current, that is, for conditions where the positive current density and the total current are the same.

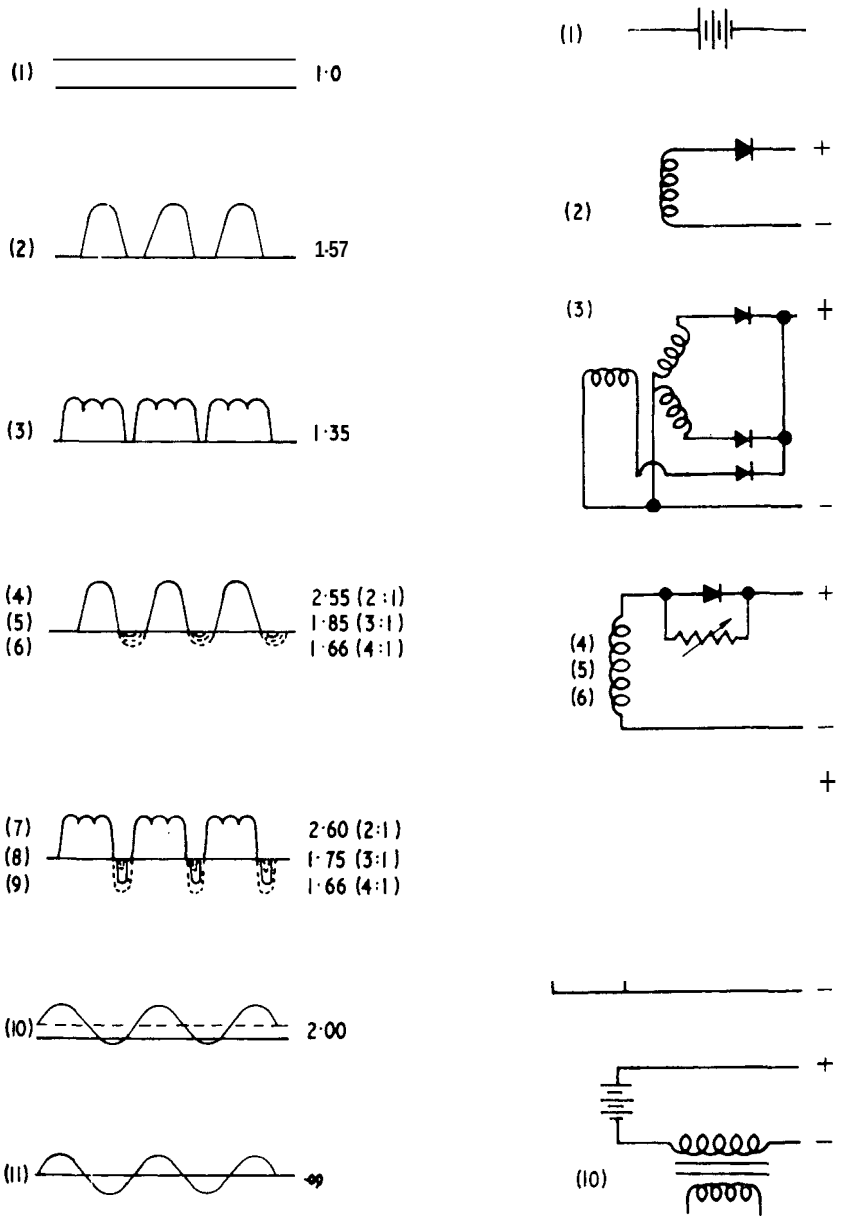


Fig. 7-34. Various wave forms applied by Fukushima et al[135] and their circuit diagrams

TABLE 7-13

Properties of sulphuric acid films[135]

H_2SO_4 15 wt.%, 30°C, 1 A/dm² (mean positive current), 30 min.

Current Form	*Voltage*		*Coating ratio*	*Thickness (μm)*	*Density*	*Abrasion** resistance (sec)*	*Hardness (μ Vickers)*	*Appearance*
	dc (V)	*ac (V)*						
Direct current (battery)	13.0	–	1.16	8	2.46	455	78	Non-coloured transparent
1-P Half wave	13.5	14.5	1.25	8	2.66	435	84	Non-coloured transparent
3-P Non-reversed interrupted	13.0	15.5	1.22	1.5	2.76	640	80	Non-coloured transparent
1-P Imperfectly rectified (2:1)*	4.0	10.0	1.10	7	2.32	205	54	Light yellowish-gold, opaque
1-P Imperfectly rectified (3:1)	4.5	10.0	1.13	7	2.32	225	46	Light yellowish-gold, opaque
1-P Imperfectly rectified (4:1)	4.5	10.0	1.16	7	2.42	280	64	Light yellowish-gold, opaque
3-P Imperfectly rectified (2:1)	5.5	11.5	1.04	6.5	2.38	175	48	Light yellowish-gold, opaque
3-P Imperfectly rectified (3:1)	6.5	11.5	1.08	6.5	2.46	165	47	Light yellowish-gold, opaque
3-P Imperfectly rectified (4:1)	8.0	11.0	1.09	7	2.25	185	47	Light yellowish-gold, opaque
Superimposed (ac + dc)	10.0	10.0	1.13	7	2.50	370	78	Non-coloured transparent
Alternating (ac)	1.6	11.0	1.04	5.5	2.70	155	43	Light yellowish opaque

* ratio of positive (1 A/dm²) and negative current

** specified by Japanese Industrial Standards (JIS-H 8601)

Low voltage anodizing in sulphuric acid

An interesting development by Alcoa[136] has been the production of a coloured anodic coating in a sulphuric acid electrolyte by anodizing at low voltages. The work is first anodized conventionally in, for example, a 15% (wt) sulphuric acid electrolyte at a voltage of 12-20 volts to a thickness of about 15 microns. The voltage is then reduced over a period of 0.5-5 minutes, at a typical rate of voltage reduction of about 4 volts/min, to a level of not more than 3 volts. Anodizing is then continued at this low voltage for times of 4 to 12 min. This treatment is said to increase the thickness of the barrier layer, and it is this increase of thickness combined with the composition of the layer, and the constituent incorporation that takes place, that is believed to produce colour. With the extrusion alloys such as 6063 and 6061 light bronze or grey coloured finishes are produced, according to the concentration and temperature of the electrolyte.

Low voltage anodizing has been used for another purpose by Thomas.[137] After conventional anodizing he reduced the anodizing voltage under a.c. conditions to a value of about 4 V, in order to detach anodic films from their aluminium substrate. He found that, having reduced the voltage, switching off the power supply and allowing a short time for chemical dissolution completely detached the film. The rate at which this happened depended on the terminal voltage used and on the attacking power of the electrolyte under the conditions chosen, but films produced at a final voltage of 3 volts could be detached in about 15 minutes. In practical terms these observations could be of importance in continuous anodizing, or in situations where the voltage is interrupted or work stays in the anodizing bath after the current is switched off.

Additions to sulphuric acid electrolytes

Many additions have been made to sulphuric acid electrolytes to try to change the properties of the anodic films produced. In particular reduction of the dissolving power of the sulphuric acid electrolyte has been desirable, in order to reduce temperature sensitivity and increase film hardness. Oxalic acid is the chemical most frequently added to achieve this aim, and sulphuric acid-oxalic acid electrolytes are increasingly being used.

Early work concentrated on their use for hard anodizing applications as the very low temperatures normally needed for hard anodizing were not essential with such electrolytes. Typically a 12% (wt) sulphuric acid, 2% (wt) oxalic acid electrolyte was used. In other work a 5% (vol) sulphuric acid, 5% (wt) oxalic acid electrolyte was used to give hard anodized finishes with reasonable dyeing properties.[138]

In more recent times, however, interest in sulphuric-oxalic acid electrolytes has widened to include anodizing for decorative and protective purposes in, for

example, architectural applications. Work by Jenny[76] showed the relationship between current density and film thickness with increasing aluminium content with both sulphuric acid and sulphuric-oxalic acid electrolytes (Fig. 7-35). He found that the addition of oxalic acid extended the useful life of the anodizing electrolyte, though he was assessing this in terms of the effect of aluminium content on the voltage current density relationship. In practice the presence of oxalic acid reduces chemical dissolution of the anodic film and therefore decreases the rate of build-up of aluminium in the electrolyte, and this can mean a longer electrolyte life. Sacchi[139] and Bosdorf[140] have studied sulphuric-oxalic acid electrolytes in detail, and additions of 10-40 g/l oxalic acid to 150-250 g/l sulphuric acid electrolytes are recommended. Under these conditions anodizing in the mixed electrolyte at 30°C can produce films of equivalent hardness to those produced in a normal sulphuric acid electrolyte at 20°C. Göhausen has demonstrated the beneficial effects of oxalic acid additions in work on abrasion resistance of anodic coatings[141] (Fig. 7-36).

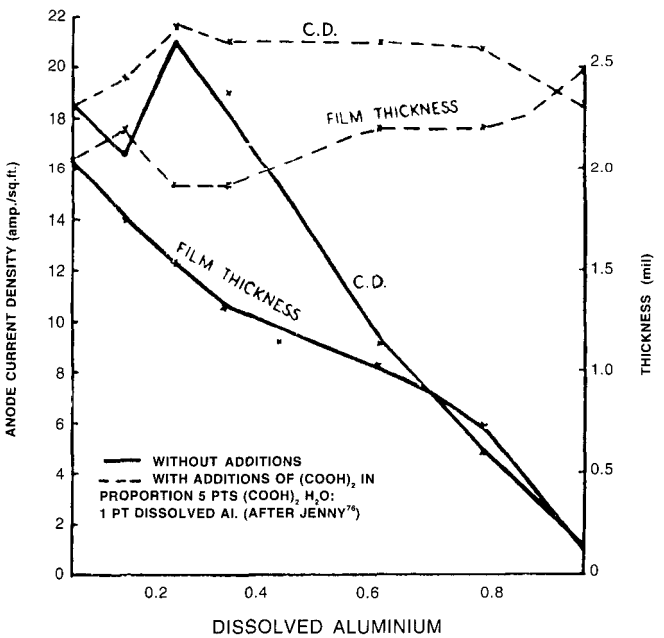


Fig. 7-35. The relation between current density and film thickness with increasing metal content, showing also the effect of oxalic acid additions (after Jenny[76])

1 amp/sq ft ≈ 0.1 A/dm^2 1 mil = 25.4 μm

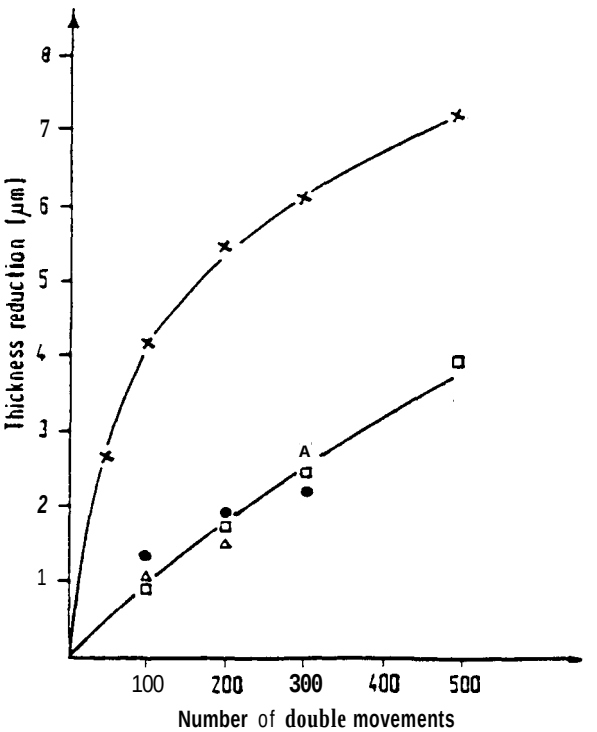


Fig. 7-36. Loss of thickness as a result of abrasive wear in the abrasive wheel test with coatings produced in sulphuric acid electrolytes (24°C, 1.5 A/dm^2, 20 µ) with and without oxalic acid additions[141]

Thickness reduction (pm) Number of double movements

x = 170 g/l H_2SO_4
● = 170 g/l H_2SO_4 + 5 g/l oxalic acid
△ = 170 g/l H_2SO_4 + 10 g/l oxalic acid
□ = 170 g/l H_2SO_4 + 15 g/l oxalic acid

The current Qualanod Specifications"* recognise the use of sulphuric acid-oxalic acid electrolytes in architectural applications, and recommend a maximum free sulphuric acid content of 200 g/l, and oxalic acid content of 7 g/l and a maximum aluminium content of 20 g/l. This bath can be used at a maximum temperature of 24°C.

The main limitations of oxalic acid additions are the relatively high cost of the acid and the fact that it can be decomposed during electrolysis, thus giving a

relatively high rate of consumption. As a result of reduced coating attack it may also affect dye uptake and hence reduce the durability of dyed finishes, but overall the beneficial effects of oxalic acid additions on coating quality are important, particularly when producing relatively thick coatings (25 microns).

A different approach, but with the same purpose, has been proposed by Reynolds.[142,143] They suggest the addition of glycolic acid and glycerol to a sulphuric acid electrolyte to reduce film dissolution. **A** typical electrolyte contains 15-24% (wt) sulphuric acid, 1.2%(vol) glycolic acid and 1.2%(vol) glycerol. Mannitol and sorbitol are alternatives to glycerol. Using this electrolyte they show that hard anodizing, bright anodizing or architectural anodizing can be carried out in the same electrolyte, with only the current density and anodizing time needing to be adjusted. High anodizing current densities can be used when necessary without burning, and difficult alloys, such as those with high copper content, can be anodized more readily than with conventional electrolytes. This 'multi-purpose electrolyte' has been used in a number of plants in the **U.S.A.** and experience with it in one particular plant has been reported.[144]

In Japan deliberate additions of sulphates such as aluminium sulphate or magnesium sulphate have been shown to decrease chemical dissolution of the film.[145] In an extensive study, Fukuda and Fukushima showed that increase in sulphate concentration suppressed chemical dissolution, giving a more even film surface with reduced film porosity. This generally gave a harder film, except at very high sulphate concentrations where the rise in surface temperature at the anode gave high rates of film attack. Tajima and Umehara[146] used ammonium sulphate as an addition to reduce film dissolution, but with the added benefit that the complex alum formed, aluminium ammonium sulphate, precipitated out at a level of about 5 g/l of dissolved aluminium. In effect this gives a 'long-life' anodizing electrolyte, as the alum can be filtered off on a batch or continuous basis. An addition of 1.50-200g/l of ammonium sulphate is made to a 15% (wt) sulphuric acid electrolyte, and this can be used at temperatures up to 35°C without serious loss of film properties. Other Japanese workers[147] have used additions of nickel sulphate and sodium potassium tartrate (Rochelle salt).

Acorn Anodising Co. have proposed sulphuric acid-nitric acid electrolytes[148,149] and a typical bath contains 140 g/l sulphuric acid and 14 g/l nitric acid. This is said to allow the use of lower operating voltages for a particular current density and therefore saves electrical energy. It is particularly suitable for anodizing difficult alloys such as those containing large amounts of copper or silicon, and, as with the Reynolds process, the electrolyte can be used for hard anodizing as well as for decorative anodizing.

Many other additions have been proposed including lignin sulphonic acid,[150] 2-amino ethyl sulphuric acid,[151] taurine (2-amino ethane sulphuric acid),[152] peat extract,[153] an extract from the guebracho tree,[154] and sugar alcohols.[155] Softer coatings are claimed to be produced by the addition of wetting agents such as aromatic sulphonic acids, and these may also help to reduce spray. **A** 15-20% glycerol addition is said to produce films of higher elasticity,[156] as are ammonium sulphate,[157] aniline hydrosulphate[158] and aliphatic carboxylic acids.[159]

5. CHROMIC ACID PROCESSES

Bengough-Stuart process

The first chromic acid process was developed in Britain by Bengough and Stuart in 1923, and this, as well as later modifications, including that covered by a standard specification,[160] is still in extensive use.

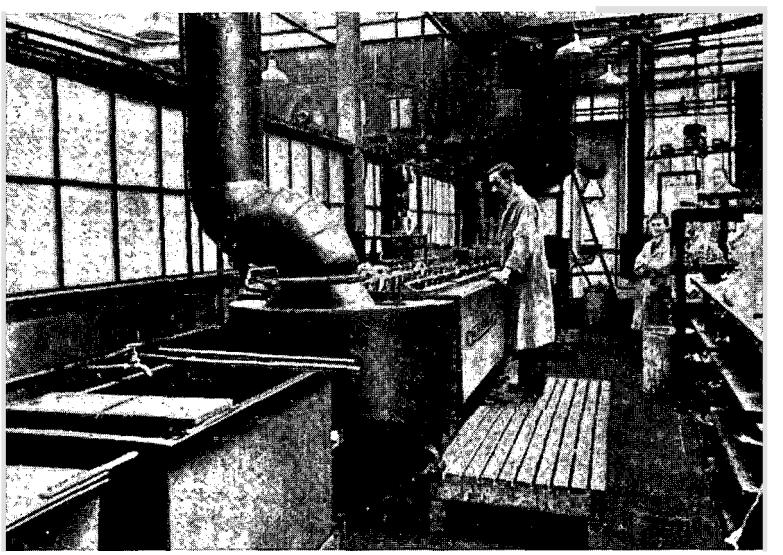


Fig. 7-37. Typical Bengough-Stuart anodizing plant

Cleaning

The work is cleaned by vapour degreasing and, where necessary, is given an additional alkaline cleaning treatment in, e.g., a 38-50 g/l (6-8 oz per gallon) mixture of trisodium phosphate and sodium meta-silicate at 90°C.[160] Where the work will stand it, grit blasting or scratch-brushing may precede cleaning. After a final rinse in clean running water, the work is ready for anodizing.

Process details

The standard chromic acid process is outlined in Defence Specification DEF-STAN 03-24/3,[160] which states that the electrolyte shall consist of a solution containing 30-100 g of chromic acid per litre (4.8-16 oz/gal). The purity of the

chromic acid shall be not less than 99.5% CrO_3. Chloride in the electrolyte shall not exceed the equivalent of 0.20 g NaCl per litre and sulphate shall not exceed the equivalent of 0.50 g Na_2SO_4 per litre. The free chromic acid shall not fall below 30 g per litre. The electrolyte may be regenerated by the addition of chromic acid provided that the total chromium in solution does not exceed 100 g per litre calculated as CrO_3. The operational temperature of the electrolyte shall be within the range 38-42°C.

Current shall be applied so that the voltage across the bath is increased in steps of not more than 5 volts from 0-40 volts in the first 10 minutes, maintained at 40 volts for 20 minutes, gradually raised to 50 volts in the next 5 minutes and maintained at 50 volts for 5 minutes. These times shall be regarded as minima.

The cathode shall be mild steel or stainless steel in the form of plates, or the tank itself. The anode:cathode area ratio is not critical, but less chromic acid is consumed at the higher ratios. Values varying from 5:1-10:1 are generally suitable. Where the tank acts as the cathode, the sides and bottom may, if desired, be partially covered by glass or other chemically inert insulating materials.

In the treatment of certain casting alloys the voltages and temperature given above may not be suitable. In this case the temperature is reduced to 25-30°C and the bath voltage is increased in steps of not more than 5 volts from 0-40 volts in 10 minutes and the voltage maintained at 40 volts for 30 minutes.

In the case of high zinc containing aluminium alloys in the over-aged condition, the temperature of the electrolyte should be 35 ± 2°C, and the bath voltage should be raised to 20 + 2, - 1 V and held at that level for a minimum of 30 minutes; the rate of voltage increase should be 3 to 4 volts per minute.

The anodizing current is controlled by the voltage and the cycle must be adhered to strictly in order to avoid etching. The original Bengough-Stuart cycle, which took 60 minutes, is, however, no longer in extensive use. The average current density over the 40 minutes is approximately 0.3-0.4 A/dm^2 (3-4 A/ft^2). Because of the complex voltage cycle, rectifiers with automatic voltage controls and appropriate timers to suit the cycle employed are desirable.

The Bengough-Stuart process cannot be used on alloys containing more than 5% copper, but is especially suitable for work with rivets, joints, etc., which is difficult to rinse, as chromic acid residues are not harmful to the corrosion resistance of the metal.

The Bengough-Stuart coating is thin (averaging 2-5 μm; 0.08-0.2 mil) and, because of this, is relatively softer than those produced by other processes. The coating contains only a little chromium, and the average current consumption in producing it is 0.2 kW h/sq ft of surface. The corrosion resistance of the film is excellent relative to its thickness, but the abrasion resistance is poor and the film is easily damaged. The colour is more or less dark grey, depending on the composition of the basis metal, and it does not dye well. The chromic acid coating is not normally sealed, due to its low porosity. For the same reason, the dissolution rate of the coating is high compared to the growth rate, and while the limiting film thickness is low, the metal usually loses in weight by anodizing.

Constant voltage chromic acid process

This process was developed in the U.S.A. by the National Bureau of Standards[159,161] in an attempt to develop a process which would work at constant voltage and which would avoid rapid exhaustion of the solution. It was found that at a chromic acid content of 5-IO%, the Bengough-Stuart cycle is not required, but that a constant voltage of 40 may be employed for a much reduced treatment time. Table 7-14 gives the relationship between treatment time and current efficiency of the process.

The current efficiency, of course, decreases with time until the limiting film thickness is reached, when the rate of growth is equal to the dissolution rate.

The changes in dimensions produced on three aluminium alloys by the accelerated chromic acid process were determined by Edwards and Keller.[162] The alloys were 1200-0 (commercial purity aluminium), 2024-T (an Al-Cu-Mg-Mn alloy) and an Al-4.5%Cu-0.8%Si casting alloy (195-T4), and they were treated in 8% chromic acid solution at 35°C, 40 volts for 30 minutes. The same treatment produced coatings of thickness 0.14 mil (3.5 pm) on 1200-0, 0.12 mil (3.0μm) on 2024-T and 0.10 mil (2.5 pm) on 195-T4. The changes in the diameter of the test-piece anodized varied according to the alloy and the position on the test-piece, but in no case exceeded 0.08 mil.

TABLE 7-14

Bengough-Stuart process and accelerated process compared[163]

Chemical acid content	*Voltage*	*Current density*	*Temp, ("C)*	*Time (min)*	*Apparent current efficiency*	
					*Removal of Al**	*Formation of Al_2O_3*
3%	Bengough-Stuart cycle	0.3 A/dm² av.	40	60	102.0	45.9
9%	40 V	0.3 A/dm²	30	30	101.8	52.2

* The weight of the film only accounts for 60 to 80% of the aluminium lost while 20 to 40% is dissolved, confirmed by gas analysis figures.[161]

The coatings produced by the accelerated process may be sealed in hot water at 82-93°C or, alternatively they may be dyed and subsequently sealed in nickel acetate (0.4 oz/gallon; 2.5 g/l) at pH 5.0.[57]

According to Prelinger,[164] a free chromic acid concentration of between 5.0-6.0 oz/gallon (31-37 g/l) is the minimum which will give from the concentrated chromic acid anodizing bath an anodic coating capable of withstanding the 240 hours salt spray requirement of the original U.S. military specification MIL-A-8625A.

Due to its advantages, the constant voltage process, operated with a 9- 10% chromic acid solution, has almost entirely replaced the Bengough-Stuart process in the U.S.A. It has been tested in Britain by Brace and Peek[165] who, at 54°C and 30 volts, obtained 5 μm coatings in 20 minutes and 10 μm coatings in one hour as indicated in Fig. 7-38. The current efficiency would appear to be about 30% from the figures quoted. Good results were obtained on super-purity (S1), 1200 (SIC), 6063 (HE9), 6082 (HE30), 3103 (N3), 5251 (N4), 5154 (N5) and 5056A (N6) alloys. Slightly grey films were formed on 3103 (NS3), while thin and rather softer films were obtained on 2014A (H15). On gravity die-castings in LM4M, LM5M, LM8, LMIOW, LM11W and LM16W, satisfactory coatings were formed provided the castings were substantially free from porosity. As distinct from those produced in the Bengough-Stuart process, the coatings are attractive and, being opaque, present an enamel-like appearance. This is due to the fact that the aluminium is etched slightly during anodizing. Attractive finishes are obtained by dyeing the coating, and yellow, bronze, orange, blue, turquoise, green, red and black shades have been obtained using organic dyes. The flexibility of the coating is markedly superior to that of sulphuric acid coatings and, while the abrasion resistance is inferior, the film withstands thermal changes better.

Harris[166] also examined the 10% chromic acid process at about the same time by using single phase rectified current to check the efficiency of film formation, or the amount of aluminium appearing in the coating expressed as a percentage of the total aluminium which takes part in the reaction during the period of anodizing. His results, summarised in Fig. 7-39, indicate that the best operating temperature for efficiency is 30-40°C with this strength of acid but that the coatings are thin. The very thick coatings formed under different conditions are produced at very low efficiency, down to 22%, indicating excessive dissolution of the coating and, therefore, poor quality. The inconsistent shape of the curves suggests unstable conditions and the degree of agitation will determine how much of the oxide formed remains on the surface as coating. Rather better results were obtained with hexaphase rectified current but still at low efficiency. It must be observed, too, that in the case of both these results and those obtained by Brace and Peek, the thickness determinations were by stripping and weighing with an assumed density of 2.5, which may not be a valid assumption for coatings formed at low efficiency.

It is strange that the chromic acid process should have survived for more than half a century with remarkably little change. While operators of the sulphuric process have felt free to experiment with, and use to good effect, the whole gamut of processing conditions, some peculiar inhibition has operated

to preserve an almost ritualistic repetition of the complex voltage cycles in the Bengough-Stuart process, the precise reason for which is lost somewhere in the past, and may even be connected with the original limitations of the power supply. It is equally strange that some basic features of the chromic acid process were discovered so late and realised so little. For instance, the important role of the sulphate content was not explained until 1945;[167] that the coating which is perfectly transparent on pure metal should always be considered as opaque; that the process works very badly with fluctuating voltages; or that the appearance is always bright and clear when the basis metal contains even quite small amounts of copper unless etching takes place, which the Bengough-Stuart process ensures very nicely when the copper is high.

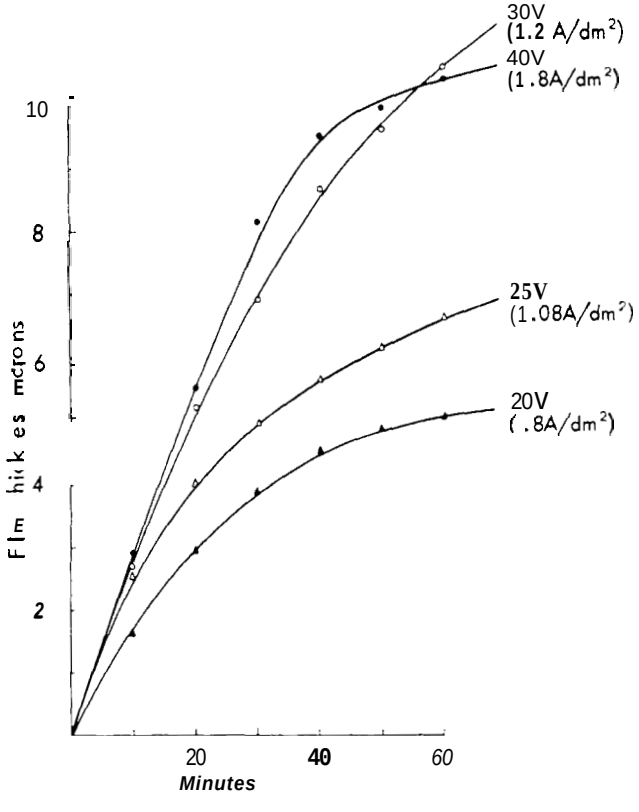


Fig. 7-38. Effect of anodizing voltage on film thickness obtained for anodizing times up to 60 minutes in 10% CrO_3 at 54°C[165]

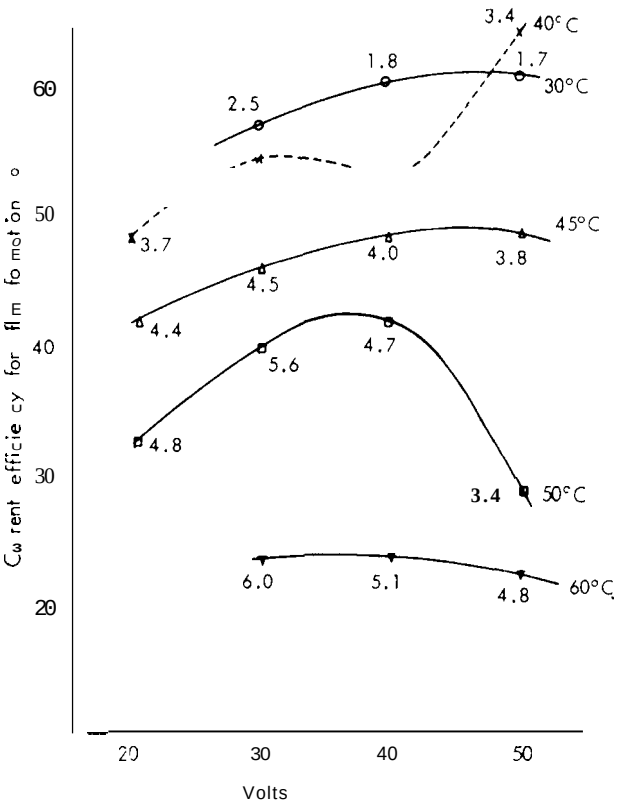


Fig. 7-39. Current efficiency for anodizing in 10% chromic acid. (Single phase full wave rectification).[166] Film thickness in microns shown for each point

Scott and Thomas[168] have operated the chromic acid process as a constant voltage one for over 30 years, and latterly at constant current for certain alloys. They use a composition of 30 g/l chromic acid at 45°C, and raise the voltage to 45 as soon as the rectifier or generator output will allow, to get a current density of 0.5 A/dm^2 (5 amp/sq ft) which provides a coating thickness of 5 μm (0.2 mil) in 60 minutes. Indeed for copper alloys it is recommended that the voltage be raised as quickly as possible with a considerably higher current in order to gain control of the anodic process and avoid excessive etching. In a particular case of constant voltage operation on 2014A alloy (4½% Cu) a film thickness of 4 μm was obtained in 45 minutes compared with only 1.9 μm by the Bengough-Stuart cycle, while the film was also considerably harder and the appearance clear and bright.

Fig. 7-40 shows the voltage-time cycle required to maintain 0.5 A/dm^2 for 1 hour when anodizing an L65 casting (4½% Cu, 6% Mg, 0.7% Si, 0.8% Mn) in 3% chromic acid at 45°C. The voltage must be raised to 70 as compared with a steady 45 volts for pure aluminium, but the coating is of good quality.[24]

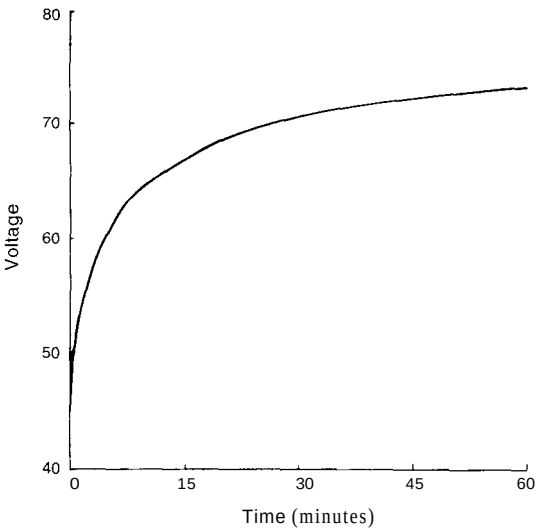


Fig. 7-40. Chromic acid anodizing of L65 casting alloy (4½% Cu) with constant current.[166] 3% chromic acid. Temperature 45°C. Current 0.5 A/dm^2

Aluminium Français[169] have described a process using 15-19% (wt) chromic acid at low bath temperatures (below 30°C) and low anodizing voltages (21-23 V). A small cathodic surface is required and is related to electrolyte volume. With this process the consumption of chromic acid is said to be very much reduced as a result of peroxidic reactions occurring at the anode, and addition of hydrogen peroxide to the bath is apparently beneficial. The rate of anodizing is slow but films up to 6 microns in thickness can be produced after 120 minutes anodizing. A later Péchiney patent"' claims a rapid chromic acid anodizing process in which an 100-200 g/l chromic acid electrolyte is used at 55-70°C, a constant direct voltage of between 35 and 45 V and an anode current density in the range 3.5-5 *Al* dm^2. The anode surface area is in the range 1.7B-2.3B dm^2 and the cathode area is not more than 0.06B dm^2, where B denotes the volume of electrolyte in litres. Under these conditions a growth rate of the oxide of about 1 micron per minute can be obtained, and films with good opacity, dyeability and flexibility are said to

be produced. The anodizing time should not exceed 10 minutes but films up to 10 microns in thickness can be formed.

The production of thick coatings by chromic acid anodizing has also resulted from U.M.I.S.T. work.[171] This work uses a 30-40 g/l chromic acid electrolyte at 55-70°C and very high anodizing voltages of about 90-150 V. A constant current density of about 1.5A/dm^2 is used, and this is relatively high for chromic acid anodizing. Films up to 25 microns in thickness have been produced this way in anodizing times of up to 90 minutes. Anode:cathode ratio is given as 15-30:1 and very vigorous air agitation directed towards the anode is required. Mohler[172] looked at the chromic acid anodizing of aircraft alloys of the 7000 (Al-Zn-Mg) and 2000 (AI-Cu) series and concluded that a constant 22 V anodizing process was best. British Aerospace[173] have also claimed the benefit of high temperature chromic acid anodizing, where temperatures of above 55°C are said to give increased pore diameter, and hence improved preparation for adhesive bonding.

Impurities in chromic acid baths

During an investigation of the impurities of chromic acid solutions, Buzzard and Wilson[161] found that chloride present in the electrolyte causes etching, while the chromic acid was exhausted mainly by neutralization with dissolved aluminium. The hexavalent chromium content, which is called the *free* chromic acid content, decreases with time, while trivalent chromium and aluminium content increase, the former being formed by cathodic reduction. To avoid this, the cathode area should be kept down as far as possible. When the free chromic acid content is low, the corrosion resistance of the coating is low and a brown deposit, consisting probably of an aluminium or chromium chromate, settles out at the bottom of the tank. In the presence of trivalent chromium, the dissolution of the aluminium is retarded. The optimum operating conditions depend on this dissolution, and hence on the ***free*** chromic acid content.

Attempts have been made to rejuvenate the electrolyte by anodic oxidation of the trivalent chromium as is done in chromium plating. The solution is electrolysed between lead anodes and iron cathodes, at 2.5 amp/sq ft (0.25 AI dm^2) for 24 hours or until the pH drops from 1.5 to 0.2. According to another account[146] the anode:cathode area ratio should be 40:1 while the anode area should be within the region of 0.5-1.0 sq ft per gallon (1-2 dm^2 per litre).

Jackson[167] has studied the effect of sulphate content in the Bengough-Stuart chromic acid bath and has found that the colour of the coating varies significantly with the amount of sulphate present. Thus, while a semi-opaque film is formed at less than 0.01% H_2SO_4, opaque films formed at 0.01-0.03% H_2SO_4 go over to transparent coatings above 0.03% H_2SO_4.

In practice, the sulphate may come from hard water, and although anodizing is possible up to a sulphate content of 0.5% H_2SO_4, it is inefficient and the water

supply should therefore be tested and measures taken to soften it if necessary. The life of the chromic acid solution is shortened in the presence of sulphate, as in its absence an insoluble film of chromium dichromate is formed on the cathode which is permeable only to the small hydrogen ion and hence permits the liberation of hydrogen without reduction of the $Cr_2O_7^{2-}$ ion, which is too large to diffuse through the film. The presence of the bisulphite anion facilitates dissolution of this cathode film and hence increases reduction of the hexavalent chromium. Provided, however, that the cathode current density is large enough (i.e., the cathode area is small), the influence of the sulphate ion is negligible. In this way, Tarr, Darrin and Tubbs[174] worked with cathodes of only 2% of the anode area (using high chromic acid solutions) and obtained coatings of similar weight of Al_2O_3 (i.e., similar anode efficiency) as with cathodes twenty times the anode area.

To precipitate sulphate from the solution, barium hydroxide or carbonate may be added as in the case of chromium plating solutions. As the precipitate does not as a rule interfere with anodizing, it is often allowed to remain at the bottom of the tank. In the precipitation it may be assumed that 1 lb of barium hydroxide will reduce the sulphate content of 100 gallons of solution by 0.2 g/l (1 g of barium hydroxide per litre of solution will reduce sulphate by 0.2 g/l). This will, however, depend to some degree on the chromic acid content, as barium chromate may partly precipitate. For this reason, if the precipitate is to be removed, time should be allowed for barium in chromate form to be converted into the less soluble sulphate before decanting the solution. Scott has pointed out that by adding strontium hydroxide the solubility of the strontium sulphate will automatically ensure the correct sulphate content for obtaining opaque-appearing coatings.[168]

Chromic-sulphuric acid process

The effect of sulphate in chromic acid solutions, however, is not necessarily detrimental. During the last war a modified chromic acid process was developed by Chisholm *et al.* at the San Diego Naval Air Station, **U.S.A.,** with the purpose of saving chromic acid which was then in short supply, a process investigated later at the Battelle Memorial Institute by Slunder and Pray.[175]

In the normally high chromic acid bath, approximately half the Al_2O_3 formed by electrolysis is dissolved by the free chromic acid. In this way it has been stated that 90% of the chromic acid consumed is used to neutralize dissolved aluminium and to maintain the pH.[176]

The decrease in efficiency is shown by a rise in pH and a drop in the current density at constant voltage. Ordinary additions of chromic acid build up the chromium content, and after a time the bath is exhausted and is either entirely discarded or replaced in part, the latter method being preferable as it enables a constant pH and chromium content to be used. In the modified process, on the other hand, though the bath initially contains chromic acid only, the pH is maintained by additions of sulphuric acid.

In the process as used by Chisholm, a 3% chromic acid solution in distilled water is used and chromic acid added as necessary to maintain a current density of not less than 0.15 A/dm^2 (1.5 amp/sq ft). After the CrO_3 content reaches 10%, the solution is maintained by additions of concentrated sulphuric acid to keep the current density between 0.15 and 0.25 A/dm^2 (1.5-2.5 amp/sq ft). The current density is measured on 2024T (Al-Cu-Mg-Mn) anodes of known surface area or by a current density meter. The solution is operated at 35±2°C and the voltage is gradually taken up to 40 volts. Examples of operating times are 50 minutes for propeller blades, 30 minutes for 2024T sheet structures, and 40 minutes for 3003 (1¼% Mn) alloy as well as for rivets and bolts anodized in containers. Coatings of 2.5 μm (0.1 mil) are usually aimed at.

According to Chisholm, mild steel tanks, which are used as cathodes, are suitable for this anodizing solution, though Slunder and Pray preferred lead-lined tanks with carbon ca hodes.

Slunder and Fray worked with a stock solution containing:

hexavalent chromium (Cr^{6+})	50.3%
trivalent chromium (Cr^{3+})	0.3%
aluminium oxide (Al_2O_3)	14.8%
sulphate (SO_4)	4.7%
at pH	1.0

to which varying amounts of aluminium sulphate were added.

While, in the case of 2024T, sulphuric acid additions can be made by time alone, the relationship is mc re complicated with some other alloys as the sulphate content increases. At constarit pH, variations in sulphate content may cause pronounced changes in the curren : density-voltage relationship and, in practice, the thickness of the film **is** controlled by maintaining the operating conditions to give a constant anode current density. This is usually done by changing the pH or the bath voltage as the sulphate content increases.

The variation in the current density/voltage relationship with sulphate content means that different alloys cannot be anodized at the same time unless the voltage is kept down to 15-20 volts. The coatings are transparent and have the appearance of d.c. sulphuric acid filins.

Kochegarov[177] has reported good anodic coatings on quenched Y-type alloy in chromic-sulphuric acid baths at high current densities.

Chromic acid-dichromate bath

A solution containing:

chromic acid	12.5 g/l
potassium dichromate	37.0 g/l

has been used by Tomashov[178] and his co-workers at 20-60°C and 1-6 amp/sq ft (0.1-0.6 A/dm^2) for assemblies, as traces of this solution show rather less corrosive attack than the normal chromic acid bath.

Regeneration of chromic acid solutions

As the anodizing bath is used, the aluminium content of the solution will rise and there may also be an unwanted rise in the trivalent chromium concentration. Rise in aluminium content may be countered by addition of chromic acid according to the free chromic acid content measured by the titration value (see end of this chapter) which should not be allowed to fall below 3 except when the solution is about to be discarded, when it may fall to as low as 2. Once the total chromic acid concentration has exceeded 10% by weight, the voltage required to work the bath becomes excessive and the corrosion resistance of the coating may suffer. In practice the bath will have to be discarded unless it is regenerated.

Regeneration can be carried out by means of cation exchange and is usually well worth investigating if the bath volume is above approximately 300 gallons (1300 litres).

Fig. 7-41 shows diagrammatically the type of plant used in cation exchange. The hydrogen exchanger consists basically of a cation exchange resin, normally polystyrene sulphonates or less frequently resins containing carboxyl groups. These resins have the property of taking up cations from solution and replacing them by hydrogen ions. The order in which they do so is approximately as follows[179] (ions towards the right displacing those on the left in the resin):

$$Hg^{2+},\ ZrO_2^{2+},\ Li^{+},\ H^{+},\ Na^{+},\ K^{+},\ Rb^{2+},\ Be^{2+},\ Cd^{2+},\ Mn^{2+},\ Mg^{2+}$$
$$\text{and}\ Zn^{2+},\ Cu^{2+},\ Ni^{2+},\ Co^{2+},\ Sr^{2+},\ Pb^{2+},\ Ba^{2+},\ Al^{3+},\ Th^{3+}$$

A number of proprietary cation exchange resins of this type are on the market and are usually stable in solutions containing up to 25% (wt) chromic acid. In practice, a portion of the bath is withdrawn at daily or two-daily intervals and passed through the ion exchanger. When the resin is exhausted, it is itself regenerated by passing sulphuric acid through the column when, due to the high H^+ concentration, the resin is converted back to the hydrogen form. By this method it may be possible to keep the aluminium concentration as low as 0.2 g/l (as Al_2O_3). In practice, the exchange column and piping are generally PVC-lined steel. Steel, or in special cases Duriron, pumps may be used. The effluent sulphuric acid which carries the extracted metal ion is then discarded. Compact units of the type made possible by reciprocal flow ion-exchange systems (p. 135) can also be used for chromic acid recovery.[180]

The economies of cation exchange regeneration have been discussed in a number of articles.[181,182,183,184,185] Particularly in the case of the larger plants, they have often been spectacular, while an additional advantage consists in the closer

control of the anodizing operation facilitated by operating at a constant aluminium content.

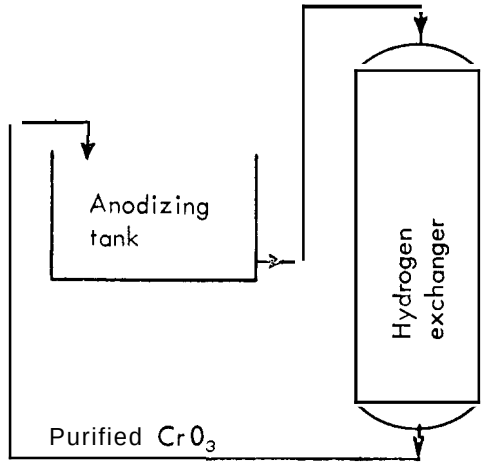


Fig. 7-41. Flow diagram for utilisation of cation exchange in the purification of chromic acid anodizing solutions

Disposal *of* chromic acid solutions

Chromic acid anodizing wastes create a disposal problem whose seriousness will vary with local regulations. In many cases it is essential to extract the chromic acid from the effluent before this is passed to waste and in some cases the chromic acid may be recovered for re-use.

A number of methods have been devised for treating chromic acid-containing wastes including: (1) reduction by ferrous sulphate, sulphur dioxide or sodium metabisulphite, barium sulphide, iron or zinc;[186,187,188] (2) precipitation with barium chloride or hydroxide;[189,190] (3) evaporation to a small volume;[191,192,193] and (4) anion exchange.[180,181,194,195,196] **A** full description of all these methods has been given elsewhere.[197] While choice of method must be made according to individual conditions, anion exchange has the advantage of being perhaps most easily combined with the systems described earlier.

A plant used for combined regeneration and waste treatment is shown in Fig. 7-42. To the left of this picture is the cation exchange unit for extracting aluminium and trivalent chromium. To the right is the anion exchanger which is of identical construction. The waste waters are introduced into the anion exchanger column which holds a resin which usually contains quaternary ammonium groups $N(CH_3)_4^+$ and is regenerated with caustic soda. The resins used, which are stable in

solutions containing up to 20 ppm CrO_3, extract the chromate from the solution and replace it by hydroxyl ions. When the resin is exhausted, caustic soda or more rarely ammonium hydroxide or sodium carbonate solution is passed through the bed to regenerate it. In doing this the chromate ion is released and may be recovered as chromic acid by passing the regeneration effluent through the cation exchanger.

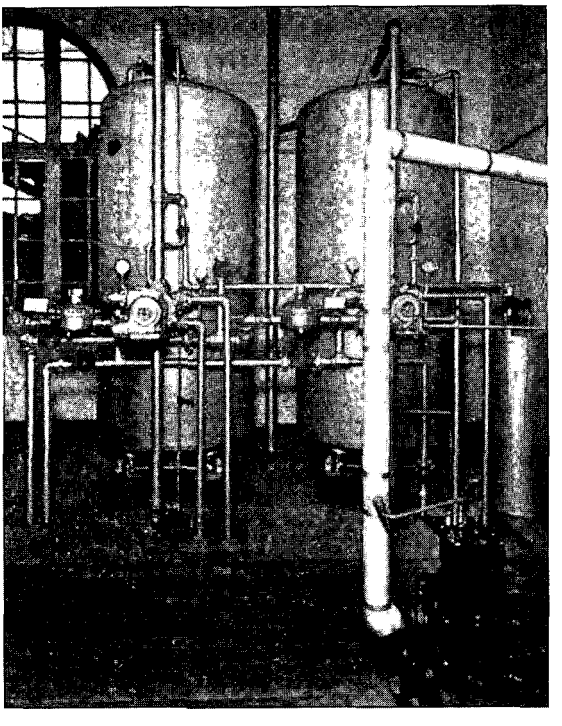


Fig. 7-42. Typical ion exchange installation for treating and recovering chromic acid

An example of the rate of the process is shown in Fig. 7-43. In this case'" the effluent concentration of aluminium was 6.94 gm per litre (as Al_2O_3) at a chromic acid concentration of 100 gm per litre.

The pressures against the use of hexavalent chromium for health and safety reasons probably mean the demise of chromic acid anodizing in the long term, but the continued defence and aerospace use of the process, particularly in Europe, means that this will not happen quickly.

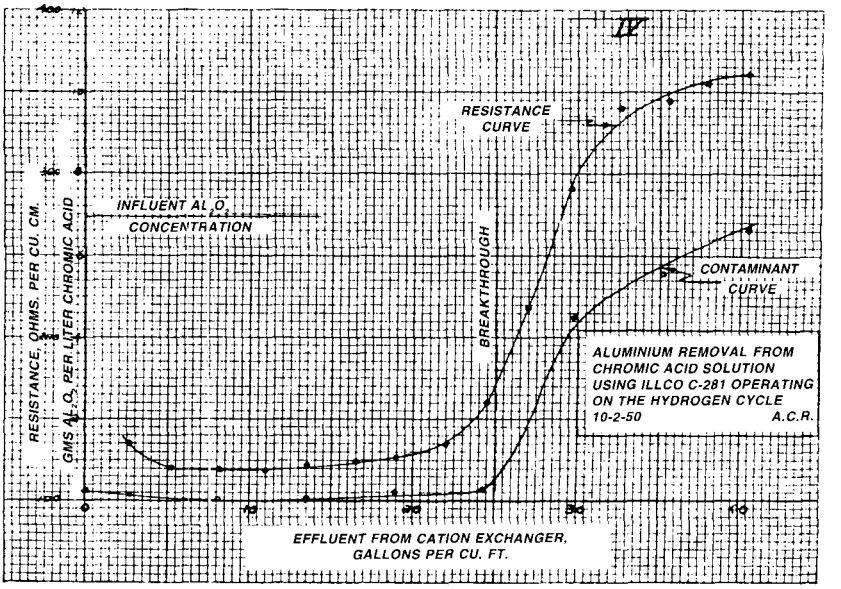


Fig. 7-43. Aluminium removal from chromic acid solution on the hydrogen cycle

6. OXALIC ACID PROCESSES

These were first (developedin Japan and later introduced into Germany where at one time they were in extensive use. Their main interest today is for producing relatively hard coatingi which are usually gold or light bronze coloured according to the basis metal. Thus, an aluminium-0.2-0.5%Cr alloy (Fe + Si below 0.35%) may be given an attractive gold or bronze finish.[198] Oxalic acid anodizing can also have advantages for anodizing wire (see Eloxal WX below).

The oxalic acid processes are more expensive than the sulphuric acid processes both in chemicals and power consumption, but thicker coatings of up to 60 μm (2.4 mil) may be obtained without the use of special techniques, increase of film thickness being almost linear with time during the first hours of treatment. Hence oxalic acid has been used to some extent in hard anodizing (see Chapter 9).

The four standard German processes using solutions containing 3-5% oxalic acid were operated as follows:

Eloxal GX – was the basic d.c. process and current densities of 10-20amp/sq ft (1 - 2 A/dm^2) were applied at 40-60 volts. This bath was kept at 18-20°C and the treatment time was 40-60 minutes. The coatings obtained were yellow in colour on aluminium and alloy; not containing heavy metals, and were of good wear resistance.

Eloxal GXh – was a modification of the Eloxal GX process in which the temperature was raised to 35°C with a resulting drop in voltage to 30-35 volts. The treatment time was shorter, 20-30 minutes, as at the increased temperature the limiting thickness was reached earlier. Coatings produced by the GXh process were almost colourless, and this and their increased porosity made them more suitable for dyeing and for photographic processes. They were, however, somewhat softer and thinner.

Eloxal WX – was the a.c. process, operated at 20-30 amp/sq ft (2-3 A/dm^2) at 20-60 volts. The bath temperature was 25-35°C and the time of treatment was 40-60 minutes. The coatings were much softer and found application in anodizing wire and elastic **strip.** The work was alternately anode and cathode and the voltage had to be increased gradually from 20 to about 60 volts. The coatings were yellow on aluminium and somewhat darker on heavy-metal-containing alloys.

Eloxal WGX – was a combination of the GX and WX processes, and the proportions of a.c. to d.c. could be varied according to the hardness and colour required. The normal range was 20-30 amp/sq ft d.c. at 30-60 volts, and 10-20 amp/sq ft a.c. at 40-60 volts (2-3 A/dm^2 d.c., 1-2 A/dm^2 a.c.). Temperatures of 20-30°C could be used, and the operating time was 15-20 minutes. On aluminium-manganese alloys this process gave coatings of greater wear resistance than any other. Neither of the processes using a.c. was in wide use, chiefly due to the high cost.

Oxalic acid anodizing was used for many years in Japan and typical conditions have been described by Tajima.[199] The normal method was to employ a 3% (wt) solution at 1-2 A/dm^2 and 25-35°C for 30-80 minutes using 15-30 volts d.c. and 60-100 volts a.c. with lead or graphite cathodes for the d.c. A common practice was to follow anodizing by steam sealing under 50 kN/m^2 (7 p.s.i.) pressure for 30-60 min. The coating could be lightly buffed after sealing and was light gold in colour.

In Britain and America oxalic acid solutions of slightly higher acid content, 5-10% (wt), have occasionally been used, and such an electrolyte was the basis of Alcan's Alcanodox process.[200] The electrolyte contained 80 g/l to 100 g/l oxalic acid and gold and light bronze finishes could be produced according to the alloy used. In a further development[201] it has been proposed to superimpose on the d.c. operation substantially square pulses of current at a frequency of 1½-20 per second with peak current values up to 21 A/dm^2 (200 A/ft^2) and 3-6 times the mean anode current density of 1.1-3.8A/dm^2 (10-36 A/ft^2). These conditions gave much darker colours, with the ratio of peak current density to mean current density strongly affecting the result. At high peak to mean ratios very dark bronzes and even black could be obtained.

As with the sulphuric acid processes, tanks are usually lined with rubber, plastics or lead, and separate stainless steel, lead, aluminium or graphite electrodes are used. Agitation, power supplies and cooling are in principle the same as for sulphuric acid anodizing, but much higher voltage rectifiers and higher capacity refrigeration units are required.

As the electrolyte is not corrosive, the oxalic acid process may be used for parts with crevices, joints, etc., in which case after anodizing and rinsing, the work may be dipped in 1% ammonia or ammonium bicarbonate.

Additions and impurities

The virtues of adding small proportions of sulphuric acid to the oxalic electrolyte in order to obtain deeper and more controlled colour effects have been exploited by Aluminum Company of America[202] in a procedure that stipulates a ratio of oxalic acid to sulphuric acid, which is to be maintained at a value between 9 and 13 according to the temperature of the operation, given by the formula:

$$R = 2\left(1 - \frac{2T}{15}\right)$$

where T is in °F.

Additions of formic acid to oxalic acid have also been studied for the rapid formation of thick anodic films on aluminium and its alloys[203] which is a technique developed by Herenguel many years ago.[204]

Campanella[205] investigated the effect of additions of various proportions of dioxane to the oxalic acid electrolyte. He observed increases in the hardness, the degree of crystallinity, and the resistance to acid and alkaline corrosive conditions with increasing dioxane concentration, but at the same time a decrease of sealing hydration and of the amounts of adsorbed electrolyte anions.

It has also been proposed in Japan to add selenic acid or selenates to the oxalic acid electrolyte,[206] and workers at Kinki University in Japan[207] have suggested the addition of calcium sulphate to the electrolyte to reduce the yellow colour of films.

Many workers have used films produced in oxalic acid for fundamental studies on the mechanism of anodic film formation, notably the work at U.M.I.S.T. described in Chapter 6. Nagayama, Tamura and Takahashi[208] studied the dissolution rates of porous coatings formed in oxalic acid, separating the effects on pore walls from the effect on the pore bases. Dissolution from the pore base is field-assisted and increases with temperature, the apparent energy of activation being about 16 kcal/mole. Dissolution from the walls did not change with current, not even when it was interrupted. More recent work by Manhart and Mozelewski[209] supports this work and shows how the slow attack of the pore walls in the oxalic acid electrolyte leads to a tapered pore structure.

Electrolyte purity is probably of greater importance in the oxalic than in the sulphuric acid process, and pitting occurs more readily. Elze[210] has examined the role of chloride and found that pitting tends to take place around foreign inclusions when the chloride exceeds 4 mg/l in the case of d.c. treatment and when the inclusions are of Fe, Ni or Pt, but that pitting takes place in the absence of such inclusions when the chloride content is about 200 mg/l, which is about the same as for sulphuric acid. Schenk[6] has also reported the sensitivity of oxalic acid electrolytes

to chloride and states that they must not contain more than 40 mg/l when anodizing unalloyed aluminium and not more than 20 mg/l when treating Al-Cu-Mg-Mn alloys.

Effect of operating conditions

In general most of what has been said about the influence of operating conditions on anodic oxidation in sulphuric acid will apply also to oxalic acid anodizing.

As in other processes, the anode efficiency and the maximum film thickness vary with the temperature, both in the d.c. and a.c. processes. In a 5% oxalic acid solution, for instance, 1.2 A/dm^2 (11 amp/sq ft) d.c. produces no coating at all at above 50°C, while a.c. at 4 A/dm^2 (37 amp/sq ft) will form a coating at up to 60°C.[211]

The effect of temperature and pH of oxalic acid electrolytes on the film thickness is shown in Fig. 1-44. These results, which were obtained by Hübner,[212] show that as the temperature increases the coating thickness decreases. With increase in pH at high temperatures, the coating thickness curve goes through a maximum and the optimum is shown to lie between pH 1.5 and 2.5. The best anodizing conditions are, however, at lower temperatures, between 25 and 40°C, where the optimum pH value is approximately 0.5-1.0, corresponding to approximately 3-8% oxalic acid.

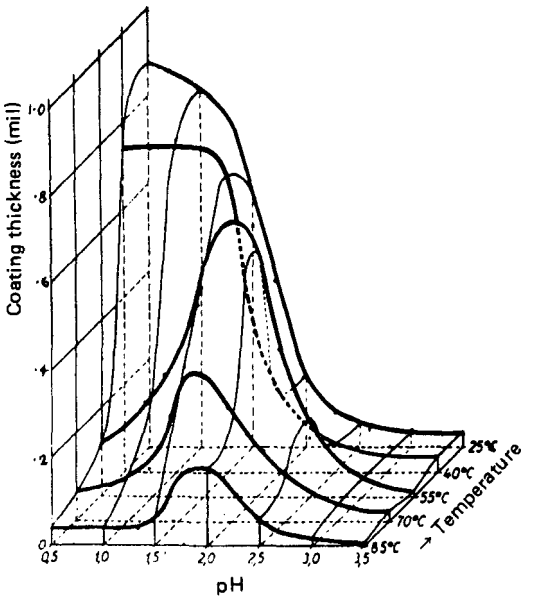


Fig. 7-44. Effect of variations of temperature and pH of oxalic acid electrolytes on film thickness produced on 99.5% aluminium (Hübner[212])

The relationship between oxalic acid concentration, voltage and coating thickness has been examined by Jenny[76] for both the d.c. and a.c. processes. In general, d.c. anodizing gives much higher coating thicknesses due to the greater heat developed in the coating, partly due to the rectification effect and partly to oxygen evolution.

Addition of oxalic acid may be made on the basis of current consumption. Approximately 0.1.3-0.14 gm oxalic acid are used per amp-hour while 0.08-0.09 gm aluminium per amp hour go into solution,[6] forming aluminium oxalate. 5 parts by weight of oxalic acid are added for each part by weight of dissolved aluminium. As the aluminium content rises, the current density is decreased and the solution is discarded when 3% aluminium is present.

7. OTHER DECORATIVE AND/OR PROTECTIVE PROCESSES

Sulphamic acid process

This process was developed by R. Piontelli[213] who also applied sulphamic acid to many electroplating processes. Piontelli employed solutions containing 20% sulphamic acid, NH_2SO_2OH, at 30-40°C. Current densities of 1 A/dm^2 (10 amp/sq ft) are used, while the voltage is gradually increased during the operating time of 45 minutes. The coatings are denser and less porous than those produced in sulphuric acid and do not require sealing. The solvent action of sulphamic acid on the anodic oxide coating is markedly weaker than that of sulphuric acid. As a result higher bath temperatures are required.

Fukushima,[214] who anodized various alloys of aluminium in 5-20% sulphamic acid at 10 amp/sq ft (1 A/dm^2), found that at temperatures around 20°C local attack tended to occur at weak points of the coating, allowing current break-through leading to pitting and local corrosion.

In the **U.S.A.**, a sulphamic acid process was developed by the Reynolds Metal Co. who used a 5-10% solution at 6-25 amp/sq ft (0.6-2.5 A/dm^2). The bath temperature was kept at 40°C. Tanks were of stainless steel or steel lined with acid-resisting materials. Separate lead cathodes were used. The voltage was raised from 5 to 45 volts within the first 3-5 minutes and maintained at this for 15-40 minutes. In this process, the coating was porous and was sealed in the usual way, or it could be dyed.

However, the cost of sulphamic acid in this country is high and the process is not economically competitive with sulphuric acid.

Sulphuric acid is formed in small quantities by hydrolysis and there is evidence that its presence is necessary to obtain a satisfactory coating.[215]

Andrus[138] investigated a 5% sulphuric acid electrolyte containing 5% sulphamic acid. This produced films having a narrow temperature range for dyeing and an abrasion resistance which dropped rapidly with rise in temperature.

The sulphamic acid process has also been the subject of a detailed study in Russia[216] to establish the optimum conditions of operation. The procedure adopted is said to give better results than those published elsewhere, and the quality of the anodic layers is not inferior to that obtained in the sulphuric and oxalic acid processes.

Malonic acid process

Use of malonic acid, $CH_2(COOH)_2$, has been investigated by Kape.[217,218] As may be expected, this acid will give coatings which are somewhat similar to those produced in oxalic acid. However, the solubility of malonic acid is greater in water and its solvent action on the oxide coating is lower. In cold dilute solutions, thin films (below 2.5 μm; 0.1 mil) of low porosity are formed, and to achieve commercially acceptable films a 12.5% (wt) solution has to be used at 40-60°C with vigorous agitation with carbon cathodes and a plastic tank. Table 7-15 overleaf gives conditions for malonic acid anodizing a number of aluminium alloys.

Hardness values between 400 and 500 DPH are obtained with malonic acid coatings. Hardness decreases with increasing current density and anodizing time, and while the abrasion resistance is good, it decreases with increase of anodizing temperature (Fig. 7-45). The corrosion resistance of the coatings compares well with those obtained in other anodizing baths (Fig. 7-46). As malonic acid coatings have a very low porosity they are not very suitable for dyeing.

Phosphoric acid processes

Whilst phosphoric acid anodizing is rarely used to produce decorative or protective finishes, it is being increasingly used as a preparative treatment for subsequent application of organic or plated coatings.

One of its most widespread uses is in the preparation of lithographic plates for printing purposes (see also Chapter 4), and with some plates it has largely replaced the previously used sulphuric acid electrolytes. Thus Howson-Algraphy[219] describe an anodizing process based on a 10-30% (wt) phosphoric acid electrolyte used at a temperature of 15-30°C. A current density of 0.5-2.0 A/dm^2 (5-19 A/ft^2) at voltages from *0-50* volts is applied for 2-20 min. Plates produced under such conditions are said to be more stable in storage, and, because of improved adhesion of the light sensitive coating, to give longer printing runs. A similar development by Hoechst[220] uses a mixed sulphuric acid-phosphoric acid electrolyte containing 25-150 g/l H_2SO_4, 10-50 g/l H_3PO_4 and 5-25 g/l Al^{3+}. It is used at 4-25 A/dm^2 at temperatures of 25 to *65°C*. Another suggestion, from Fuji Photo Film Co.,[221] is the use of a.c. anodizing in phosphoric acid and Vickers[222] claim the use of sulphuric acid anodizing followed by phosphoric acid anodizing. Kodak[223] also recommend phosphoric acid anodizing.

TABLE 7-15

Conditions for anodizing aluminium alloys in 12.5% w/v malonic acid[217]

Alloy	Current density		Time (min)	Temp.		Voltage	Coating thickness		Colour
	(amp/sq ft)	(A/dm^2)		(°F)	(°C)		(mil)	(μm)	
NT3 ½H (3003)	12	1.3	30	131	55	115-120	0-2	0-50	Opaque yellow-white
NS4 ½H (5251)	12	1.3	30	104	40	101-110	0.25	6.3	Pale yellow
	24	2.6	60	122	50	105-110	1.2	30	Brown
HE 9W (6063)	15	1.6	30	131	55	110	0.15	3.75	Pale yellow
	15	1.6	60	131	55	110	0.4	10	Light brown
HE 20 WP (6061)	15	1.6	30	131	55	120	0.2	5	Opaque yellow-white
HS 10 W	24	2.6	30	131	55	120	0.2	5	Opaque yellow-white
H 15 WP (2014A)	12	1.3	30	149	65	68-120	0.06	1.5	White
	12	1.3	30	158	70	66-84	0.1	2.5	White
D.T.D. 683	12	1.3	30	131	55	70-84	0.25	6.3	Opaque white-yellow
	24	2.6	60	131	55	106-120	1	25	Opaque off-white
5%% Si alloy	24	2.6	30	131	55	115-120	0.2	5	Grey-yellow

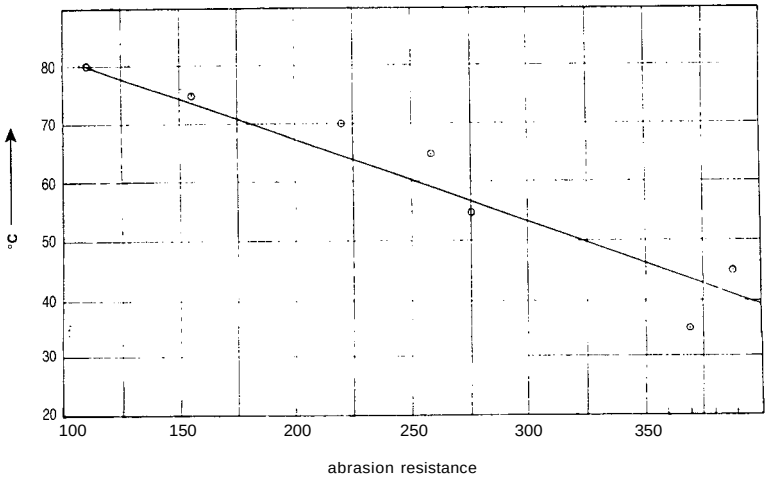


Fig. 7-45. Effect of bath temperature on abrasion resistance of coatings produced in 12.5% w/v malonic acid at 12 amp/sq **ft** (1.3 A/dm^2)

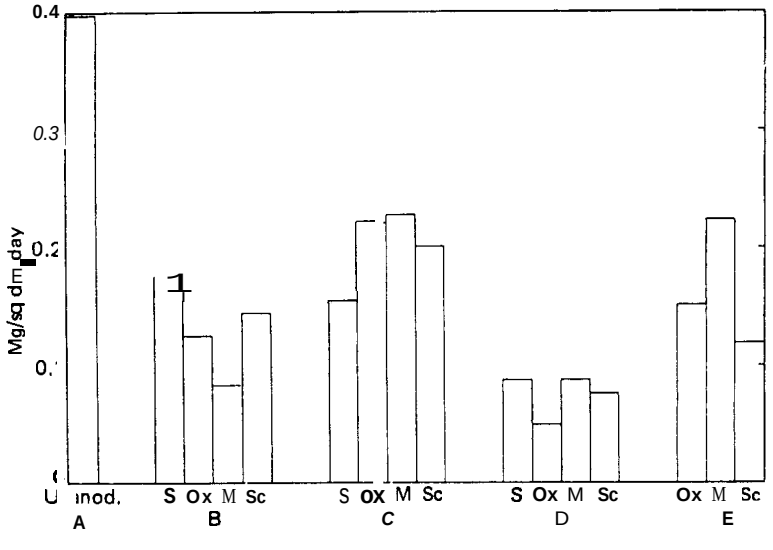


Fig. 7-46. Variation of corrosion resistance with anodizing and sealing methods. Loss in weight on immersion in salt water

S	sulphuric acid anodized	**A**	unanodized
Ox	oxalic acid anodized	B	sealed in water
M	malonic acid anodized	**C**	sealed in dichromate
Sc	sulphamic acid anodized	D	sealed in lanolin
		E	unsealed

In quite a different context phosphoric acid anodizing is becoming recognised as an excellent preparation for adhesive bonding in the aerospace and automotive industries. This work has been pioneered by Boeing[224] and it is becoming known as the Boeing Process in that industry. In this process anodizing is normally preceded by a sodium dichromate/sulphuric acid etching treatment (FPL etch), which is carried out for 15-30 min at 68°C in a 33 g/l sodium dichromate 330 g/l sulphuric acid solution. After rinsing the work is then phosphoric acid anodized in a 10-12% (wt) phosphoric acid electrolyte at 10-15 V and a temperature of 21-24°C for 20-25 min. Such a treatment is said to give adhesive bonds which are consistent in quality and have greater durability under adverse conditions[225] than conventional surface preparation methods such as chromic acid or sulphuric acid anodizing (Fig. 7-47). This process has become an ASTM standard under the designation of D3933-93. Later a two-step anodizing process,[226] first involving phosphoric acid anodizing, and then anodizing in a sulphuric acid /boric acid electrolyte was described, and a similar patent but using only anodizing in sulphuric acid and boric acid as an alternative to chromic acid anodizing has been covered by Boeing.[227]

A detailed comparison of phosphoric and chromic acid anodizing, as pretreatments for bonding and painting, has been reported by Thompson and Heaton.[228] They concluded that the phosphoric acid treatment was superior and that this was particularly true when using epoxy-based adhesives. This field was reviewed by Kozma and Olefjord,[229] and a very broad ranging review of pretreatments for bonding purposes has been produced by Critchlow and Brewis.[230] In another study the same authors[2”] confirm the superiority of phosphoric acid anodizing with epoxy adhesives.

The importance of this development in the U.S. aerospace industry has sparked off a great deal of investigational work aimed at identifying the particular features of phosphoric acid anodizing that are responsible for the improved adhesion. Venables and colleagues at Martin Marietta have been particularly active in this work and have examined the morphology of phosphoric acid anodized films in detail.[232] They show oxide whiskers or protrusions on the phosphoric acid anodized surface, and assume that this interlocks with the adhesive (Fig. 7-48). However other authors question the significance of these whiskers and believe that it is the hydration resistance and stability of the coating produced by phosphoric acid anodizing that is the most important factor.[225] Detailed SEM pictures of phosphoric acid anodized surfaces were produced by Arrowsmith *et al.*[233] and microtomed cross-sections of phosphoric acid films have featured in some of the UMIST work reported in Chapter 6.

In the automotive field Alcan[234,235] have done a great deal of work on phosphoric acid anodizing as a pretreatment for adhesive bonding of vehicle structures, and they propose a continuous phosphoric acid anodizing process[234] in which the aluminium strip is passed through the electrolyte at between 25 and 80°C with a contact time of not more than 15 seconds at a current density of at least 250 A/m^2. This film, which has large open pores (Fig. 7-49), is said to form an excellent substrate for lacquer, paint or adhesive. The use of this material for vehicle fabrication is covered in an associated patent.[235]

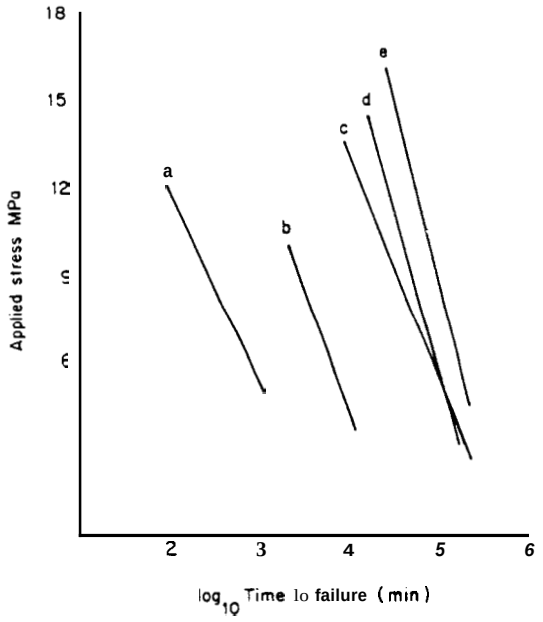


Fig. 7-47. Effect of pretreatment on the durability of aluminium joints bonded with a nitrile-epoxide and subjected to applied stress at 52°C and 100% R.H. (a) degreased; (b) sulphuric acid-anodized (unsealed); (c) chromic acid-etched; (d) chromic acid-anodized; (e) phosphoric acid-anodized[225]

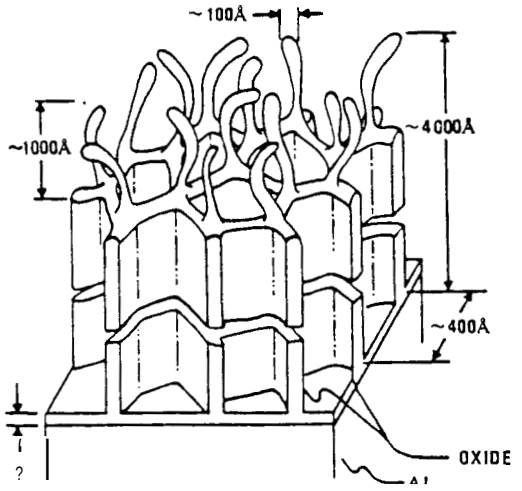


Fig. 7-48. Schematic representation of phosphoric acid anodized surface oxide by Venables *et al.*[232]

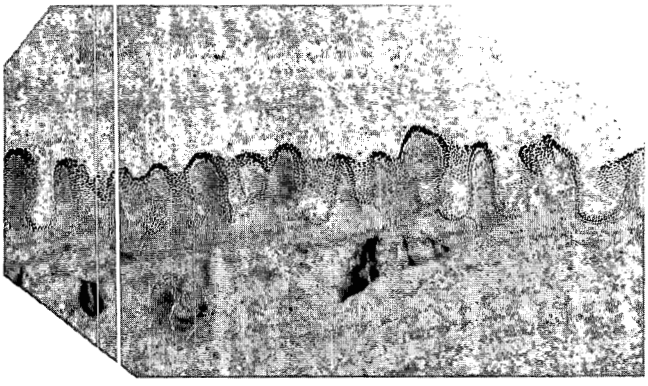


Fig. 7-49. Phosphoric acid anodized film produced as a substrate for adhesive bonding [courtesy of Alcan International Ltd.]

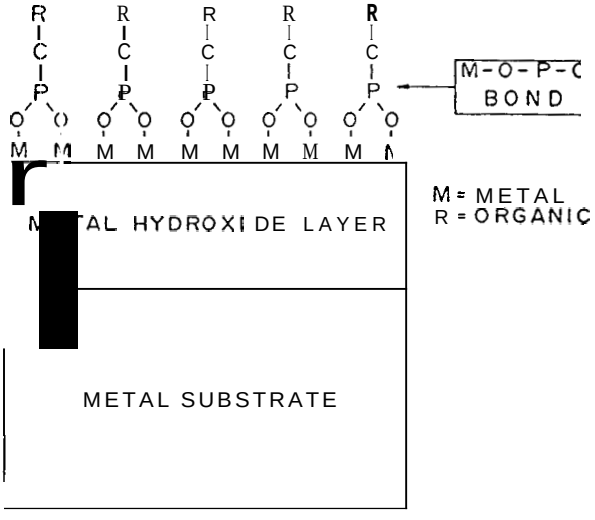


Fig. 7-50. Functionalised layer of organic compound on anodic film surface. [237]

Alcoa[236] have patents based on phosphorous acid anodizing, again as a pretreatment for bonding or organic coating, and in a range of similar pretreatment patents[237] they claim the use of organic phosphonic acid anodizing or phosphorous acid esters. These are said to form a non-porous barrier layer with a functionalised layer of organic compound on the outer surface (Fig. 7-50). A related double anodizing treatment[238] in which the material is first anodized to produce a

conventional porous film, and is then anodized in an aqueous organo-phosphorous compound, is said to give either chemically resistant surfaces or those suitable for organic coating.

Alcan[239] have also used phosphoric acid in electrolytic cleaning treatments where the balance of anodizing is adjusted towards dissolution of the film as fast as it is formed. This process is described in more detail in the electrolytic cleaning section of Chapter 4. In the same field there is similar work reported by Boeing[240] and by Felisari.[241]

Phosphoric acid anodizing has also been used as a pretreatment for electroplating, and this is discussed in Chapter 13. Spooner and Seraphim[242] studied this process in detail and recommended a 250 g/l phosphoric acid electrolyte used at a current density of 1.1-1.6 A/dm^2 and 25°C for a time of 10 minutes. A film thickness of about 3 microns was produced under these conditions.

Finally a quite different application of phosphoric acid anodizing has been developed by Alcan,[243] in which a phosphoric acid anodized film, separated from the basis metal, is used as a porous filtration membrane. This is described in more detail later in this Chapter in the section on Functional Anodizing, but essentially superpurity aluminium is anodized in a 5-150 g/l phosphoric acid electrolyte at a voltage of 40-200 V and a temperature of 5-50°C. The film produced has a very uniform pore structure and can be over 100 microns in thickness, and it is separated from the metal substrate using a controlled voltage reduction programme. The separated film can then be used as a microfiltration membrane.

Opaque coatings

Most important of these was the Ematal process developed by Schenk,[244] and used mainly in Switzerland, which employed an oxalic acid solution containing salts of thallium, zirconium or titanium. These salts hydrolyse in the coating, the hydroxides producing a milky, opaque, non-metallic appearance which somewhat resembles porcelain enamel. The bath was operated at 2-3 A/dm^2 (19-28 amp/sq ft) d.c., and 120 volts. The operating time was 20-40 minutes, and the solution was kept at 50-70°C. The pH of the solution was critical and must be kept at 1.6-3.0.

The corrosion resistance was claimed to be superior to that of sulphuric acid coatings, and the coatings could be dyed satisfactorily, especially to pastel shades. Most wrought alloys containing less than 2% copper, and casting alloys containing less than 1% Mn, 1% Fe, 1% Ni, 2% Cu and 8% Zn or Mg, are suitable for treatment by the Ematal process.

The addition of over 3% zirconium to sulphuric or oxalic acid electrolytes has been described by Freud and Frasch[245] for producing coatings similar to the Ematal process and by the same sort of mechanism. These authors add zirconium in the form of a sulphate complex $[ZrO(SO_4)_6].H_2O$ to the sulphuric acid solution which is operated at 35°C, 18 volts, 8 A/dm^2 (75 amp/sq ft) for 30 minutes with lead cathodes. Anodizing is followed by sealing for 10 minutes in boiling water.

In an improvement of the Ematal process by Contraves A.G.[246] it was proposed to add cobalt acetate to the electrolyte mixture containing boric, citric and oxalic acids with potassium titanium oxalate. This was also a high voltage process and the coating was said to be extraordinarily abrasion resistant. There was a correct manner for preparing the electrolyte, the cobalt acetate being added from a prepared solution only when the bath was in use and 'activated'. Two electrolytes were suggested, one suitable for alloys of low copper content and the other for use when the copper content of the alloy was high (see Table 7-16).

TABLE 7-16

Improved Ematal process[246]

	1. Alloys low in Cu	*2. Alloys with Cu*
Potassium titanium oxalate	45 g/l	*50-55* g/l
Boric acid	12	14
Citric acid	0.8	1.5
Oxalic acid	1.5	1.8
Cobalt acetate	1.2	0.5-1
Temperature	58-60°C	35-38°C
Voltage	110 V	110 V

In a later version the electrolyte contained potassium-titanium oxalate, cobalt acetate, nickel acetate, nickel sulphate and 0.3-0.6 ml/litre sulphuric acid. The coating formed was said to be electronically conductive.[247]

Similar opaque coatings can also be obtained in a mixture containing:[248]

chromic acid 3% (wt)
boric acid 0.1-0.2% (wt)

at 0.3 A/dm^2 (3 amp/sq ft), 40-60 volts, 40-55°C, and in the following mixed electrolytes:

	I	II
chromic acid (% wt)	10	5
oxalic acid (%)	2	0.5
boric acid (%)	–	0.2-0.5
phosphoric acid (%)	2	–
water	balance	balance
current density (amp/sq ft)	5-8	8-10
voltage	20-30	25-40
temperature (°C)	30-50	30-50

The French BF4 anodizing process, which was also based on a mixture of chromic, oxalic and boric acids, was used at 42-48°C, 40-50 volts and 0.8-1 A/dm^2 (7-9 amp/sq ft), and was reported to be employed in the French aircraft industry.[249] The opaque coatings obtained were built up to 20 μm (0.8 mil) in 60 minutes and could be dyed. Superimposed a.c. could also be used to obtain a white or grey-yellow film.

Mellitic acid process

Mellitic acid $C_6(COOH)_6$, as well as being used as an additive to the sulphuric acid bath for hard or architectural anodizing, can be used on its own to obtain high density coatings which have the property of reflecting radar.[250] Such solutions were used at about 164 g/l at 40 volts.

Other acids used for anodizing

In addition to what might now be regarded as the traditional acids used for anodizing, there has been a widespread search for viable alternative systems, generally for commercial rather than technical reasons. Acids which have featured in binary or more complex mixtures include:

sulphosalicylic acid	maleic acid
sulphophthalic acid	succinic acid
substituted succinic acids	sulphoresorcinol
naphthalene disulphonic acids	chromotropic acid
sulphamic acid	citric acid
lignosulphonic acid	formic acid
cresolsulphonic acid	proprionic acid
sulphoanthranilic acid	tartaric acid
sulphomaleic acid	

Most of these are referred to later in Chapter 8 in the section on integral colour anodizing.

No one has contributed as much, in public at least, to the study of the lesser known acids as Mr. J.M. Kape. In 1961[218] he formulated the proposition that all satisfactory acids for anodizing are dibasic with a dissociation constant of at least 10^{-4} for the second hydrogen ion, and, in addition, their solubility needs to be sufficiently high to give a reasonably low anodizing voltage, or pitting will occur. Monobasic acids containing a –COOH or $-SO_3H$ group usually produce pitting even when anodizing super-purity metal.

In a later study[251] Kape examined a series of acids having at least 1% solubility in water at 20°C and containing two –COOH or $-SO_3H$ groups, or one of each. These acids fall into the following groups:

1. Dibasic saturated acids
2. Dibasic unsaturated acids
3. Hydroxy-dibasic or polybasic acids
4. Derivatives of oxalic acid
5. Aromatic carboxylic acids
6. Aromatic sulphonic acids.

The results of attempting to use these acids singly are given in Tables 7-17 to 7-21, while Table 7-22 lists the pH values, dissociation constants and conductivities of the solutions.

The graph in Fig. 7-51 plots the results on a dissociation constant/conductivity continuum to indicae that the various types of anodic reaction are located in specific areas.

Kape concludes that anodic polarization of aluminium occurs in most organic dicarboxylic and tricarboxylic acids. If the pH value of the solution is much below 2.0 pitting occurs. There is also pitting if the first dissociation constant ($-\log K_1$) is more than 3.0. Thick oxide coatings can be obtained in oxalic, malonic and glyoxylic acids provided the conditions **are** such that chemical dissolution of the oxide does not occur at too high a rate: indeed this factor is of prime importance in most systems. Pitting also occurs if the conductance of a 5% solution falls much below 3200 microsiemens.

Kape suggests that a simple measurement of conductance in mixed acids should indicate whether pitting is likely to occur in anodizing, and conversely that a number of practicable systems can be devised by arranging for the electrolyte to have the right characteristics. This theory was demonstrated by mixing oxalic acid in various amounts with several acids which tended to pit or form barrier layers when used alone until coatings of 25-35 μm could be obtained (Table 7-23). In this way he was able to propose, on the basis of these principles, a number of anodizing systems which should and could produce thick anodic coatings of good quality. These are given in Table 7-24 together with the abrasion resistance of the coating. The use of mixed acid systems is considered in more detail in Chapter 8.

TABLE 7-17

Results of anodizing in electrolytes composed of dibasic saturated organic acids in water[25]

Acid	*Concentration (%)*	*Voltage range*	*Temperature (°C)*	*Remarks*
Adipic	Saturated	30-40	20	Pitting, no film formation.
Malonic (pH 1.7)	1	155-168	20	Dark bronze-grey coating. Heavily profiled.
	2.5	142-160	20	Dark bronze-grey coating. Less profiling.
	5.0	138-150	20	Dark bronze, fairly smooth coating.
	7.5	130-146	20	Dark bronze, smooth coating.
	10.0	120-140	20	Dark bronze, smooth coating.
	10.0	110-130	40	Bronze-yellow.
	10.0	104-115	40	Yellow-brown.
	10.0	95-102	50	Yellow-brown.
	10.0	84-92	60	Yellow-ochre.
Glutaric (pH 3.1)	0.1	220-280	20	Barrier layer, iridescent.
	1.0	150-280	20	Iridescent coating, pitting.
Succinic (pH 2.9)	1	210-285	20	Iridescent coating, pitting.
	3	160-280	20	Iridescent coating, pitting.
	10	135-280	20	Iridescent coating, pitting.
Diglycollic (pH 1.5)	5	120-180	20	Iridescent, grey film 7.5 μm thick.
	5	130-250	30	Iridescent, grey film 7.5 μm thick.
	5	156-220	40	Iridescent, grey film 7.5 μm thick.
	5	172-275	50	Iridescent, grey film 7.5 μm thick.
	5	170-270	60	Iridescent, grey film 7.5 μm thick.
n Butyl malonic (pH 4.5)	1	50	20	Burnt, pitting.
	5	50	20	Burnt, pitting.
	10	45	20	Burnt, pitting.

Fukushima and colleagues[252] in Japan have also studied the monocarboxylic acids, which in general are less suitable for use in anodizing systems. Using 99.99% aluminium sheet anodized at 1.87 A/dm^2 they carried out experiments from 20°C to boiling point in aqueous solutions of the acids which ranged in strength from 0.01 mol/litre to saturation. They found that formic acid was rather different from the rest of the members of the series in that porous and thick anodic coatings were uniformly formed in formic acid at relatively high temperatures and concentrations. At low temperatures and concentrations they obtained pitting of the anode by local corrosion, as also did Kape.[251] The uniform formic acid coating possessed porous structures similar to those obtained in sulphuric acid, and they could be easily coloured with

TABLE 7-18

Results of anodizing in electrolytes composed of dibasic and tribasic unsaturated organic acids[251]

Acid	*Concentration*	*Voltage range*	*Temperature (°C)*	*Remarks*
Aconitic (technical grade) (contains H_2SO_4)	2.0	45	20	Pitting. Constant current difficult to maintain.
	4.0	30	20	Thick dark coating at isolated points. Resembles anodizing in very dilute H_2SO_4.
	6.0	30-55	20	Thick dark coating at isolated points. Resembles anodizing in very dilute H_2SO_4.
Maleic (pH 1.4)	2.5	150-300+	20	Thin greyish coating.
	2.5	Over 200	40 to 50	10 microns thick, greyish rough coating.
	5.0	95-160	20	Iridescent greyish coating (2.5 microns)
	5.0	78-116	30	Iridescent greyish coating, constant current difficult to maintain.
	5.0	78+	40 to 60	Iridescent greyish coating, constant current difficult to maintain.
Citraconic	5.0	83-235	20	Iridescent coating. Thin deposit of a brownish material.
		145-220	50	Iridescent coating. Solution decomposing to a yellow compound.
Itaconic (pH 2.2)	5.0	110-125	20	Iridescent coating, pitting.
	5.0	130-140	50	Iridescent coating, pitting.
	10.0	105-100	20	Pitting. Very little film formation.
	10.0	100-140	50	Pitting. Very little film formation.
Acetylene dicarboxylic acid	1.0	80	20	Pitting.
	5.0	70	20	Blotchy brown coating.
	10.0	60-65	20	Yellow oxalic type coating.

organic dyestuffs. In other acids such as acetic, propionic, butyric, valeric and benzoic acids, it was impossible to form uniform coatings and corrosion of the anode was always observed. The same authors then studied the dicarboxylic acids.[253] They concluded that uniform coatings could be obtained in baths of succinic, fumaric, glutaric, adipic, pimeric, suberic, azelaic, sebacic and phthalic acid, and thick coatings could be obtained at relatively high concentrations and temperatures in malonic acid and maleic acid.

TABLE 7-19

Results of anodizing in electrolytes composed of dibasic and tribasic hydroxy organic acids in water[251]

Acid	*Concentration*	*Voltage range*	*Temperature (°C)*	*Remarks*
Malic (pH 2.2)	5	205-130	20	Grey iridescent coating, 2.5 microns thick. Fine pits (one large hole right through one specimen).
	5	230-280	50	Hard grey-bronze coating, 10 microns thick. Profiled.
	10	200-230	50	Hard grey-bronze coating, 10 microns thick. Profiled.
	10	224-230	20	Greyish coating, 10 microns thick. Hole burnt right through one specimen.
Thiomalic (pH 2.5)	2.5	105-170	20	Yellowish 'tracery' type coating. Very irregular. Minute pits.
Mucic acid (pH 2.6)	1	130-290	20	Iridescent coating, pits.
	1	300+	50	Iridescent coating, no pits
Tartaric (pH 1.8)	5	180-267	20	Greyish coating, 2.5 microns thick.
	5	192-241	30	Greyish coating, 2.5 microns thick.
	5	182-215	50	Greyish coating, 2.5 microns thick.
	5	195-215	60	Greyish coating, 2.5 microns thick.
	10	Over 100	20	Iridescent coating, barrier layer.
Citric	2.5	200-300	20	Thin iridescent coating.
	5.0	220-280	20	Thin iridescent coating.
	5.0	230-280	30	Greyish, iridescent coating, 2.5 microns max.
	5.0	230-280	40	Greyish, iridescent coating, 2.5 microns max.
	5.0	150-240	50	Greyish, iridescent coating, 2.5 microns max.
	5.0	198-240	60	Clear iridescent coating.
	10.0	200-250	20	Greyish coating. Very thin.
	10.0	200+	55	Greyish coating. Thick yellow in places.
	10.0	200+	90	Greyish coating. Thick yellow in places.

TABLE 7-20

Results of anodizing in electrolytes composed of derivatives of oxalic acid[251]

Acid	*Concentration*	*Voltage range*	*Temperature (°C)*	*Remarks*
Glyoxylic (pH 1.7)	2.5	160-185	20	Some pitting. Greyish bronze patchy film (about 25 microns).
	5.0	160-170	20	Patchy greyish-bronze film (about 25 microns), slight pitting.
	10.0	130-150	20	Grey-brown, patchy coating 25 microns.
	15.0	130-145	20	Bronze coating, fairly smooth.
	25.0	130-140	20	Bronze coating, smooth.
	35.0	125-130	20	Bronze coating, smooth.
Glyoxal (used as 40% aqueous solution)	2.5	22-40	20	Thin clear coating. Large number of small pits.
	5.0	30-35	20	Thin clear coating. Large number of small pits.
	10.0	25	20	Thin clear coating. Large number of small pits.
	40.0	21-23	20	Thin clear coating. Large number of small pits.
Oxamic (pH 1.9)	Saturated (< 1%)	10-20	20	Uncontrollable current. Considerable pitting.

TABLE 7-21

Results of anodizing in electrolytes composed of derivatives of aromatic carboxylic acids in water[251]

Acid	*Concentration*	*Voltage range*	*Temperature (°C)*	*Remarks*
Phthalic (pH 2.4)	Saturated (< 1%)	150-252	20	Iridescent (barrier layer) (pH 2.4).
		175-225	50	Iridescent coating, less than 2.5 microns.
Trimellitic	Over 1%	90-190	20	Very thin iridescent coating
Pyromellitic	1.5	70-180	20	Very thin iridescent coating

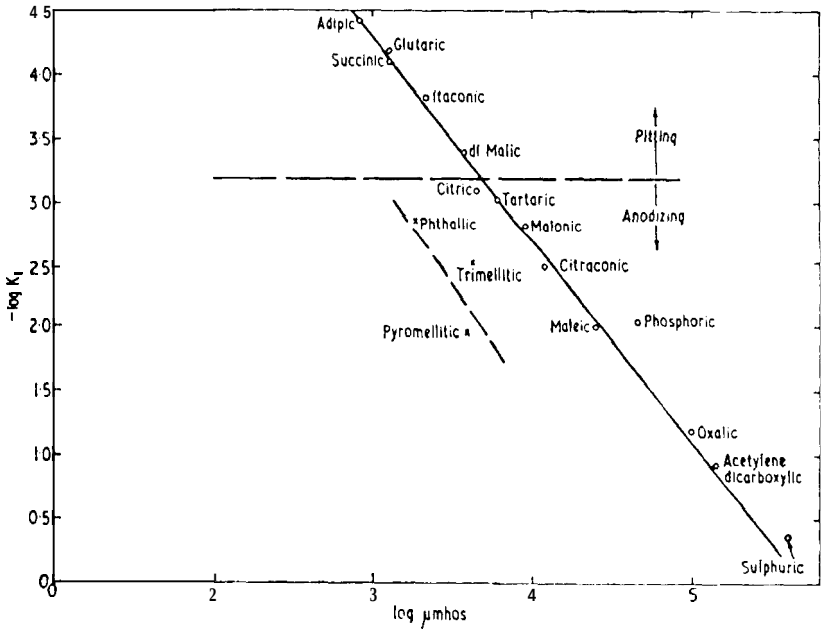


Fig. 7-51. Anodic reaction, acid dissociation constant and conductance of various acid electrolytes[251]

Anodizing in electrolytes based on organic solvents

Very little work has been carried out on the use of organic solvents as a basis for anodizing electrolytes, but Kape[254] has examined such systems in detail. He studied a range of mixtures primarily based on sulphuric acid or oxalic acid dissolved in organic solvents which were miscible with water. He found that few of these mixtures conducted electricity and few serviceable coatings were obtained until the solutions were diluted with water. Oxalic acid electrolytes containing water together with formamide, dimethyl formamide, dimethyl sulphoxide and sulpholane produced hard, integrally coloured coatings. Results for a range of such electrolytes are shown in Table 7-25.

TABLE 7-22

A comparison of some physical properties of solutions of organic acids in comparison with their reaction towards aluminium[251]

Acid	*pH of 5%* or saturated solution	*–log* K		Anodic reaction*	*Conductivity of a* **5%** solution *(μS)*	$log_{10}\mu S$
Oxalic	1.2	$K_1 = 1.19$,	$K_2 = 4.21$	Thick, porous, anodic coatings, 60-80 V	65000	4.81
Malonic	1.7	$K_1 = 2.85$,	$K_2 = 6.10$	Thick, porous anodic coatings, 100-150 V	9100	3.95
n-Butyl malonic	4.5	K_1 = ?	K_2 = ?	Pitting at 40-45 V		
Succinic	2.3	$K_1 = 4.19$,	$K_2 = 5.57$	Thin iridescent coating, pitting, 130-280 V	1400	3.15
Adipic	2.9	$K_1 = 4.43$		Pitting, 30-40 V	720	2.86
Glutaric	3.1	$K_1 = 4.34$		Thin iridescent coating, pitting, 150-280 V	1330	3.11
Diglycollic	1.5	K_1 = ?	K_2 = ?	Porous anodic coatings. 150-300 V Max. thickness 7.5 microns	5750	3.76
Maleic	1.4	$K_1 = 2.0$,	$K_2 = 6.26$	Barrier layers, tendency to give thicker coatings up to 10 μ at over 100 V.	25000	4.4
Acetylene dicarboxylic	0.1	K_1 = ?	K_2 = ?	Pitting at 1%, thick coatings at 10%		
Citraconic	1.8	$K_1 = 2.48$		Barrier layer 150-250 V.	11900	4.08
Itaconic	2.2	$K_1 = 3.40$,	$K_2 = 5.55$	Pitting. Tendency to barrier layer formation at 100+ V.	2200	3.34
dl-Malic	2.2	$K_1 = 3.40$,	$K_2 = 5.05$	Pitting. Tendency to form thick porous coatings at 200+ V.	3900	3.59
Mucic	2.6	$K_1 = 3.21$		Pitting. Tendency for form barrier layer at 300 V.	400	2.6
Tartaric	1.8	$K_1 = 3.02$,	$K_2 = 4.54$	Thick barrier layer (?) porous coatings at 180-210 V.	6200	3.19
Citric	2.0	$K_1 = 3.06$, $K_2 = 4.74$	$K_3 = 5.40$	Thick barrier layer 200+ V.	4500	3.65
Phthalic	2.4	$K_1 = 2.89$		Barrier layer, 150-250 V.	1750	3.24
Trimellitic	ca 2.0	$K_1 = 0.52$, $K_2 = 3.85$	$K_3 = 5.20$	Barrier layer, 90-190 V.	4200	3.62
Pyromellitic	ca 2.0	$K_1 = 1.92$, $K_2 = 2.89$	$K_3 = 4.49$ $K_4 = 5.64$	Barrier layer, 70-180 V	5800	3.76

* N.B. The term 'barrier layer' is used in a general sense to imply a thin essentially non-porous oxide structure.

TABLE 7-23

Voltage range and colours produced by adding various concentrations of oxalic acid to aqueous solutions of organic carboxylic acids, at 20°C, 18 amp/sq ft (2 A/dm²) for sufficient time to obtain a coating of 25-35 microns[251]

Electrolyte mixture. % of each component acid	*Voltage range*	*Colour of coating and remarks*	*Conductivity (μS)*
10 Malonic	125-135	Dark sepia-brown, rough	11500
10 Malonic + 0.1 oxalic	135-140	Dark brown, rough	12000
10 Malonic + 0.2 oxalic	130-140	Dark brown, smoother	12800
10 Malonic + 0.3 oxalic	125-135	Med. brown-bronze, **smooth**	
10 Malonic + 0.4 oxalic	110-130	Med. bronze	
10 Malonic + 0.5 oxalic	125-130	Med. bronze	15000
10 Malonic + 0.6 oxalic	110-120	Light med. bronze, very smooth	
10 Malonic + 1.0 oxalic	100-115	Light med. bronze, very smooth	18000
10 Malonic + 2.0 oxalic	85-110	Light bronze	
10 Malonic + 3.0 oxalic	85-110	Light bronze (almost like oxalic acid coating)	29000
10 Malonic + 4.0 oxalic	75-85	Very light bronze (almost like oxalic acid coating)	
10 Malonic + 5.0 oxalic	70-80	Dark gold (similar to oxalic coating, 35 μm thick)	39000
10 Glyoxylic	130-150	Grey-brown, patchy, rough	7200
10 Glyoxylic + 0.1 oxalic	140-160	Dark greyish, partially burnt	8000
10 Glyoxylic + 0.2 oxalic	130-150	Grey-brown, rough	
10 Glyoxylic + 0.3 oxalic	115-140	Bronze, smoother	9900
10 Glyoxylic + 1.0 oxalic	90-130	Bronze	15500
35 Glyoxylic	125-130	Bronze-brown, smooth	9500
35 Glyoxylic + 0.3 oxalic	120-130	Bronze	10200
35 Glyoxylic + 0.5 oxalic	120-135	Bronze-brown	11100
35 Glyoxylic + 1.0 oxalic	115-130	Med. brown-bronze	13000
5 Tartaric	180-267	Thin grey coating, 2.5 μm thick	5800
5 Tartaric + 0.2 oxalic	170-247	Dark grey, roughish	8000
5 Tartaric + 0.3 oxalic	110-155	Med. grey, smooth	
5 Tartaric + 0.6 oxalic	100-146	Brown-grey, smooth	12000
5 Tartaric + 2.0 oxalic	80-107	Greenish yellow (cf. oxalic acid films)	25000
2 Oxamic + 0.2 oxalic	8-10	Pitting	15000
2 Oxamic + 1.0 oxalic	8-10	Pitting	17000
2 Oxamic + 1.6 oxalic	8-10	Pitting	25000
5 Citric	220-300	Barrier layer, iridescent	4400
5 Citric + 0.15 oxalic	140-180	Med. grey-brown	6200
5 Citric + 0.3 oxalic	110-180	Med. grey-brown	8200
5 Citric + 0.6 oxalic	100-170	Grey	11400
5 Citric + 1.2 oxalic	85-104	Greenish yellow (cf. oxalic acid films)	17500
5 Diglycollic	120-180	Thin grey coating, 7.5 μm thick	6300
5 Diglycollic + 0.15 oxalic	165-240	Dark grey, streaky	7750
5 Diglycollic + 0.3 oxalic	148-197	Med. grey, slightly streaky	
5 Diglycollic + 0.6 oxalic	120-175	Bronze-grey	13600
5 Diglycollic + 1.2 oxalic	100-140	Yellow-brown	
5 Diglycollic + 1.8 oxalic	85-110	Greenish yellow (cf. oxalic acid films)	24000
10 Malic	Erratic	Greyish iridescent, 10 μm thick, pitting	5000
10 Malic + 0.1 oxalic	220-261	Dark bronze-grey, profiled	6000

Electrolyte mixture. % of each component acid	*Voltage range*	*Colour of coating and remarks*	*Conductivity (μS)*
10 Malic + 1.0 oxalic	198-200	Dark grey, profiled	14000
10 Malic + 3.0 oxalic	85-103	Greenish yellow (cf. oxalic acid films)	27000
2 Pyromellitic	70-180	Thin iridescent film	6250
2 Pyromellitic + 0.1 oxalic	150-175	Pale grey	7800
2 Pyromellitic + 0.2 oxalic	115-150	Pale grey-brown	8800
2 Pyromellitic + 0.6 oxalic	120-155	Pale yellow-grey	13500
2 Trimellitic	90-190	Iridescent coating	5000
2 Trimellitic + 0.1 oxalic	150-200	Light grey	6800
2 Trimellitic + 0.2 oxalic	100-150	Grey-beige	8100
2 Trimellitic + 0.4 oxalic	100-130	Very light grey	10500
2 Trimellitic + 1.2 oxalic	50-90	Yellow-green (cf. oxalic acid films)	19000
10 Succinic	135-280	Iridescent coating and pitting	2000
10 Succinic + 0.1 oxalic	150-275	Grey-bronze, mottled	3200
10 Succinic + 0.2 oxalic	100-150	Grey	6000
1.0 Glutaric	150-280	Iridescent coating and pitting	–
1.0 Glutaric + 0.1 oxalic	165-280	Grey	–

An oxalic acid (3-7% (wt)), formic acid (2% (vol)) mixture dissolved in a 66% (vol) water and 33% (vol) formamide solvent showed particular promise, and reproducible yellowish brown, bronze or grey coatings were produced. The electrolyte could be used between 20 and 30°C and peak voltages between 90 and 140 V were required to give current densities of 0.5-2.4 A/dm^2. Coatings produced in this way had a very high abrasion resistance and were considered suitable for architectural or hard anodizing applications.

Anodizing in alkaline electrolytes

Comparatively little work has been done on the use of high pH electrolytes for the formation of porous anodic coatings. Bogoyavlenskiy[255] investigated the corrosion resistance of films produced on clad Duralumin in 15% sodium carbonate using a.c., d.c., and pulsating and fluctuating current. He concluded that the best films were formed at less than 100 volts but that their protective value was inferior to that of coatings formed in sulphuric acid. Subsequently Bogoyavlenskiy[256] determined the optimum temperature and concentration for anodizing in carbonate and found that the best results were produced in 5% Na_2CO_3 at 30°C in 25-30 minutes at 0.5 A/dm^2 with a voltage of 110-105. The coatings were matt in appearance and their corrosion resistance was not inferior to sulphuric acid coatings. Corrosion resistance in these tests was determined by the time taken for a drop of acid reagent, containing K_2CrO_7 3 g, HCl (d. 1.16) 25 ml, H_2O 75 ml, to turn green.

TABLE 7-24

Properties of hard, thick coatings obtained in mixed acid systems[251]

Electrolyte	*Thickness of coating (μm)*	*Specific abrasion resistance. (g SiC/μm)*
8% Sulphuric	25-35	2.0
9% Oxalic acid dihydrate	25-35	3.75
10% Malonic	25-35	6.6
10% Malonic + 0.2% oxalic	25-35	5.25
10% Malonic + 0.6% oxalic	25-35	5.0
6% Tartaric + 1.5% oxalic	20	7.5
5% Citric + 1.5% oxalic	25	6.9
5% Itaconic + 1.5% oxalic	25	6.9
5% Maleic + 1.5% oxalic	27	8.1
5% Malic + 1.5% oxalic	25	7.45
5% D.G.A. + 1.5% oxalic	25	7.25
5% Thiomalic + 1.5% oxalic	25	7.6
5% Tartaric + 0.3% oxalic	20	6.75
5% Citric + 0.3% oxalic	15	8.3
5% D.G.A. + 1.2% oxalic	30	10.5

Neufeld and Ali[257,258] have reported on the formation of thick porous coatings in electrolytes containing borax at pH 9-11. By operating in the range of 60-80°C they obtained coatings on 99.5% aluminium which did not differ radically in sealing, corrosion or abrasion resistance from conventional films formed in sulphuric acid. The typical electrolyte contained 5% borax at pH 10, used at 70°C and 10-50 volts. At less than 20 volts the films were similar in appearance to sulphuric acid films, but above 20 volts they resembled chromic acid films. It appears practicable to form coatings up to about 15 μm which might find some useful application, but probably not for architectural work, and results on copper-containing alloys were not at all promising. These authors also used 5% solutions of sodium carbonate, sodium silicate, sodium citrate, and potassium-sodium tartrate but in no case were they able to produce similar thick porous coatings. The same authors have examined the effects of anions in alkaline electrolytes on anodic film structure.[259] They concluded that, at elevated temperatures, film growth beyond the normal barrier layer thickness and development of a well-defined pore structure was not

TABLE 7-25

Mixed Solvent Electrolytes[254]

ml Solvent	ml Water	ml H_2SO_4	Per Cent of Sulphuric Acid On Solvent	On Water	On Total Solvent	Voltage Range	Remarks and Appearance of Test Piece
Cellosolve							
800	15	80	10	340	9.5	60	Brown deposit. Smells. Pitting.
800	64	80	10	82	9.0	30-38	Pitted and profiled, no coating.
800	120	80	10	66	8.5	less than 3	High current, pitted and profiling, no coating.
Dimethyl formamide							
500	6	11	2.2	183	2.19	89	Nonadherent yellowish coating.
500	15	11	2.2	73	2.13	80	Nonadherent yellowish coating.
500	70	11	2.2	157	1.92	69-79	Profiled bronze coating 2 mil thick (50 micron).
500	120	11	2.2	9.2	1.78	67-77	Coating appears as a feathery type of pattern. Very patchy.
500	170	11	2.2	6.5	1.64	62-61	Coating appears as a feathery type of pattern. Very patchy.
500	270	11	2.2	4.1	1.44	56	Coating appears as a feathery type of pattern. Very patchy.
500	370	11	2.2	3.0	1.24	52	Coating appears as a feathery type of pattern. Very patchy.
500	470	11	2.2	2.33	1.11	48-50	Coating appears as a feathery type of pattern. Very patchy.
500	670	11	2.2	1.64	0.98	45-50	Coating appears as a feathery type of pattern. Very patchy.
500	670	31	6.0	4.6	2.85	28	Paler colour, smoother; tendency for dilute sulphuric electrolyte 'ink blob' pattern.
500	670	51	10.1	7.8	4.68	27	Almost normal H_2SO_4 coating.
Dimethyl sulphoxide							
500	2	50	10	2500	9.8	80-90	Dark brown sticky film. decomposes in air and reacts with water.
500	15	50	10	350	9.6	90	Dark brown sticky film, decomposes in air and reacts with water.
500	30	50	10	166	9.4	75	Dark brown sticky film, decomposes in air and reacts with water.
500	45	50	10	110	9.2	75	Dark brown sticky film, decomposes in air and reacts with water.
500	150	50	10	33	7.7	50	Dark brown sticky film, decomposes in air and reacts with water.
500	300	50	10	16	6.25	45	Bronze-coloured coating.
500	400	50	10	12	5.5	38-40	Patchy, bronze coating.
500	550	50	10	9.5	4.7	32	Dilute H_2SO_4 'ink blob' type coating.

TABLE 7-25 continued

ml Solvent	ml Water	ml H_2SO_4	Per Cent of Sulphuric Acid On Solvent	On Water	On Total Solvent	Voltage Range	Remarks and Appearance of Test Piece
Formamide							
600	50	3	0.5	6.0	0.45	0-85	Current uncontrollable. Brown film which wiped off.
Sulpholane							
375	10	10	2.1	100	2.6	115-290	Profiled. Yellow grey deposit.
375	40	10	2.1	25	2.5	100-over 20	Protiled. Yellow grey deposit.
315	100	10	2.7	10	2.1	81-150	Grey coating 0.5 mil (12.5 micron). Rather patchy.
375	200	10	2.7	5	1.7	25-50	Profiled. Grey coating. Pitted.
Cellosolve							
800	75	80	10	108	9.5	205-280	Greyish-yellow coating. Some pitting.
800	175	80	10	48	8.2	120-150	Yellow coating. Typical type of oxalic film.
800	215	80	10	29	7.4	85	Yellow coating. Typical type of oxalic film.
Dimethyl formamide							
500	10	50	10	500	10	190-230	Grey coating, covered with tine pits.
500	30	50	10	166	9.8	150-235	Smooth grey coating 0.8 mil (20 microns) thick
500	60	50	10	83	9.4	110-140	Grey-bronze coating.
500	160	50	10	44	7.8	110-140	Grey-bronze coating.
500	260	50	10	20	6.6	100-130	Grey-bronze coating.
500	410	50	10	12.5	5.5	86-130	1.2 mil (30 micron) (average) coating. Bronze.
500	560	50	10	9.0	4.6	85-120	1.2 mil (30 micron) (average) coating. Bronze.
500	660	50	10	7.5	4.25	85-125	1.2 mil (30 micron) (average) coating. Bronze.
500	910	50	10	5.5	3.8	68-115	1.2 mil (30 micron) (average) coating. Bronze.
500	1160	50	10	4.3	3.0	55-177	1.2 mil (30 micron) (average) coating. Bronze.

ml Solvent	ml Water	ml H_2SO_4	Per Cent of Sulphuric Acid On Solvent	On Water	On Total Solvent	Voltage Range	Remarks and Appearance of Test Piece
Dimethyl sulphoxide							
500	10	50	10	500	10	280+	Profiled coating, somewhat burnt.
500	30	50	10	166	9.4	200+	Profiled coating, somewhat burnt.
500	50	50	10	100	9.1	170-240	Very uneven bronze-coloured coating 0.6-1.0 mil (15-25 micron) thick.
500	70	50	10	72	8.6	120-300	Bronze-grey coating 0.8-1.4 mil (20-37 micron) thick.
500	90	50	10	55	8.2	100-240	Bronze-grey coating 1.0-1.4 mil (25-37 micron) thick.
500	130	50	10	39	7.9	140-170	Bronze-grey coating 0.5-1.0 mil (12-25 micron) thick.
500	200	50	10	25	7.1	130-160	Very variable thickness. Bronze-grey coating.
500	400	50	10	12.5	5.5	85-115	Uniform bronze-coloured coating 1 mil (25 micron).
Formamide							
700	10	50	7.1	500	7.0	70-150+	Grey powdery film.
700	30	50	7.1	166	6.9	70-170	Grey powdery film.
700	80	50	7.1	63	6.4	110-265	Dark bronze 1 mil (25 micron).
700	180	50	7.1	30	5.9	110-180	Dark bronze 1 mil (25 micron).
700	380	50	7.1	13.8	4.6	110-120	Bronze coating 1 mil (25 micron).
700	580	50	7.1	8.6	4.0	100-125	Bronze coating 1 mil (25 micron).
700	780	50	7.1	6.4	3.3	105-120	Bronze coating 1 mil (25 micron).
700	1000	50	7.1	5.0	2.9	85-100	Light bronze.
Sulpholane							
600	60	60	10	100	9.9	105-115	Yellow patchy coating 1.2 mil (30 micron).
600	70	60	10	85	9.8	205-250	Yellow patchy coating 1 mil (25 micron).
600	110	60	10	55	8.4	150-160	Yellow patchy coating 1 mil (25 micron).
600	140	60	10	43	8.1	115-125	Yellow patchy coating 1 to 2 mil (25-50 micron)

uncommon, but only borate solutions supported the growth of films of a thickness comparable to commercial acid-based anodizing processes. 5% (wt) solutions of sodium tetra-borate (borax), sodium metasilicate, sodium carbonate, potassium sodium tartrate, and sodium nitrate (2%) were used at 70°C. Most electrolytes produced porous films but only borate allowed film growth of more than a few microns and only metasilicate inhibited pore formation completely. In the case of citrate solutions a transition from porous film growth to electropolishing was observed. More recent work using borax electrolytes has been patented by Aerospatiale[260] They claim a 30-70 g/l borax electrolyte used at 25-65°C and a pH of 9-11. The voltage used is 20-60 V with an anodizing time of 10-40 minutes. The benefit claimed is improved fatigue properties with anodized components.

The publication of a later work on the use of alkaline solutions in the U.S.S.R.[261] on certain pecularities of the anodic oxidation of aluminium in medium carbonate solutions seems to indicate a continuing interest in high pH solutions in that country.

Japanese workers are increasingly examining alkaline electrolytes and they report[262] the formation of anodic coatings on 99.5% aluminium by using alternating current in caustic soda solution (0.I-0.4%) to which 5-14% of sodium glycollate has been added, prepared by reduction of oxalic acid. The thickest and hardest coatings of 9.5 μm were obtained by electrolysis for 30-60 minutes at 3-6 A/dm^2 in 0.3-0.4% caustic soda containing not more than 12% sodium glycollate, and using a stainless steel counter electrode. Their colour tone was similar to that of coatings produced in sulphuric acid-oxalic acid electrolytes. When a lead counter-electrode was used under the same conditions a black coating was produced, the thickest and hardest film being obtained in 0.1% caustic soda. The depth of colour increased with the time of treatment and was due to the formation of chelate compounds by counter electrolysis of glycollic acid.

The same authors[263] also investigated a.c. treatment in 0.1 M caustic soda to which various oxidizing agents had been added – potassium permanganate, ammonium vanadate, potassium dichromate, potassium thiosulphate, hydrogen peroxide, and potassium ferricyanide (hexacyanoferrate 111). The thickest and hardest coating was obtained in 0.1 M caustic soda solution containing 0.05 M potassium permanganate. A bright black coating was obtained in the alkaline solution of 0.22 M caustic soda containing $K_3Fe(CN)_6$ and $K_2Cr_2O_7$. The optimum conditions were: pH 11-12; current density 0.8-1 A/dm^2; anodizing time 30 minutes. The corrosion resistance of this black coating was higher than that of a coating produced in sulphuric acid. Qualitative analysis showed the presence of iron, chromium and aluminium in the coating.

Later work by Yoshimura and Hirochi[264] seems to have centred on alkaline baths containing hydrogen peroxide, and sodium hydroxide, trisodium phosphate, sodium fluoride and sodium carbonate baths containing hydrogen peroxide have been studied. Relatively low coating ratios were produced (0.20-0.79), but the presence of hydrogen peroxide increased the abrasion resistance and the alkali resistance of the coatings. The addition of phosphates to the electrolytes reduced

pitting effects which otherwise occurred with some alloys, and it also reduced the decomposition of the hydrogen peroxide.[265] A typical bath contained 0.1-0.3 M NaOH and I-4% (vol) H_2O_2 and was used at temperatures of 10-20°C, voltages from 30-70 V and a current density of about 2 A/dm^2. Under these conditions films several microns in thickness could be produced and these could be electrolytically coloured to give a range of finishes using conventional nickel or tin based electrolytes.

Other Japanese workers have carried out anodizing in borax-sodium hydroxide, borax-sodium carbonate and disodium hydrogen phosphate-sodium hydroxide solutions at various pH values from 9 to 12,[266] and also in sodium phosphate solutions Containing salts such as sodium tartrate, sodium citrate, sodium gluconate, ammonium borate and ammonium sulphate.[267] More recent Japanese work[268] compared films produced in a barium hydroxide bath with those produced in sodium carbonate or sodium hydroxide baths. Additions of sodium aluminate and sodium tetraborate were added to the barium hydroxide electrolyte, and the barium hydroxide / sodium tetraborate bath was found to give the greatest film hardness and best alkali resistance. Other workers at Kinki University have used ammonium fluoride baths,[269] often containing ethylene diamine[270] or benzylamine.[271]

8. BARRIER-TYPE ELECTROLYTES

The thickness **of** the porous-type anodic oxide films obtained by the usual anodizing processes, viz., sulphuric, chromic or oxalic acid processes, may be a disadvantage in cases where the metal is very thin and would be dissolved during normal film growth. Such an example is provided by the aluminium deposits obtained by evaporation in high vacuum[272] and commonly used for reflectors in optical instruments as well as in car headlamps, electric torches, etc. For such deposits, which are usually below 0.5 μm (0.02 mil) in thickness, solutions must be used which produce barrier-type coatings.

However by far the most important industrial application of barrier films is the one that exploits their inherent properties of being tenuously thin and at the same time withstanding very high voltages by using them as the dielectric material in electrolytic capacitors. The aluminium employed is of very high purity in the form of foil of 0.085-0.10mm gauge, and many millions of square metres are anodized annually to find their way into components, each of which contains no more than a few grammes of the metal.

Barrier films on aluminium have also attracted a great deal of attention from research workers because of the theoretical problems which they pose as a member of the group of valve metals, and many studies, some of which have been referred to in Chapter 6, have investigated the coating formation, properties and structure of the oxide, ion transport mechanisms, electronic current, electroluminescence, and dependence of the residual leakage current upon electric field.

Ammonium tartrate solutions

The most commonly-used barrier type electrolytes for protective purposes are ammonium tartrate and boric acid solutions. The former have been employed with success by Holland and Sutherland in England[273] and by Hass and Scott[274] in the U.S.A.

Holland and Sutherland[273] used a solution containing *3%* ammonium tartrate at pH *5.5* for protecting aluminium coatings produced in the production of mirrors by vacuum evaporation. Aluminium cathodes were used in the form of very thin films as the aluminium deposits were themselves only 1-10 mil *(25-250* μm) thick. In the solution given, the film thickness was increased by 1.3 nm per volt **applied** and in measuring the reflectivity at various film thicknesses at a number of wavelengths, the most achromatic mirror over the widest range of incident angles was shown to be obtained with anodic oxide films 140 nm thick, which also gave good abrasion resistance.

The arrangement used by Hass and Scott is shown in Fig. *7-52.* The solution used is similar to that employed by Holland and Sutherland and contains *3%* tartaric acid plus ammonium hydroxide to bring the pH to *5.0-5.5.*

The evaporated aluminium surface is anodized using an aluminium cathode. The starting current is approximately *20* amp/sq ft *(2* A/dm^2) which decreases to a few milliamps/sq ft in approximately 1 minute, after which the film virtually ceases to grow. By this method films up to approximately 500 nm (0.5 μm) thick can be obtained. However, the film thickness depends on the voltage as is shown in Fig. *7-53.*

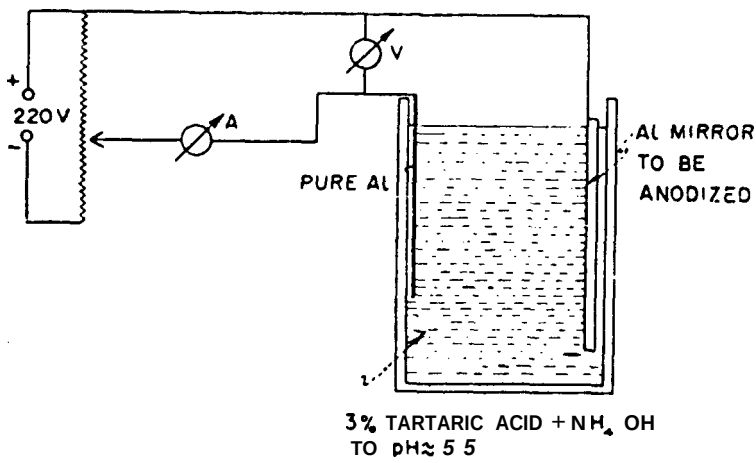


Fig. 7-52. Arrangement for anodizing vacuum-deposited aluminium film (Hass and Scott"')

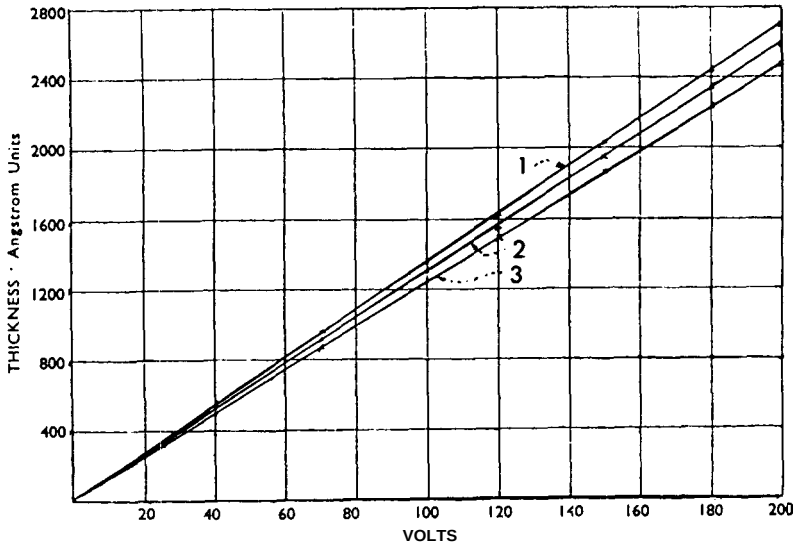


Fig. 7-53. Film thickness-voltage relation for barrier-type coatings[274])
1. 15 min anodizing t = 1.35 nm/V. 2. 2 min anodizing t = 1.30 nm/V.
3. 30 sec anodizing t = 1.22 nm/V.
1 nm = 10^{-3} mm

Films of 1.2-1.3 nm/V were obtained, which compares very well with a theoretical maximum of 1.4 nm/V when the solvent action of the electrolyte on the oxide is nil.

In practice, anodizing of the aluminium mirror[275] submits the film to a severe test and weakly-adherent films are removed from the glass on immersion in the electrolyte. The technique, therefore, requires a high degree of control and the aluminium coating must be free from impurities which otherwise cause pin-holing. The reflectivity of the anodized mirror is shown in Fig. 7-54 as a function of the coating thickness and wavelength.

As is seen, it by no means follows that the thicker the film the lower the reflectivity, as the interference maximum and minimum shift to longer wavelengths with increasing film thickness. In fact, the best reflectivity in the visible range is obtained at approximately 120 volts for 2 minutes giving a coating thickness of 156 nm. The infra-red and ultra-violet reflectivity are practically equal to that of unprotected aluminium.

Hass and Bradford[276] applied combinations of aluminium oxide and titanium oxide films and found that, provided each was approximately the thickness of a quarter of the wavelength of light, the visible reflectivity of the evaporated aluminium deposit could be increased by 5%. To produce such a coating, the titanium oxide is evaporated on to the aluminium. This first decreases the reflectivity

by producing a strongly light-absorbing oxide of formula (TiO_x) which is anodized in a 3% ammonium tartrate solution to the non-absorbing TiO_2. Part of the aluminium is oxidized to Al_2O_3 underneath the titanium oxide. The voltage used is *75* V and the finished coating has good protective properties. Much work has been carried out on a variety of valve metals deposited on aluminium surfaces[277,278] as these are of interest in electronic applications.

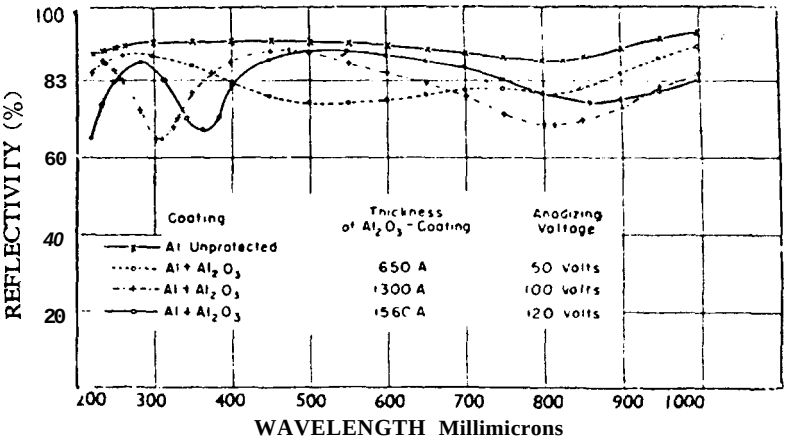


Fig. 7-54. Reflectivity of barrier-type coatings'"

Boric acid solutions

Similar results to those of Hass and Scott were obtained by Vasicek[279] who used a saturated boric acid solution for anodizing at 50 volts, and by Altenpohl[280] who obtained coatings approximately *0.67* μm thick, with good properties, by anodizing in a solution of

boric acid	10% (wt)
borax	0.1%

at 80-100°C at 500 volts for *35* minutes. Improved results were obtained by interrupting the current after 20 and *30* minutes for 1 minute in order to allow gas to escape.

The abrasion resistance of such coatings is stated to be very good. They cannot be damaged by strong rubbing with rough linen and are resistant to scratching by most metals. On the other hand they are sensitive to boiling water and salt spray.

It is of incidental interest to observe that a thin but highly protective coating can also be obtained by boiling aluminium for 20 hours in distilled water,[281,282] a

process which cannot, however, be applied economically in practice. Of possible practical interest is the thickening of the barrier-type coating under the normal sulphuric acid anodic coating by, e.g., boric acid anodizing in order to obtain a further improvement in corrosion resistance. Boeing[283] have used a sulphuric acid /boric acid electrolyte to produce thin anodic coatings as an alternative to chromic acid anodizing.

With the development of thick, protective vacuum evaporated aluminium coatings both in the U.S.A. and in Gt. Britain, it may be possible to confer the advantages of anodized aluminium coatings to steel or other metals.

Silicon oxide films

As an alternative to the use of anodizing in the applications, a thin layer of silicon monoxide (SiO) may be evaporated on to the aluminium to a thickness of approximately 150 nm, giving excellent heat resistance at a reflectivity only approximately 1% below that of unprotected aluminium. Such films are frequently heated to 200°C or above to counteract brittleness due to internal stress.[284]. Again the wear resistance is very good and the resistance to salt spray and boiling water even somewhat better than that of anodized coatings. Silicon dioxide films are also used in Germany.[285]

Electrolytic capacitors

The anode material in electrolytic capacitors is generally 99.99% purity aluminium foil of 85-100 μm gauge; formerly (and occasionally now) the purity is 99.8%. The electrolyte is a boric acid solution buffered to a near neutral pH with sodium or ammonium borate, the composition used depending on the working voltage and function of the final component.

During anodizing to form the barrier film, when the selected voltage, which may be anything from 3-650, is reached the current falls rapidly as the insulating layer is built up (see page 333) and tails off exponentially to a prolonged decline over a period of days until the final steady leakage current is reached, which will be no more than a few microamps per cm^2, most of which is assumed to be electronic with no further influence on film formation.

A capacitor consists of two parallel metal plates separated by a dielectric or insulating layer, the: electrical capacity of the system in absolute units being $C = KA/4\pi D$, where A is the area, K the dielectric constant or permittivity of the insulator, and D the distance separating the plates. In the case of an electrolytic capacitor, D becomes the thickness of the anodized layer, while the aluminium anode constitutes one plate and the electrolyte the second, although there must of course be a cathode plate in order to make electrical contact. There are several reasons for the extremely high capacities which can be obtained with electrolytics. Firstly, at only 14 Å (1.4 nm) per volt, which makes a 500 volt coating 0.7 μm

thick, the thickness is nearly two orders less than any alternative paper or plastic insulation would have to be to withstand the same voltage, and when it comes to low voltage operation the values of D are so low that they could not be produced by any other means. Since D is in the denominator, the capacity can become very large indeed. Secondly, the aluminium oxide coating is favoured with a very high dielectric constant in the 8-10 region, which provides a further substantial advantage. Thirdly, by etching the anode it is possible to multiply the capacity by a further factor of 10 or so. The result is that an electrolytic capacitor can be microscopic compared with the size and weight that its equivalent would need to be if made with paper or plastic insulation.

Electrolytic capacitors were first introduced in the early 1930s and the original wet electrolytics comprised a lead or aluminium can containing the aqueous electrolyte plus the loosely coiled anode foil and a seal to keep the solution in place. The natural self-healing properties of this miniature anodizing bath ensured a quite remarkably reliable performance from these components. The so-called dry types were introduced some years later, and here the electrolyte was a viscous solution of boric acid in glycerol or ethylene glycol, and the construction method was to sandwich a strip of porous paper soaked in the electrolyte between the anode and an auxiliary plain cathode foil; this ensemble was rolled up and potted in a metal can or cardboard tube, with, of course, external connections. Manufacture of such capacitors has been described by Jackson[286,287] Morley[288,289] and Bernard.[290]

The use of etched anodes was introduced about 1945. The etching procedure in sodium chloride has been described on page 194. The original four- or five-fold increase in surface area now reaches as high as 10 for high voltage capacitors, while for the low voltage types now common in transistorised circuits the increase in surface area can be much more than this. Thus, about 30% of the foil weight is removed, with a tremendous advantage which helped not a little in putting men on the moon.

In practical units, with **A** = area in cm^2, D = 14 Å per volt and K = 8, the capacity C in tnicrofarads = $\frac{5.05A}{V}$. During the formation of an anode foil, C is therefore proportional to 1/V, which means that for 10 volts formation the capacity is 50 times greater than for 500 volts. It is of obvious advantage then to use the lowest formation voltage consistent with the application. In its present day low voltage circuitry, capacitors of enormous value can be of really miniature dimensions. In 1969 the 1 Farad capacitor (1,000,000 μF) was announced by Nitsuko in Japan.[291]

The penalties that must be paid when using electrolytics are:

(a) The component is polarised and it is important to connect it the right way round and to maintain a voltage on it.
(b) There is a small but continuous residual leakage current.
(c) The stated working voltage must not be exceeded.
(d) It is subject to an initial surge when switching on since the dielectric layer must be reformed after a period of idleness.

(e) There is slow deterioration when not in use which imposes a heavier load on power supplies during the recovery period after switching on.
(f) The shelf life is limited to approximately two years after which it is no longer safe to use the component.
(g) It must be manufactured from very high purity material under clinical conditions.

None of these factors has prevented electrolytic capacitors from being used by the million. Originally 99.8% foil was used exclusively, but 99.99% was introduced about 1950 and has now almost completely displaced the lower purity foil except in countries where import restrictions rule otherwise. Leakage currents are thereby reduced to about one third of their value with 99.8% anodes, the recovery times are much improved, and the shelf life extended to two or three times as long. More recently the deliberate addition of trace quantities of specific elements to high purity foils has been claimed to give improved capacitor foil. Thus additions of In or Cd,[292] Pb or Bi,[293] Ga,[294] Ti,[295] Ti plus B,[296] V,[297] Cu,[298] Cu + Sn,[299] Mn[300] Cr[301] and Ca[302] have all been described.

It is the usual practice to do the preliminary forming of foil in a continuous process using hot electrolyte of about 10% boric acid at 95-100°C and with a high current density. The foil is in fact introduced into the solution with the full voltage applied and the speed adjusted to keep the current within the limitations of the equipment. The final forming and ageing of the wound and impregnated component may take up to three weeks at about 10% above the registered working voltage.

The non-aqueous electrolyte used in the capacitor requires careful preparation since glycol and boric acid form an ester, with water as one of the reaction products, and it is necessary to reduce the water content to a lower value by prolonged boiling until the boiling point has reached a predetermined value. Cracks in the thin film produced during assembly of the capacitor are sealed by oxide formed during use by virtue of the presence of electrolyte in the capacitor."' The boric acid is a special quality (SO) grade prepared by recrystallization three times,[304] and water of very high purity must be used for the aqueous electrolyte. It has been shown by Church that the effect of chloride can be detected down to 1 part in 100 million.[305] His method was to examine the dry rims by evaporating a thin layer of aluminium on to the oxide and to count the number of breakdowns at weak spots as the voltage was progressively raised, each spot becoming isolated as a result of arcing. Fig. 7-55 indicates the fault density/voltage characteristics with barrier-type films formed to 750 V in aqueous electrolyte with chloride at two levels, both very low. The effect of chlorides in the forming electrolyte has also been investigated by Sharp and Panitz[306] and Nadkarni *et al.*[307]

Increased demands from electronic component manufacturers have meant changes in the working electrolyte, and the glycol-borate mixture has now been replaced by electrolytes based on dimethyl formamide (DMF) as solvent. This material extends the temperature range of the capacitors to -55°C to +I 25°C, which allows applications which are impossible for glycol-borate electrolytes.

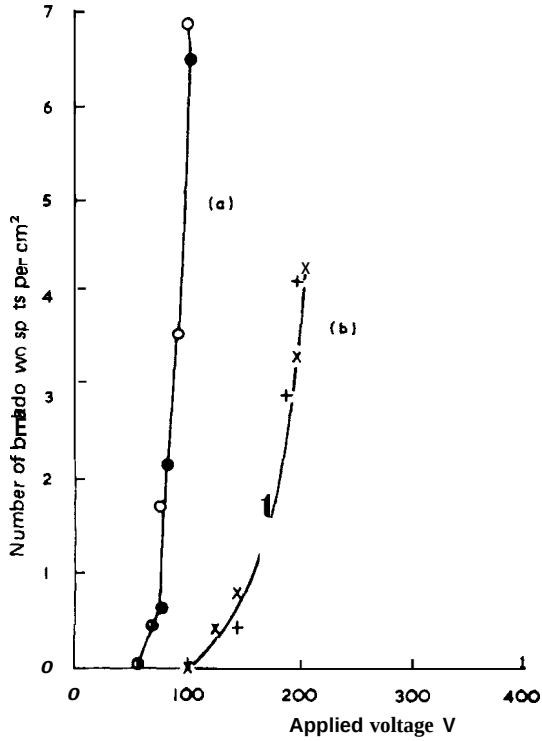


Fig. 7-55. Number of breakdowns as a function of applied voltage (evaporated electrode negative). Dependence on electrolyte purity and mode of formation (dry air at 25°C)[305]

(a) o, • Boric acid film, chloride content = 0.05 ppm
(b) **x,** + Boric acid film, chloride content < 0.01 ppm

The selection of a suitable electrolyte mixture has given rise to many patents, and mixtures of DMF with compounds such as adipic acid, trifluoroacetic acid, maleic acid, salicylic acid, citric acid, tartaric acid and formic acid have been proposed.[290] In all cases they must dissolve to give conducting solutions and have at least a limited ability to form barrier oxides when dielectric repair is needed, as well as withstanding the high fields that are imposed on the electrolyte.

More complex methods of forming the barrier layer itself have also been developed to overcome its limitations. These involve the initial production of a hydrous oxide, often formed by placing the foil in boiling water, followed by conventional boric acid anodizing.[308,309] The composite film formed consists of a layer of pseudoboehmite at the outer surface, which becomes dehydrated during

the anodizing step, and is incorporated into the conventional barrier film beneath. Such composite films, which are said to increase the capacitance of the foil, have been studied by Alwitt and Bernard[310] and Kudo and Alwitt,[311] and they confirm the dehydration of pseudoboehniite to alumina. However they also find that these composite oxides 'contain voids[311] which may occupy as much as 5% of the barrier film volume. The voids lead to electrical instability which can result in a serious reduction of the ability of the dielectric film to sustain a high electric field, but it can be corrected by brief treatment of the freshly anodized foil in hot distilled water followed by re-anodizing at the original voltage. The reaction of the water with the oxide greatly accelerates the complete relaxation of the dielectric and re-anodizing results in a stable oxide. This process has been described by Bernard and Russell[312] and is shown in Fig. 7-56.

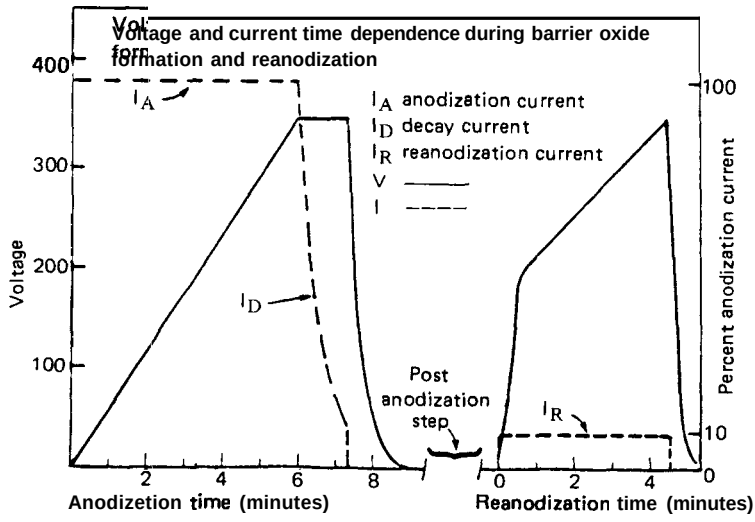


Fig. 7-56. Voltage and current-time curves for barrier oxide formation on aluminium foil. The reanodization voltage-time curve was obtained after a 5 min barrier postboil. These curves are typical of the results obtained with both polished and etched foils[312]

The aluminium is coated with a hydrous oxide layer by immersion for a short period (typically 5-10 min) in boiling water and is then anodized at several hundred volts in an aqueous borate electrolyte. If the anode foil is held at constant potential (V,) for several minutes, the current (I_D) decays to a small fraction of the anodizing current (I_A), showing the normal behaviour of a stable anodic oxide.

However, if the foil is then removed from the electrolyte, treated in boiling water for say 2 min, and returned to the anodizing cell with the application of the same current (I_D) that was measured at the termination of the oxide formation step, it will display an initial barrier voltage close to zero. A substantial passage of charge, of the order of a few per cent of the anodizing charge, will then be required in order for the anode to sustain the original anodizing voltage. Dyer and Alwitt[313,314,315] examining similar effects conclude that the electrical instability of composite oxide films is an intrinsic property of the film that arises from the presence of internal voids into which water can diffuse when the formation field is removed. Subsequent re-anodizing fills the voids with barrier oxide and stabilises the film.

Besides the use of water, it has been suggested that suitable hydrous layers **can** be produced in a hot dilute boric acid/borax mixture at pH 5.5-7,[316] or by first treating in water and then in a boiling aqueous solution of a phosphate, silicate or tartrate.[317]

Films in borate electrolytes contain some borate absorbed from the electrolyte, the proportion depending on the method of anodizing, but it is in the region of 0.6-2% B_2O_3 (corresponding to 1.6-6% $AlBO_3$) for films formed at 500 volts.[304] It is now also known that the films do not possess the perfect uniformity in thickness and structure that they were once believed to have. Research has indicated a more complex structure especially at the higher formation voltages where three forms of alumina have been identified: (1) anhydrous amorphous alumina, i.e., with crystallite size less than 10 Å constituting the bulk of the film; (2) hydrated amorphous alumina occurring as a layer at the oxide-electrolyte interface; and (3) crystalline alumina of small crystallite size occurring in agglomerates as columns of amorphous oxide readily soluble in a chromic/phosphoric acid mixture at 80°C.[318] The crystalline columns appear to be associated with points of weakness in the anodic coating where some form of electrical breakdown is incipient. The distribution of the anion is also not uniform and has been indicated in Chapter 6 but in every case the anion containing layer is in the outer part of the film and an anion-free layer, consisting of relatively pure oxide, is retained at the aluminium/oxide interface.[319] The thickness of this layer is dominated by the anion which was present in the anodizing electrolyte.

The anodic coating thickness is controlled fairly precisely at 12-15Å per volt, or 0.7 μm at 500 volts. The capacity is inversely proportional to the forming voltage (or film thickness) and is about 0.015 μF at 500 volts, 0.15 μF at 5 volts, and pro rata.

The dielectric strength varies with film thickness from 11.0×10^6 volt/cm at 100 Å[320] to 3.5×10^6 volt/cm with thicker films.[321]

Lomer has given the following values for dielectric strength:[322]

13.4	Å	11.0×10^6 volt/cm
195	Å	9.9×10^6 volt/cm
580	Å	7.5×10^6 volt/cm
830	Å	6.3×10^6 volt/cm
1540	Å	5.2×10^6 volt/cm

The dielectric constant of films formed in ammonium pentaborate, according to Bernard and Cook,[303] is 8.4± 0.2; Harkness and Young[323] give the value for thin films formed in aqueous borate solutions as 9.8 ± 0.5. The latter also give the refractive index of the coatings at a wavelength of 5900 Å as 1.57-1.58 which is very close to the value of near 1.60 accepted for porous anodic coatings. Haas[324] has quoted a value of 1.64 at 5000 Å.

The steady state ionic current density through the oxide agrees with the formula:[323]

$$I = \frac{I_{o}e\,(W - qaE)}{kt}$$

where E is the field strength, q the valence charge 3e, and I_o, W and a are respectively 2.24×10^7 A/cm², 1.3 eV, and 2.95 Å.

Alternative electrolytes mentioned in connection with electrolytic capacitors have been an aqueous alkaline biphthalate bath, 0.1-5%, suitable for use with anodes made from sintered aluminium powder;[325] a solvent of dimethyl formamide or homologues containing picric acid and/or alkaline picrate;[326] and an electrolyte suitable for use at either low or high temperatures consisting of a bicarboxylic acid, e.g., adipic acid, phosphoric acid and/or a phosphate.[327] Other electrolytes include a non-aqueous ethylene glycol, ammonium pentaborate, ortho-phosphate electrolyte,[328] boric acid containing a hydroxycarboxylic acid,[329] and a mixture of citric acid, ammonia and phosphoric acid.""

It has also been proposed to dispense with an electrolyte and use a gas plasma of oxygen ions for forming an oxide coating.[331,332] Using a low pressure gas plasma Tibol and Hull[333] ,anodized films of aluminium evaporated onto glass, forming 22 Å per volt at low voltages and less at over 50 volts. Using aluminium counter-electrodes the capacitors were almost entirely free from pinholes or other faults, and had very low, nearly non-polar leakage currents. Operated at 20 volts and 150°C the life perfformance was excellent. Miles and Smith[334] also found plasma films to be robust, stable and to obey predictions based on a simple electron tunnelling theory. These authors also carried out solid state anodizing in contact with tin which had oxygen dissolved in it.

The field strengths in the oxide during plasma anodizing have been compared with conventional anodizing by Olive, Pulfrey and Yound,[335] and Ramasubramanian[336] has studied the effects of specimen size, configuration and forming voltage during plasma anodizing.

As an alternative to anodizing, aluminium oxide films of very similar electrical properties have been applied to aluminium capacitor electrodes by evaporation of aluminium in oxygen at a partial pressure of 10^{-3} mm Hg. Da Silva and White[337] believe that a suboxide is first formed (possibly AlO), but that after exposure to air, the: evaporated oxide film is similar in composition to an anodic coating, and values obtained for the dielectric constant appear to bear out this conclusion.

Maddocks and Thun[338] have evaporated a number of other films for capacitor application including silicon monoxide and dioxide, magnesium, lanthanum and certain fluorides, cerium dioxide and zinc sulphide. Haas[339] has published a study of the use of SiO_2 as a dielectric, and the use of aluminium fluoride has been the subject of a patent.[340,341] The aluminium may be reacted with HF vapour at 520°C[340] or be anodized in pyridine fluorohydrate in pyridine.[341]

A.C. boric acid process

An a.c. process for producing barrier films for electrolytic condensers has been used in the U.S.S.R. Both two- and three-phase circuits are stated to be practicable. In the former, anodizing tanks are used arranged as shown in Fig. 7-57. Each pair of tanks forms one anodizing unit. *If* the composition of the two solutions is identical, the voltage in the first tank will be less than in the second due to the lower resistance of the bare foil passing into the first tank. Three solution compositions have been used containing 100, 50 and 30 g/l boric acid with 0.5, 0.25 and 0.05 g/l borax respectively, and they are operated at voltages up to 550, 550-650 and 650-800 volts at temperatures between 89 and 95°C.

The tank material is important as it must not be attacked during the anodic phase, and a stainless steel containing 1.1% carbon, 18% chromium, 9% nickel and 1% titanium has proved most suitable. **A** three-phase system is also in use and is shown in Fig. 7-58.

For low temperature operation of the capacitor, at which boric acid electrolytes become viscous and less conductive, ethylene glycol has been added but this causes rapid deterioration at higher temperatures. Similarly, the electrolytic capacitor is not suitable for operation at temperatures above about 85°C.

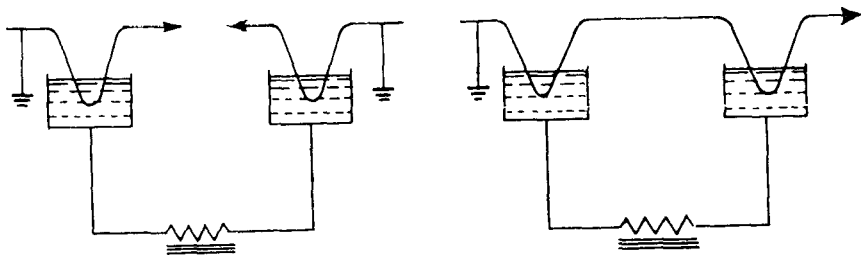


Fig. 7-57. Circuit diagrams of two-phase continuous foil anodizing plants

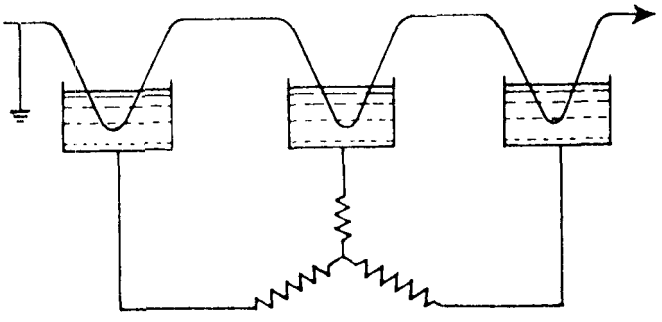


Fig. 7-58. Circuit diagram for three anodizing tanks used in three-phase foil anodizing

Solid state electrolytics

For dry capacitors, which will work at a wider temperature range, it is necessary to apply a more stable oxide film as, in the absence of electrolyte, the film is not self-healing. For this purpose Wilson reports[342,343] that the combination of oxalic acid anodizing followed by boric acid anodizing has given good results. Cleaning is important and, for the achievement of a smooth clean surface, it was found necessary to clean in hot concentrated hydrogen peroxide solution. The electrolyte must be made up with very pure chemicals. **A** Japanese patent suggests a first electrolyte of adipic acid and ammonia, followed by anodizing in phosphoric acid and ammonia.[344]

By using this technique, oxide of much greater insulation resistance has been obtained which is also less sensitive to moisture. For the production of the dry capacitor, the second electrode, which must be in intimate contact with the oxide, is a thin layer of vacuum deposited aluminium.

There would be considerable advantage in dispensing with a liquid electrolyte since most of the difficulties with electrolytic capacitors arise from drying out, freezing, evaporating or corrosion by the electrolyte. Dry capacitors have been made by evaporating aluminium onto the oxidized foil as a counter-electrode; points of short circuit can be cleared by applying a voltage which evaporates the aluminium in their vicinity, but better results have been obtained at some sacrifice in capacity by first adding a very thin supporting layer of a resin from a dilute solution. The successful system in recent years however has been to employ a solid electrolyte of manganese dioxide in some form. Post has described the preparation, construction and characteristics of these capacitors,[345] in particular the 35-40 volt range prepared from foil pre-anodized to 110 volts, as also has

Morley.[289] In the 1960's Mullard Ltd.[346] marketed a range of solid electrolytics from 12 μF, 40 V d.c. to 100 μF, 4 V d.c. which could operate at from –80 to +85°C and were stated to have improved impedance characteristics at high frequencies and better electrical stability during their service life than the equivalent conventional types.

The manganese dioxide can be applied by wetting the anodized foil with manganese nitrate, vacuum drying and heating in several cycles;[347] applied from a solution in isopropyl alcohol at 70°C and decomposing by pyrolysis;[348] or by using an aqueous manganese carbonate suspension followed by an aqueous manganese nitrate solution and heating to 300-400°C.

Miscellaneous organic barrier film electrolytes

Like many other organic electrolytes, malic, glycollic and citric acids produce barrier-type films[138] and require voltages of 300-500 for continuing film formation. Another requirement is a low chloride content (less than 20 mg/l) to avoid pitting. In the presence of 2.5% sulphuric acid, a porous film is formed with fair hardness and dye absorption properties."'

Wood and Patrick[349] have studied a boric acid-formamide electrolyte containing small additions of water, by means of electrochemical, a.c. impedance and metallographic techniques. In the presence of small amounts of water the formation of porous film occurs. In Japan an electrolyte containing both boric acid and oxalic anhydride has been patented,[350] and another containing holmamide and boric acid or borate.[351]

Anodizing in molten salts

A limited amount of work has been carried out on the anodizing of aluminium in molten salt solutions, particularly nitrate or nitrate salts. Early work used a low temperature melt containing, for example, 2 mol pts potassium bisulphate to 1 mol pt sodium bisulphite at 180°C.[352 353] Anodizing at 1 A/dm^2 (up to 160 V) for 30 minutes produces a white, matt anodic oxide coating, which is in fact, a highly porous and very hard corundum. The latter is not attacked by hydrofluoric, sulphuric or phosphoric acids or by caustic soda in any concentrations, nor can the film be dyed or sealed.

X-ray diffraction patterns clearly indicate the α-Al_2O_3 structure with a slight amount of γ-Al_2O_3, and its formation is believed to be due to the high local temperature produced on the anode, the absence of water and the presence of a slight amount of γ-Al_2O_3.

The high porosity of the film is indicated by its density which is 2.96 compared with 4.0 for solid α-Al_2O_3, and a hardness of 350-450 Vickers was measured under a load of 50 g.

Increase in current density reduces the current efficiency. Under the conditions stated above, a film 8.3 μm (0.33 mil) thick was grown in 30 minutes, which increased to 10.5μm (0.42 mil) in 1 hour.

The coating ratio (see page 480) of the process varies between 1.76 and 1.81, which is close to the theoretical value ($Al_2O_3/2Al$ = 1.89) and compares with approximately 1.2 for sulphuric acid anodizing.

The corundum coating is, in fact, allied to the barrier film and the porosity is due to local film breakdown caused by the high forming voltage.

Campanella and Conte[354,355,356,357,358,359] have studied the use of molten alkaline nitrates for anodizing at temperatures of 300°C. They obtained films which were very hard and compact with a non-porous structure and partially recrystallized. It was noted that the corrosion resistance in acid and alkaline solutions was superior to that of coatings produced in sulphuric acid. They measured the specific gravity, reflectivity and dielectric constant of coatings formed on 99.99% aluminium sheet at 24 volts in melts containing sodium nitrate 45, potassium nitrate 55 mols %, as well as determining the coating ratio and rate of film growth."'" In a subsequent study the coating properties were examined when lithium salts were added to the molten electrolytes,[356] followed by an examination of the electrochemical behaviour of aluminium in molten calcium nitrate tetrahydrate, $Ca(NO_3)_2.4H_2O$.[357] Ikonopisov has used molten nitrites.[360]

Lovering[361,362] has also done much work with molten nitrates and has summarised the conditions used and the benefits obtained. He suggests uses in aerospace and electronics applications and lists the potential benefits of molten salt anodizing as shown in Table 7-26.

Eutectic mixtures of salts are often chosen to minimise the melting point, and typical mixtures are 32.2% (wt) lithium nitrate ($LiNO_3$) and 67.8% (wt) potassium nitrate (melting point 133.5°C) or 44.6% (wt) lithium nitrate ($LiNO_3 \cdot 3H_2O$) and 55.4% ammonium nitrate (m.p. approx. 80°C).

TABLE 7-26

Potential advantages offered by molten salt anodizing[362]

Molten salt parameter	*Consequences*
Non-aqueous electrolyte	Anhydrous film
Elevated temperature	Faster film growth, thicker film
Highly oxidizing electrolyte	Flaw-free. coherent film
Extremely ionic electrc lytc	Good throwing power, low voltage/high anodizing ratio
High thermal inertia	Uniform, stress-free film
Low contact angle	Uniform wetting
Environmental isolation	Atmospheric contamination minimised

The types of melt which have been employed for anodizing aluminium are shown in Table 7-27.

TABLE 7-27

Types of molten salts employed for anodizing

Melt type	*Temperature range*
Single nitrate salt or nitrate mix	100-450°C
Nitrate-nitrite	110-350 °C
Aqueous nitrate	50-100 °C
Bisulphate	130-210 °C
Nitrate-organic (e.g. urea-ammonium nitrate)	45-85 °C

Constant voltage anodizing is carried out at voltages from 10 to 100 volts and Turner and Lovering[361] showed that anodizing in dry $LiNO_3$-KNO_3 melts (140°C) produced thin, uniform, barrier type films which were transparent and consisted of amorphous alumina. In melts containing low concentrations of water, two types of anodic film were formed at 140°C, depending on the anodizing voltage. Below 50 V, 2-3 micron thick, white, friable films of crystalline oxide were produced, but, at higher voltages, thin films of amorphous alumina containing many flaws were formed. The thickest, most uniform and compact films were produced by anodizing at 50 V for 30 min in molten $LiNO_3$-NH_4NO_3 containing water at 110°C, and such films can be produced at even lower temperatures (45-85°C) in a urea-ammonium nitrate melt. It is suggested that such films would reduce corrosion-fatigue in comparison with conventional films and would be suitable as a preparation for adhesive bonding in the aerospace industries. They would also have better dielectric characteristics for electronics applications than conventional films. More recently Carlin and Osteryoung[363] have studied anodizing in aluminium chloride/alkali metal chloride melts.

In more fundamental studies, workers at UMIST[364] have found that barrier type films are produced in eutectic bisulphate melts over a wide range of conditions. However at high current densities and relatively low melt temperatures, non-uniform film growth takes place and this highlights the substrate topography. In the same way as in aqueous electrolytes, both anion and cation transport contribute to growth, and species derived from the acid anion are incorporated into the film material.

'Ruby films'

An interesting development in Japan, which uses both conventional and molten salt anodizing, is the development of films which have many of the physical characteristics of synthetic rubies.[365]

The 'ruby films' are produced in a two-step anodizing process, in which high purity aluminium is first anodized for 80 min at 1.0 A/dm^2 in a 15% (vol) sulphuric acid electrolyte. Metal ions, particularly chromium ions, are then adsorbed within the film by single or double dipping treatments in a range of metal salt solutions as shown in Table 7-28. Finally the metal pigmented films are anodized to form alpha alumina films in a molten salt mixture of sodium bisulphate and ammonium bisulphate (1:1.15 mol) at 170 °C for 10 min at 1.0 A/dm^2 It can be seen from Table 7-28 that only the chromium incorporating films had a reddish violet colour and also emitted a red fluorescence, though some other metal ions gave bright or dark violet fluorescence. The use of ammonium chromate gave the best results and a 10 g/l solution used at 70°C with an immersion time of 30 min is recommended.

TABLE 7-28

Colour and fluorescence of alumina films obtained by two-step anodic oxidation[365]

	Two-step alumina films	
Adsorbed inorganic compounds	*Colour*	*Fluorescence*
Single dipping process		
$(NH_4)_2 CrO_4$	light reddish violet	deep red
$Fe_2 (C_2O_4)_3 Na_2 C_2 O_4$	yellowish light grey	dark violet
$Fe_2 (C_2O_4)_3 K_2 C_2 O_4$	grey	dark violet
$Fe_2 (C_2O_4)_3(NH_4)_2 C_2 O_4$	grey	dark violet
Alternative dipping pro-ess		
$Pb(Ac)_2 + K_2 Cr, O.$	light reddish violet	red
$K_2 Cr, O_7 + AgNO_3$	light reddish violet	red
$AgNO_3 + K_2 Cr, O_7$	light reddish violet	red
$Ni(Ac)_2 + (NH_4)_2 S$	yellowish light grey	dark violet
$CdSO_4 + (NH_4)_2 S$	light grey	bright violet
$AgNO_3 + (NH_4)_2 S$	khaki	dark violet
$Co(Ac)_2 + Na_2 S$	light grey	bright violet
$AgNO_3 + Na, S$	yellowish light grey	dark violet
$CuSO_4 + Na_3PO_4$	light grey	bright violet
$Na, PO, + Pb(Ac)_2$	light grey	bright violet
$Pb(Ac)_2 + Na, SO,$	light grey	bright violet
$Co(Ac)_2 + KMnO_4$	light grey	dark violet

The Japanese workers have shown that the visible and infra-red absorption spectra of these films are similar to those of synthetic rubies, and they believe that the colouring of the films is caused by trivalent chromium ions which replace trivalent aluminium ions in the alpha alumina structure.

Functional anodizing

The Japanese have been particularly active in developing what they call 'functional anodizing'. These developments are concerned with highly functional films with special electrical or magnetic properties, or with films used in quite different applications such as filtration membranes. Many of these developments have been summarised by Ono and Baba,[366] and by Mizuki.[367]

They describe the development of high density, vertically magnetised films for magnetic recording media, orientable liquid crystal films, electroluminescent films, use in optical devices, magnetic recording discs, microelectrodes and porous membranes. Many of these novel applications are summarised in Table 7-29 and a number of specific applications are detailed in the sections below.

TABLE 7-29

Examples of "functional" anodizing

Property	*Phenomena*	***Examples*** [368]
Electro-magnetic	Insulating properties	Hybrid IC substrates
		Planar multilayer interconnect structure of ICs [369,370,371]
		Wiring [372,373]
	Magnetic characteristics	Disc memories [374,375,376,377,378,379,380,381,382,383,384]
		Magnetic cards
	Electronic conduction	Negative resistance switching devices [385,386,387,388,389,390,391,392]
		Metal base thin film transistor
		Rectification [393]
	Photovoltage	Thin film devices [394]
Optical	Electroluminescence [395,396,397,398,399,400,401]	Surface emitting structures & displays [402,403]
	Photoluminescence [404,405,406]	Ruby films [365]
	Electrochromism [407]	Display & recording devices
		Photograph transmission
	Colouration/light absorption	Solar collectors [408,409,410,411,412]
		Radiators
		Polychromic films
	Image formation/retention	Electrophotography [413,414]
	Attenuation	Optical circuits [415]
	UV/vacuum resistance	Space applications [416,417]
Surface chemical	Lubricating properties	Lubricating films [418]
	Hydrophilic/phobic nature	Printing plates
	Catalytic power	Anodic alumina catalyst [419,420,421,422,423,424,425,426]
	Surface charge	Electret [427,428]
		Electron emission [429,430]
		Humidity sensor [431,432]

TABLE 7-29 *(continued)*

Property	*Phenomena*	*Examples*
		Ultrasonic transducers[433,434,435]
Thermal	Conductivity	Heat exchangers[436]
		IC cooling structures[437,438]
Physical	Porosity	Microfiltration membranes[439,440,441]
		Channel plates[442]
	Containment	Liquid crystals[443,444]
		Sensors[445,446,447,448,449]

Magnetic recording discs

The commercial production of rigid disc magnetic recording systems was started by IBM in 1965, and in 1968 they disclosed a method involving the deposition of a magnetic metal such as Fe, Co or Ni on the surface of, or in the pores of, a porous, anodic film.[374] The intention was to increase the recording density and produce high density, vertically magnetised films. Since then much work has been done, in Japan and elsewhere, on plated, sputtered and electrodeposited materials.

The normal manufacturing process involves initial anodizing in oxalic or sulphuric acid, followed by enlargement of the pores and adjustment of the barrier layer thickness in a second anodizing solution. Reanodizing is usually carried out at a lower voltage than the primary film forming voltage. The pores are filled with the required metal, which is electrolytically deposited, and the surface is then polished to remove any excess metal deposits. The magnetic properties, such as coercive force or magnetic anisotropy, are controlled by the pore diameter or cell diameter of the film, and these features also affect the crystal structure of the deposited metal. In terms of practical application the main problem is to prevent film defects arising from intermetallics and impurities in the aluminium metal, so very high purity based aluminium is usually used. Thus Nippon Light Metals[450] have described use of a high purity Al-4%Mg alloy, and Alcoa[451] have developed Al-Mg alloys containing small amounts of zirconium and scandium.

The NLM workers[450] pointed out that the key features of recording discs were a high quality anodic film with minimum defects and high hardness, and the maintenance of a very smooth finish. In addition the ability to withstand heating to 300-400 °C without the film cracking was necessary in many applications.

They described a process in which the high purity Al-4%Mg alloy was cut into discs which were annealed under pressure to give very flat surfaces. These were then machined to a very fine finish. The prepared discs were degreased and chromic acid anodized to a thickness of between 8 and 15 microns. They found that bath temperature was critical and had to be closely controlled, and film thickness was critical in terms of film hardness; thicknesses greater than 8 microns

were needed to obtain adequate performance but above 15 microns film hardness started to decrease. The resistance to film cracking, which proved to be up to 400°C, was attributed to the branched pores produced by chromic acid anodizing. In this case the magnetic media was plated or sputtered onto the anodized surface, and this process has been effectively used in high density recording applications in Japan for many years.

The magnetic properties of cobalt, nickel and cobalt-nickel materials deposited in the anodic coating have been extensively studied by Kawai.[452,453,454] He found that the cobalt-nickel deposits were particularly promising and gave a recording density close to that of the existing iron oxide coatings then used.

Alcoa[455] have described a method of chemically enlarging the pores of a previously produced anodic coating, preferably using a 2%(wt) chromic acid / 5%(wt) phosphoric acid solution at 32 °C. This improved the electrolytic deposition of cobalt metal into the film. A similar process was claimed by Nippon Light Metals[456] and by Kobe.[457]

In a related field, IBM[458] describe the electroless plating of nickel onto an anodized aluminium surface for the attachment of electronic chips.

Porous membranes

The use of an anodic oxide coating as a filtration membrane is one of the few applications in which the oxide is used as a separated film, but anodizing represents an ideal way to produce such a membrane. Pore size and structure are largely dependent on anodizing voltage, and the use of different electrolytes can give pores with a diameter between 10 nm and 250 nm. Pore densities of 10^{12}-$10^{15}/m^2$ can be achieved and anodic film thicknesses of over 100 microns can be produced. This then is an ideal material to be used as a porous membrane for micro-filtration purposes. However to be used in this way the film must be detached from the metal and the barrier layer dissolved.

An early Boeing patent[459] envisages the use of an oxide membrane for desalination purposes. In this development a porous anodic oxide film is first prepared by anodizing in electrolytes such as sulphuric acid, chromic acid, oxalic acid or phosphoric acid. Thin aluminium foil is used so that after anodizing little aluminium remains and, after sealing the film, this can be etched away in a solution containing a copper salt. Finally the barrier layer is removed either in this solution or in sodium hydroxide. Clearly this was quite a delicate process to carry out.

A more practical process has been described by Alcan[439,460,461] and this process, which detaches the film by a controlled voltage reduction method, is in current production. In order to obtain a very regular pore structure, high purity aluminium sheet, normally in the bright-rolled condition, is used. This material is cleaned and degreased and is then anodized in a selection of electrolytes depending on the membrane pore size to be produced. Typically sulphuric, phosphoric, chromic and oxalic acids are again used, but Alcan has found phosphoric acid anodizing to

be particularly suitable, because the high voltages achievable and the range of pore sizes thus obtained are greater than for other electrolytes. Also the film produced contains 7.5% (wt) of phosphate anion from the electrolyte. This renders the material relatively inert to aqueous environments, a desirable property for many filtration applications.

The material is anodized in a 0.4 M orthophosphoric acid electrolyte at *25°C* using a current density of 1.5 A/dm^2, a voltage of 150-160 V for a time of about 120 minutes. This gives a film about 60 microns thick with a pore diameter of 0.15 niicrons.

After production of the desired film thickness, the voltage reduction procedure is carried out to detach the film from the aluminium substrate. This procedure can either be performed in the same electrolyte as that used for anodizing or the work can be moved to another electrolyte before or during the voltage reduction procedure. Since the detachment of the film from the substrate depends on the chemical and field-assisted dissolution, the electrolyte chosen should be effective in this role. Sulphuric acid and oxalic acid have been successfully used, but again phosphoric acid is preferred. This is partly because its dissolving power for alumina means that new pore nucleation is a faster process, and also it inhibits hydration which may occur in fine: pores. Voltage reduction is controlled with a suitable data logger to monitor current and voltage. The computer is typically set to step down the voltage in increments of 0.3 V or *5%* of the existing voltage, starting with the voltage at the end of anodizing and going down to less than 0.1 V. The rate at which the voltage is reduced is determined by the rate of change of current at that particular voltage. The voltage reduction procedure is shown diagrainmatically in Fig. 7-59, together with the sort of pore structure produced.

On completion of this procedure the film remains attached by an extremely thin barrier layer, and separation is completed by immersing in a higher concentration phosphoric acid solution at room temperature. This dissolves the remaining barrier layer and generates hydrogen which lifts the film off the sheet. After rinsing the process is complete and the aluminium sheet is reused. In this way large areas of film can be separated and then cut and shaped to fit into the appropriate holder. The film is remarkably strong and handleable, and it has been shown that it can be formed after production,[462] and even profiled membranes can be produced.[463]

The membrane produced in this way has an assymetrical pore structure with the normal 0.15 micron pores over the bulk of its thickness, and a fine pore layer down to 0.02 microns on one side (Fig. 7-59).[464] This can be converted to a membrane with an overall 0.2 micron size by dissolving this fine pore layer. The benefits of the anodic film membrane are its narrow pore size distribation, its ceramic nature and its general chemical compatibility. The membranes have found rapid use in a variety of laboratory applications.

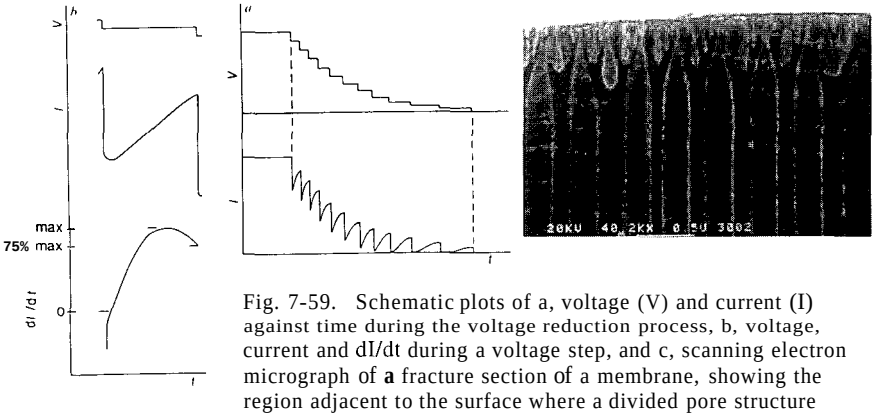


Fig. 7-59. Schematic plots of a, voltage (V) and current (I) against time during the voltage reduction process, b, voltage, current and dI/dt during a voltage step, and c, scanning electron micrograph of **a** fracture section of a membrane, showing the region adjacent to the surface where a divided pore structure replaces the original barrier layer (top). Aluminium (99.95% purity) was anodized at 160 V for 75 min in air-agitated 0.4 M H_3PO_4 at 25°C with graphite counter-electrodes to produce a film 30 μm thick. Subsequently, the voltage was stepped down from 160 to 0.1 V in decrements of 0.3 V or 5% of the existing voltage (whichever was greater). **At** each voltage step, the current fell, and then rose at a varying rate. **A** further step was effected when dI/dt had fallen to 75% of its positive maximum."'

Other miscellaneous applications

Various coatings on aluminium have been considered as solar selective coatings for solar panels. Thus Granges Aluminium[465,466] have described the use of black anodised finishes with a 1.5 micron coating, produced in a phosphoric acid electrolyte, which is then electrolytically coloured in a nickel-based electrolyte. Such a film had a solar absorptance of 0.93-0.96 and a thermal emittance of 0.10-0.20. Dornier[467] also used such films in Germany and Alcoa[468] in America, and integrally coloured coatings were studied by Sereinig and Meissner.[469] Anodizing was used as a substrate for tin oxide deposition by Roos and Georgson.[412] Many workers have also used black coloured conversion coatings on aluminium for the same purpose.[470,471,472]

Another interesting development area is the use of the optical interference finishes, described, for architectural applications, in Chapter 8, for much more functional purposes. Thus Alcan workers have proposed their use for 'tamper evident' packaging[473] and for indicators, sensors and security devices.[474] The first application, in particular, is of interest as the process used relies on great control of the anodic film structure. Optical interference effects are produced by electrolytically depositing very small amounts of metal within a film, the pores of which have usually been electrolytically enlarged at the base.[475] This process is described and illustrated on p. 719, but interference colours are produced by interference of light reflected from the metal deposit surface and from the aluminium

/ aluminium oxide interface. The degree of separation of these two surfaces controls the colour seen. It is possible to anodize beneath these deposits using a further anodizing stage, and this is used in the packaging situation to create a weak layer of film that is easily ruptured.[476] Thus if the packaging is bent or disturbed the film will break, the colour will change and the tampering will be visible.

Another new consideration for anodized products is their use in space applications. Nearly all these components are black coloured and aluminium components are usually anodized and then coated with high emittance carbon black paints. The conditions that such material has to withstand have been well summarised by Sharma *et al.*,[417] but just a few are the high temperature fluctuation, atomic oxygen erosion, outgassing from non-metallic materials and orbital debris impacts. A limitation of the high carbon paints is that they release a high percentage of condensable volatile material into the space environment, and this may condense on adjacent components and affect their performance. Various methods of black anodizing giving surfaces of high thermal emittance have therefore been evaluated. These workers found the best results with black pigmentation of a sulphuric acid anodized film in a cobalt acetate / ammonium sulphide double-dip process. Others have used black dyeing and black electrolytic colouring,[477] whilst for others the main concern has been the cracking of the oxide film under these extreme conditions.[478,479]

Whilst not a new application of anodizing, a new form of anodizing is plasma anodizing, for which various procedures have been investigated to produce anodic films for electronic devices. Thus Adama-Acquah and Swanson[480] demonstrated plasma anodizing of thin aluminium films in an oxygen environment, where the anodizing voltage increased linearly with time in a similar manner to that for barrier films. Similar work was carried out by Jaklevic[481] except that the aluminium films were overlaid by a thin metal coating, and the plasma anodizing was carried out in an oxygen or argon atmosphere with a relative humidity of 90-100%. He believed that adsorbed water diffused through the overlay to enable oxide film formation to take place. This showed a growth rate of about 1.5nm/V, similar to aqueous anodizing. In other work Matsumura[482] has described anodizing of aluminium in a microwave-discharge oxygen plasma.

9. MECHANIZATION IN ANODIZING

In continuous anodizing using automatic equipment two different types of process are to be distinguished:

(a) Continuous anodizing of wire and strip
(b) Automatic anodizing of finished products.

In both processes the sulphuric acid process has generally been used, though there is, of course, no reason why other processes should not be employed.

Anodizing wire

Early attempts to anodize wire continuously were carried out in barrier-type electrolytes and later with oxalic acid for the electrical insulation of aluminium wire, but the results were usually unsatisfactory in competition with insulated copper wire. The main difficulties are due to the high speed at which the wire is normally required to pass through the solution, requiring very high current densities to obtain coatings of adequate thickness. Thus, in an example quoted by Pullen,[483] 18 s.w.g. aluminium wire passing through a 20 ft length tank at 2,000 ft/hour would require 100 amp to give a 0.2 mil anodic coating in the 36 second treatment time (100 **A** to give a 5 μm anodic coating on 18 s.w.g. wire passing through a 6 m tank at 600 m/h). Such currents are too high to be carried by the wire using normal contacts but have been supplied by liquid contacts, in which the current is fed into the wire via the electrolyte in one bath (sometimes a specially-constructed chamber) from which the wire passes into the main tank.

A number of patents have been issued dealing with the construction of such units, in particular the electrical contacts and cooling of the solutions. Sulphuric acid is generally employed and an a.c. current may be added in some cases. In one of these,[484] wire or narrow strip is passed through an electrode chamber made of ebonite which is placed at the end of the treatment tank with its bottom cover immersed in the solution, the wire or strip being passed through via a small nozzle arrangement. The solution level in the chamber is maintained by a pump, the overflow passing into the main tank. **A** third tank is included in the plant in which the solution is cooled. When d.c. is used, the wire is made cathodic while in the entry chamber, and anodic as soon as it enters the main tank. With a.c., two electrode chambers are required, each being connected to one end of the secondary winding of the transformer, and the electrodes consist of one or more pairs of wires equally distributed between the two chambers. As mentioned previously, a.c. is often preferred to d.c. for wire as the coatings obtained are more flexible.

The dimensions of such a plant have been given by Pullen[483] as 10 ft long x 15 inches wide x 18 inches deep for the main tank (3 m x 4 dm x 4.5 dm), which is of rubber-lined steel, preceded by one or two small degreasing tanks and followed by rinse tanks. The take-up reel at the end of the sequence is provided with a variable speed drive to compensate for the continuous change in coil diameter as the wire or strip goes through. Where required, a dye bath can be included after the anodizing unit. At the currents used, which may correspond to up to 20 kW, cooling may be difficult to carry out satisfactorily in the tank itself. In consequence, a pump is normally installed which takes the solution into, e.g., an overhead cooling tank fitted with cold water coils or, where necessary, a refrigerator. **A** plant such as that described would have a capacity of 8,000-12,000 ft (2,400-3,600 m) per hour and would require about 300 amperes at 40 volts a.c. Practical experience has shown that a smaller plant is generally required where wires of diameters below 25-26 s.w.g. are to be treated.

In the type of plant described by Pullen, it has been found possible to include after-treatments such as sealing, oiling or lacquering in the main plant. Sealing, e.g., after dyeing, is carried out in this instance by immersing the finished coil in hot water for 3-4 hours followed by drying at 82°C for a similar period. Organic sealing media are best applied during reeling on to the bobbins.

A wire anodizing bath patented in France[485] contains:

sulphuric acid	20% (wt)
magnesium chloride	3.5% (wt)

and is used at up to 200 A/dm^2 (1900 amp/sq ft) with d.c. superimposed at a fifth of the a.c. current density. The use of an electrolyte containing magnesium chloride would appear to be contrary to normal practice, but it has been successfully employed in France for many years, and Reynolds[486] have also patented a sulphuric acid (30%)/oxalic acid (2.5%) mixture containing 1% sodium chloride which can be used at 40 A/dm^2. Russian studies[487] have also indicated that electrolytes containing Cl^- up to 0.5 g/l can be used for anodizing. An alternative method to providing a flexible film has been to pass the wire during anodizing over pulleys of various diameter!, and in various planes,[488] whilst Japanese workers suggest a rotating cathode to remove hydrogen from the cathode and allow anodizing at higher speeds.[489]

Applications of anodized wire

Still among the primary applications for anodized wire is electrical windings. Wire treated by the plant described above has stood up to 150 volts r.m.s. without failure, and where two such wires are twisted together according to the standard procedure and the voltage applied to the two free ends, 275 volts can be reached before failure occurs. In practice these figures are often exceeded by 50%. The main advantage of such wires is their high temperature resistance compared to organic insulated wires. On wireless-type transformers wound with anodized wire, no failures were obtained using a load of twice the normal rating for 14 months at 250°C average temperature. On the other hand, such wire is difficult to join. 'Electrical' purity (high conductivity) wire may be obtained, and, for other purposes, alloys of which the AI-Mg alloys (0.5-1.0% Mg) are perhaps the most suitable.

One outlet for anodized wire was in the decorative and domestic field and, in particular, for the production of woven wirecloth. These were woven from wire anodized in one or in several colours. A limitation was that the dyeing time allowed was very short (e.g., 3 seconds) and only pale colours could normally be obtained. This application was discontinued in about 1953.

Side fasteners on fibre tapes can also be anodized in an apparatus in which the fastener is driven over a rail.[490]

Anodizing sheet and strip

The potential advantages of continuously anodizing strip are that the process can be carried out cheaply on a large quantity of material, from which components can if necessary be formed by subsequent operations, and typical applications include lithographic plates, nameplates, decorative trim, double glazing spacers, lorry siding and roofing, architectural cladding, lighting reflectors, ceiling panels and transformer windings. Production of coil anodized material is increasing steadily and a market of more than 50,000 tonnes/year is estimated for the U.S. alone.[491] In Europe the continuous architectural line at Coil Anodizing in Belgium (Fig. 7-60) has a market of more than 10,000 tonnes per year,[492] and more than 40,000 tonnes per year of lithographic sheet is produced. Equally plants in Germany produce more than 14,000 tonnes per year of pre-anodized strip, mainly for lighting reflectors.[493] Most coil anodized material is produced at relatively low gauges, less than 0.5 mm (20 mil), but some plants are now capable of producing material up to 3 mm (120 mil) in thickness for architectural applications.[494] Equally most coil anodizing is designed to give relatively low anodic coating thicknesses, 5 μm (0.2 mil) or less, but coatings up to 25 microns (1 mil) can be produced on some lines. Continuously anodized strip can withstand moderate forming operations, including shallow drawing,[495] and is very suitable for decorative applications, but the very fine cracking of the film which occurs with thicker anodic coatings can be a limitation in corrosive environments. However 10 year exposure tests on bent specimens from the Coil Anodizing line are said to suffer no signs of corrosion.[492] Crazing is visible when bending to a 4 mm to 6 mm radius, but no serious corrosion has been detected. Such material is being sold by many of the European aluminium companies, and architectural applications have been described by Pechiney[496] and by Maxwell.[497]

In the early developments of continuous anodizing, line operating speeds were very slow (typically 2-3 m/min (6-9 ft/min)) and this was both a limitation and an advantage, as colouring, sealing or lacquering treatments could be carried out in the same line without too much difficulty. In a Norwegian plant of this type, many hundreds of tons of strip were anodized each year, mainly for aluminium food containers, and with the reservations given above, it was found that a thin coating approximately 0.06 mil (1.5 μm) thick could be produced in 10% w/v sulphuric acid using 14 amp/sq ft (1.5 A/dm^2), 15-20 volts d.c., 21-27 °C, and was sufficiently flexible to withstand forming.

Fig. 7-61 shows the sequence employed in such a strip anodizing plant which was used to produce material for the fish canning industry.[80,498]

In a different sequence also used in Norway, the anodized, rinsed and dried strip was lacquered by roller coating and baked in one cycle. In this 'lacquer sealing' sequence, cleaning of the strip was not as important as when lacquer was applied to the bare metal and could be omitted if a small amount of methyl cellulose was added to the sulphuric acid electrolyte as a wetting agent.[80]

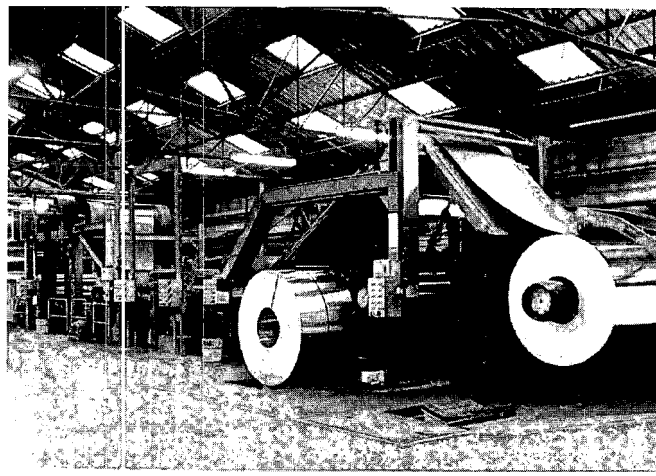


Fig. 7-60. Continuous Anodizing Line at Coil **SA,** Landen, Belgium

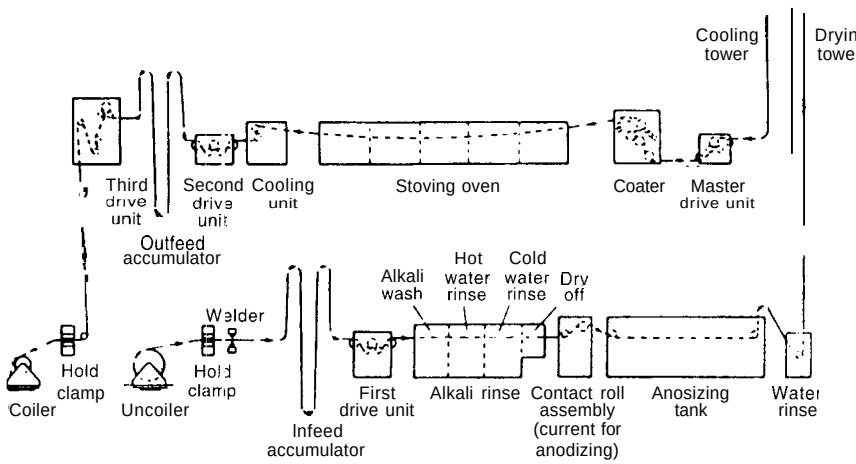


Fig. 7-61. Sequence of a Norwegian strip anodizing plant[80,498]

1 uncoil	7 sulphuric acid anodize
2 strip connection	8 rinse
3 clean	9 seal
4 rinse	10 dry
5 dry	11 rollers
6 current connection	12 coil

A similar continuous anodizing and lacquering line for aluminium strip used in the canning industry[499] was built at Alcan Industries Ltd., Rogerstone, and it was operated at a speed of 30 m/min (100 ft/min), with anodizing carried out at 12-24 V in a 15% (wt) sulphuric acid solution to give a coating thickness of about 0.3 μm

(0.013mil). Excessive drag-out was prevented by passing the strip through squeeze rolls at the end of the anodizing tank, after which the strip was rinsed, dried in hot air and air cooled, before lacquering, on one or both sides, and stoving.

More recently this type of line has been replaced by the hot electrolytic cleaning treatments already described in Chapter 4 (Fig. 4-2), as these processes can be carried out at very high strip speeds (up to 450 m/min (1400 ft/min)).

Part of the speed limitation with the early lines was the need for a contact roll to introduce current to the strip. Whilst such contact rolls are still used with some lines, they can lead to arcing problems, particularly with thin strip. In addition the current carrying capacity of the strip itself is relatively low when it is in air, so current densities which could be used were limited.

Some of the speed limitations in the continuous anodizing of strip to produce thicker anodic coatings were removed in the Lloyd process operated by International Anodizing Ltd. in Chicago.[500,501] In this the moving aluminium strip moves over a flat bed of graphite blocks connected to the power source, and is held in intimate contact with it by suction. Only one side of the sheet is anodized and the large contact area permits current densities of up to 10.8 A/dm^2 (100 amp/sq ft) to be employed with electrolyte at 43°C, a 10 μm (0.4 mil) coating being produced in 22 minutes. To assist in removing the large quantities of heat generated, a novel means of mechanical agitation has been introduced, which consists of an endless rubber belt with a serrated surface, which travels in the opposite direction to the anode strip and close to it so that the anolyte is continuously removed and replenished.[502] A diagrammatic cross section of the Lloyd process is shown in Fig. 7-62.[501] The plants are about 40 metres (130 ft) long including etching, dyeing and sealing and coatings up to 25 μm have been applied to long sheets which have been subsequently corrugated for use in certain building applications.

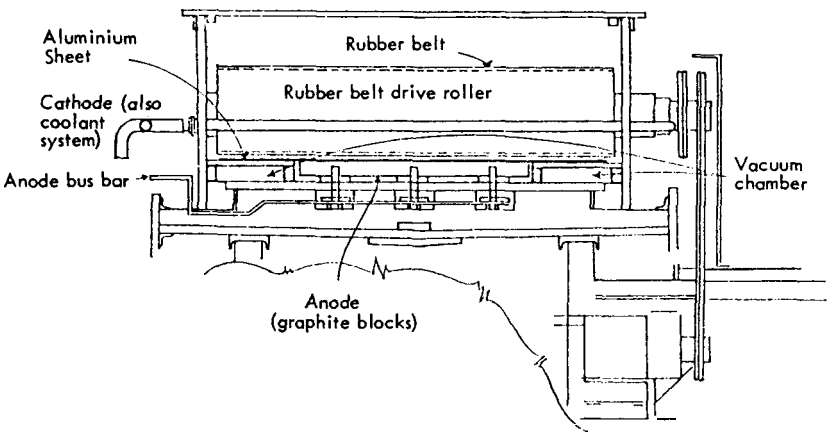


Fig. 7-62. Cross section of Lloyd process continuous anodizing chamber showing very large anode area, vacuum hold-down chambers, coolant system and rubber belt agitation system. Line speed is the only variable; all other process conditions are held constant

Barkman[503,504,505] has also tackled the speed limitations of the process in a different but fundamental way by demonstrating that aluminium strip in a liquid can carry currents up to more than 15,000 A/dm^2 (960 amp/sq inch) of cross sectional area, and investigated how much of this current could be used for anodizing. He decided that with a steadily rising current density a value of 300 A/dm^2 (2800 A/ft^2) could be reached, but in a continuous process the natural tendency is for the current density to decrease because of the current which must leave the strip as it proceeds along the tank. Barkman counieracted this tendency with a multi-cathode system whose geometry and spacing was so designed that the current density would rise along the treatment tank length according to a predetermined schedule, which had been shown in static tests to be permissible. Combining the multi-cathode design with the principle of liquid current input in an auxiliary cell, he was able to anodize at speeds of up to 30 metres/minute (100 ft/minute), achieving mean current densities of 60 A/dm^2 (550 amp/sq ft) which rose from an initial 5 to about 100 A/dm^2 (50 to about 1000 amp/sq ft) in the last cathode area.

However it is the principle of liquid contact anodizing which has allowed significant developments in continuous anodizing. The principle has been well described by Cooke[506] and is illustrated in Fig. 7-63. Current flows from the positive output of the power supply to the anode in the first electrolyte and, upon entering the solution, the usual anode reactions occur; in this case oxygen is evolved. The strip in this solution is cathodic with respect to the anode and therefore cathodic reactions will occur; in this case hydrogen is generated. The current then travels along the length of the aluminium strip until it enters the second solution where the strip is anodic relative to the cathode in this electrolyte. Anodizing of the aluminium therefore occurs in this bath and hydrogen is evolved at the cathode. The strip is bipolar, in that it is cathodic in the first section and anodic in the second, and this method of anodizing is sometimes called the 'bipolar electrode' method.

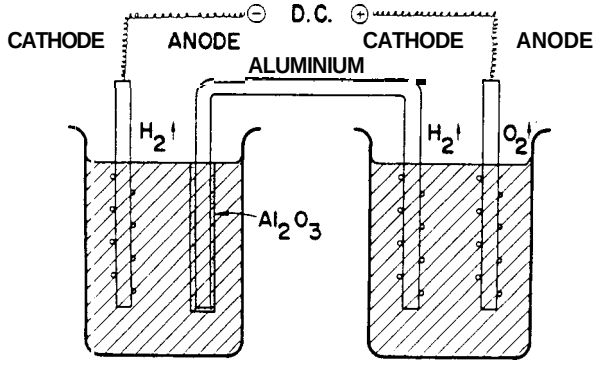


Fig. 7-63. Anodizing with a bipolar electrode[506] (liquid contact principle)

The hydrogen evolved at the aluminium surface in the cathodic section is very effective in removing rolling oil from sheet and drawing lubricant from wire, and is the basis of the electrolytic cleaning treatments mentioned earlier.

The current carried by the strip from the cathodic to the anodic section leads to an I^2R heating effect, and it is this heating that limits the amount of current which can be carried. In the extreme the strip can fuse or soften and break.

For a given alloy and cross-sectional area, the resistance, R, is proportioned to the length of strip located between the cathodic and anodic sections, and, therefore, to reduce the I^2R heating effect this length should be reduced as much as possible.

Many liquid contact systems have been described, particularly by Fromson, who has patented many cell designs.[507] He describes the operation of a relatively simple type of liquid contact system (Fig. 7-64), and described how the addition of further cells (Fig. 7-65) can allow the use of higher anodizing currents and hence higher strip speeds.[491] In this way he can also vary the processes involved, so a strip which is initially anodized can be electroplated, electropainted or electrolytically coloured in subsequent operations. Other methods of electrophoretic lacquer deposition[508] or electrolytic colouring of continuously anodized aluminium[509,510,511,512] have been described. In many of these cases, of course, both d.c. and a.c. are being applied to different parts of the same strip.

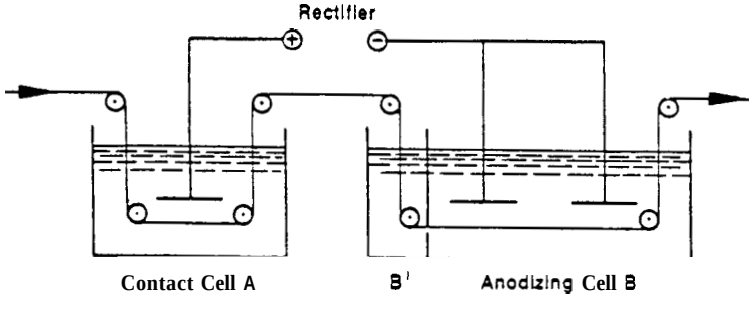


Fig. 7-64. Schematic diagram of liquid contact anodizing line[491]

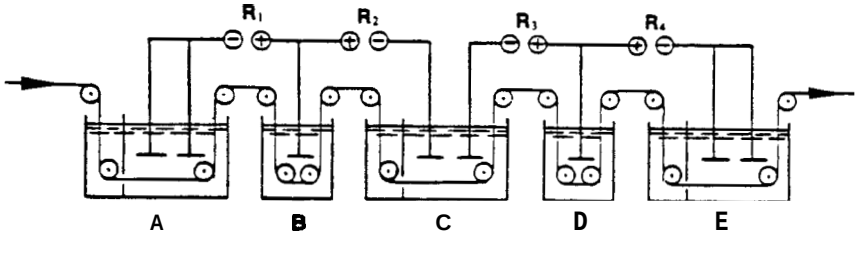


Fig. 7-65. Liquid contact line modified to include additional anodizing cells[491]

As can be seen from the above figures, the path length of the strip between cathodic and anodic sections of the cell can still be quite long, and to avoid this, in-line cells with divisions between them have been described. The most advanced is probably that developed by Alcan,[513] which is illustrated in principle in Fig.7-66. In this case the long narrow cell requires no physical division between anodic and cathodic sections, and the anodizing electrolyte can be flowed over the surface of the strip in the opposite direction to the strip movement. This is effective in removing heat from the strip surface and allows the use of very high current densities. This principle is used in the electrolytic cleaning and anodizing cells in the Alcan line at Nachterstedt,[514] which has already been described in the electrolytic cleaning section of Chapter 4. The use of mathematical modelling to help in the design of liquid contact cells has been studied by Brichau *et al.*,[515] and the principle of high electrolyte flow has been used in a cell design by Ellard and Cowieson.[516]

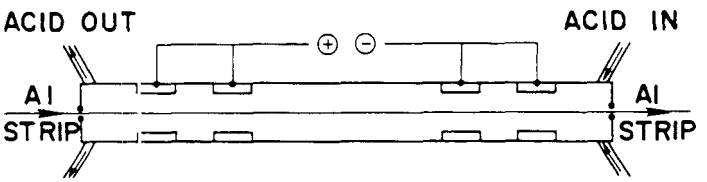


Fig. 7-66. Alcan multiple electrode cell (bipolar working electrode)[513]

Péchiney have described a process in which one side of a strip is anodized while the other is in contact with a rotating cylinder,[517] and a continuous treatment plant used in Poland[518,519] for anodizing strip conductors for electromagnets has also been described. This operated at 36 A/dm^2 (350 amp/sq ft) in an electrolyte containing sodium sulphate and sulphuric acid with an a.c./d.c. process which appears to be the system of Kholodnyi.[520] Alusuisse describe a method using a plurality of cathodes[521] and Ano-coil describe a system for continuously printing anodized aluminium rising sublimable inks.[522]

A major use of continuously anodized aluminium is in the lithographic plate making industry and many cell designs involving a.c. electrograining or d.c. anodizing have been described. These include developments from Hoechst,[523] Alusuisse[524] and Fuji Film.[525] (See also Chapter 4).

Electrical windings

The ability to continuously anodize aluminium foil or strip makes possible the use of aluminium for electrical windings of magnets and transformers.[526,527] These windings are of smaller dimensions than normally insulated copper windings for equivalent I^2R losses, while the extremely thin insulation and the use of strip instead of wire results in improved heat dissipation. As compared with copper, aluminium windings are markedly cheaper where the cross-sectional area of the conductor is above 0.015 sq inch (0.1 cm^2).

5 μm (0.2 mil) coatings produced by sulphuric acid anodizing are normally used in Gt. Britain for this purpose, and breakdown voltages of 200 volts r.m.s. can be obtained with these coatings which have an electrical strength of 472 kV/mm and a relative permeability of 7.5-8.[528,529]

Apart from its electrical properties, the flexibility of the anodized strip or foil is important. Sulphuric acid anodizing enables the production of foil 0.0035 inch (0.09 mm) thick which may be wound round a 0.125 inch (3.2 mm) diameter mandrel without damage, and this is adequate for coil winding.

Anodized aluminium windings may be operated at up to 500°C without deterioration and for this reason they have found application in atomic reactors aircraft and missiles, while for transformers and motors the safety factor on the rating of the conductor may be reduced in comparison with organic or silicone insulated wires.

Windings may be joined by spot welding, cold welding, ultrasonic welding, soldering or mechanical jointing. In soldering anodized aluminium, an ultrasonically-activated solder bath gives good results.

One of the major problems in the use of anodized flat strip for electrical windings was the tendency for short circuiting at the strip edges because coil slitting processes leave a burred or upstanding edge. It is necessary to have strip where both edges are smooth and rounded in cross section or well insulated. This problem has been tackled in a number of ways: mechanically in bevelled rollers,[530] or by edge brushing;" by flash melting,"' and electrochemically by anodizing the tightly wound coil so that the edges are converted into thick oxide before the coil is anodized.[533] Penetration of chemicals into the coil laps can be avoided by tightly winding the coil with an exponentially decreasing tension which is greater than 30% of the tensile strength of the foil,[534] and contact may be established by mounting in a cruciform rack with knife edges along the arms.[535]

Cost comparisons in America for a 200 amp welding transformer made from double glass insulated copper and anodized aluminium strip showed a conductor cost saving of 34% when aluminium was used, and the conductor weight saving was 53%, or 24.84 lb compared with 53.15 lb. Although aluminium foil or strip is widely used in coils and transformers the preferred method of insulation on the basis of cost is with paper or plastics. At one time the majority of distribution transformers in the United States were fitted with aluminium foil windings, but although excellent insulation is achieved by anodizing, the cost could only be

justified where full advantage could be taken of the high thermal stability of the windings, i.e., in dry-type transformers operating at high ambient temperatures.[536]

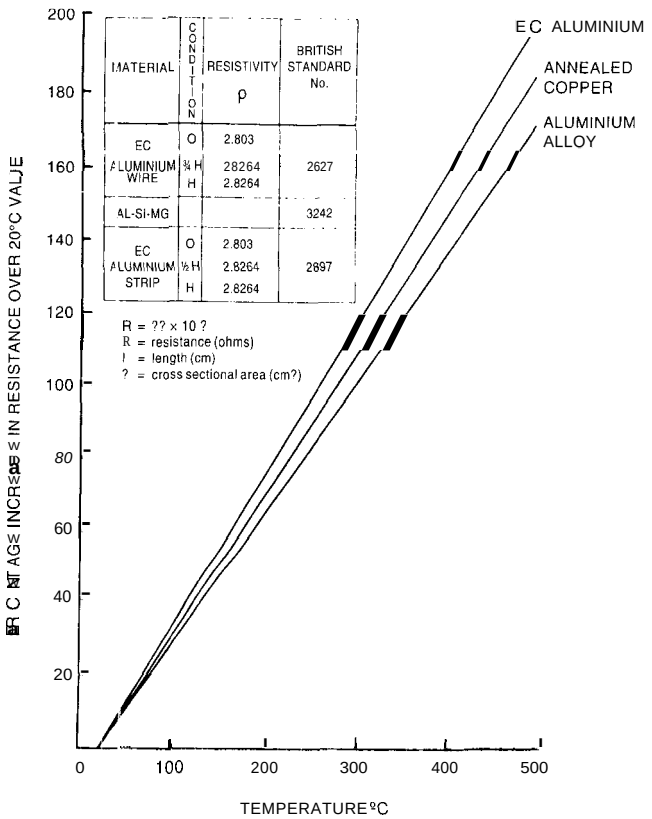


Fig. 7-67. Variations in resistance of conductor material with temperature[528]

Hard anodic oxide coatings have been used for the more extreme types of application. Thus, heating elements wound directly on to aluminium alloy supports coated with 2-3 mil (50-75 μm) anodic oxide coatings have been used at red heat without breaking clown the electrical insulating properties of the coating. As a matter of interest, short term thermal insulation, e.g., of flame jets or hot gases, is also achieved by hard anodizing.

The insulating value of an anodic coating may be severely reduced when precipitated phases, which are not oxidized in anodizing but remain suspended in the coating, are present in the basis metal. In their presence, moreover, metallic particles may become isolated by lateral oxide growth. This trouble may be largely avoided by using pure aluminium or homogeneous alloys suitable for forming a continuous protective coating.

Reflectors

The use of coil anodized aluminium for internal lighting and heat reflectors has been described by Dowell.[537] He indicates the suitability of aluminium, which has the second highest reflectance of all metals over the visible spectrum, only silver having a higher value, and with well controlled bright anodizing processes very little of this reflectance is lost. Suitable high purity based bright anodized materials have total reflectances as high as 88%, combined with a specular reflectance of 85%.

One of the factors that can be important in lighting is the appearance of iridescence when anodized aluminium is used in combination with tri-phosphor fluorescent tubes. These tubes have high light output at three distinct peak wavelengths, and iridescence can be caused by interference of light reflected from the oxide film surface with light reflected from the metal / oxide interface. This has to be prevented by careful control of anodic film thickness.

The high ultra-violet and infra-red reflectance of anodized aluminium is used in applications such as industrial drying and space heating, but film thickness is critical and is normally kept below 3 microns. Such material can have a total reflectance of over 90% for infra-red radiation of wavelengths of 1,200-1,500nm. For ultra-violet light, reflectance is around 75% for UV-B radiation and over 80% for **UV-A** radiation.

Similar applications in the U.S.A. have been summarised by Cassidy.[538]

Anodizing in situ

A novel anodizing device patented by Reynolds Metals Company[539] enables rapid anodizing to be carried out with a mobile head on flat or curved surfaces in either the horizontal or vertical planes, and by this means a hard thick coating can be applied to structures too big for normal anodizing installations to cope with. The sulphuric acid electrolyte used for this purpose is at a concentration of 30-40% and a temperature of 20-40°C, and the essential requirement is that it should flow over the surface being treated at a speed of 150-500 ft/min. This is achieved by means of the specially constructed head (Fig. 7-68) which can be moved over the surface to provide an anodic oxide coating of about 12 μm on a 15 inch length per minute. Any electrolyte leakage is collected by means of a 'vacuum shroud' and a mist filter.

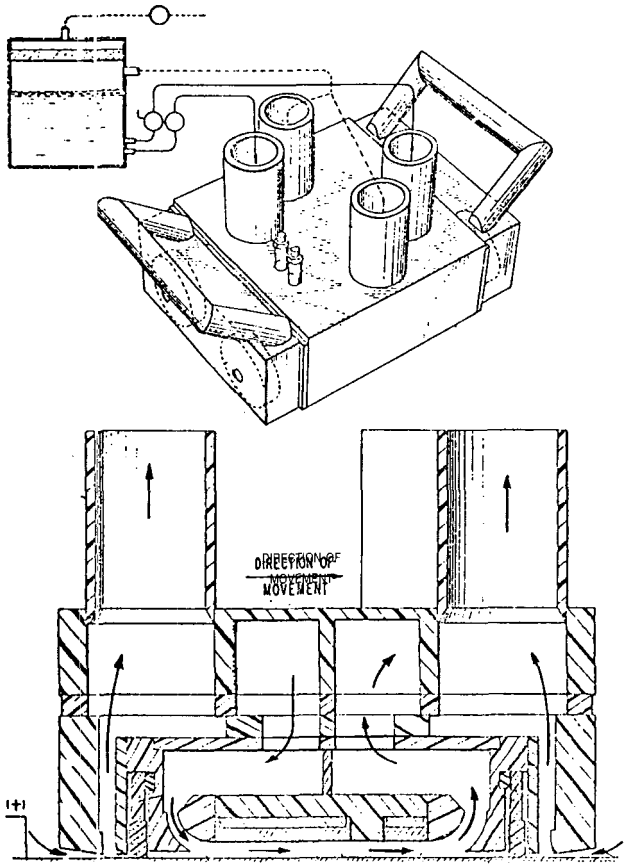


Fig. 7-68. Mobile head for in situ anodizing of flat or curved surfaces[539]

Brush Anodizing

Brush anodizing is another form of in-situ anodizing which is particularly used in the aircraft and aerospace industries, and it has been described by Norris.[540] It is not new and originates from developments of brush electroplating, but over many years it has become more accepted as a genuine localised treatment technique. It is carried out using a hand held tool and is capable of being used for phosphoric, chromic and sulphuric acid anodizing, and even of localised hard anodizing. Special power packs are used, which have high resolution meters to allow for the small areas and hence low currents required. They are automatically controlled to give a pre-determined current density or maximum voltage. The processing solutions can be used in the form of gels in the case of phosphoric acid or chromic acid anodizing, but normal solutions are used for other electrolytes.

The anodizing tool (Fig. 7-69) uses conventional brush plating graphite electrodes and solution is supplied to the work by means of a pump. The graphite electrode is covered by a polyester felt cover which holds the gel or solution. With a gel, flexible, stainless steel, perforated sheet tools are used, with the gel being forced into the absorbent covering of the tool, which is then secured to the stainless steel. The cathode covers the whole area to be anodized and coatings are applied as quickly as possible so that degradation of the electrolyte is minimised. Existing coatings in the damaged area are often removed before re-anodizing, and masking to protect adjacent areas is often necessary. In this way coatings which will meet military specifications have been produced.

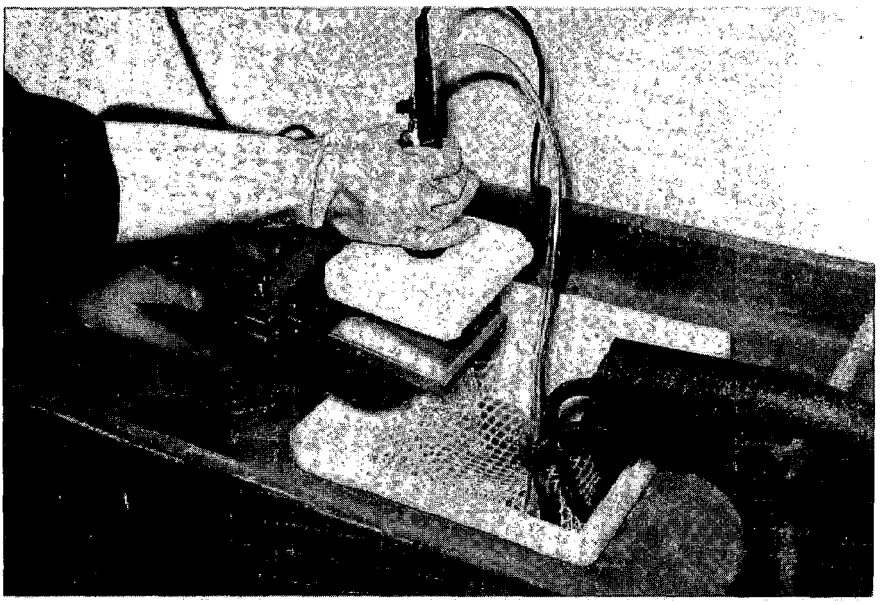


Fig. 7-69. Brush hard coating operation[54] [Courtesy Sifco Selective Plating]

Automatic anodizing of finished products

For anodizing finished products, plant essentially similar to automatic plating equipment can be employed. One such plant, shown in Figs. 7-70 and 7-71,[54] was the earliest automatic plant to be built in Britain for anodizing washing machine parts in 20% (vol) sulphuric acid at 20°C, 16 volts for 15 minutes. In the pretreatment stages, the metal was cleaned in hot alkaline cleaner and etched in hot dilute hydrochloric acid, while sealing was carried out in nickel acetate solution followed by a further hot water seal before drying in recirculated hot air.

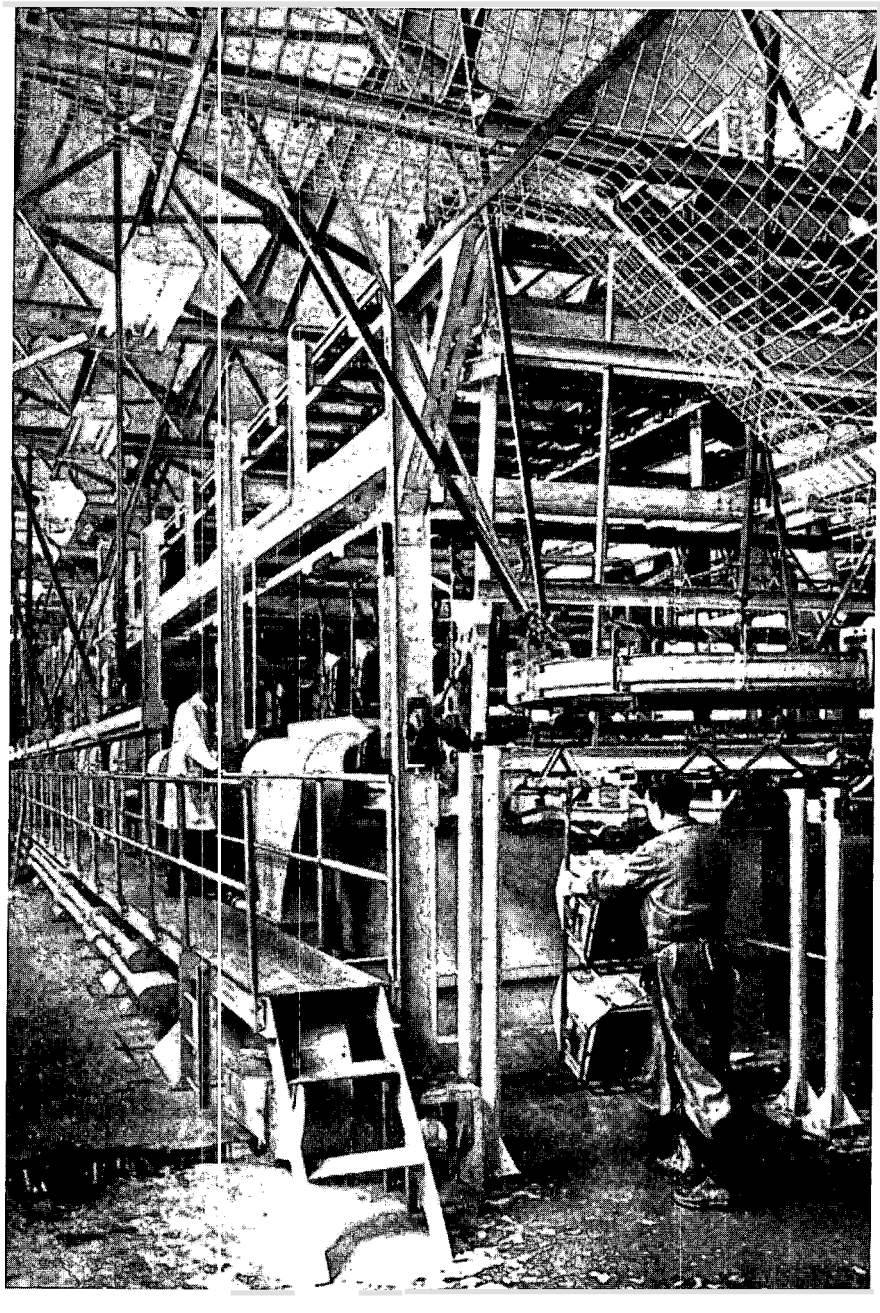


Fig. 7-70. Automatic anodizing plant for Hoover washing machine parts, showing jigs and aluminium tubs being loaded. Some of the fume exhaust hoods can be seen on the left with a trip wire for emergency stops above

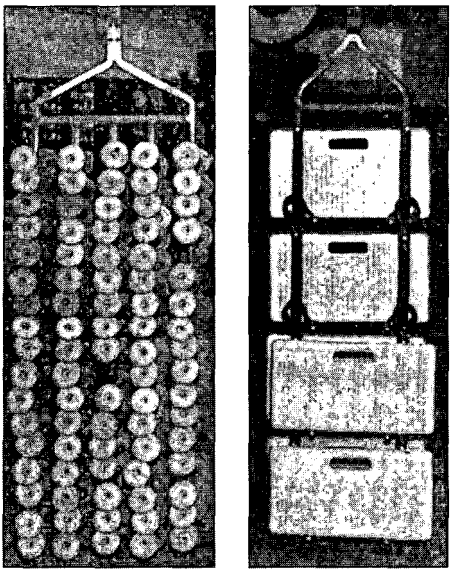


Fig. 7-71. Small components are racked and carried through the plant in Fig. 7-70 as shown here

The duplex carriage type of plant, which dealt each hour with up to 180 washing machine tubs and 135 jigs of smaller parts, was 130 ft long, 16 ft wide (tank width 9 ft) and 16 ft high, while a second line 86 ft x 42 ft x 42 ft high was installed for stripping the contact points of the insulated aluminium alloy anodizing jigs. Two banks of six 1,000 ampere, 16 volt rectifiers were employed, and the lead cooling coils in the tank were employed as cathodes. This system was adopted both in order to avoid the need for separate cathodes and also to give cathodic protection to the lead. The cooling coils consisted of 1,300 ft of 12 inch chemical lead piping and the cooling water was recirculated through a refrigeration unit operating with Arcton 6 gas. Fumes from the cleaning, anodizing and sealing tanks were drawn below floor level into trenches lined with acid-resistant brick and covered with rubber-lined steel plates. These trenches also carried the effluent into neutralization pits.

Automatic bright anodizing plant

Of great interest are a number of automatic plants which were installed for combined chemical polishing and anodizing, particularly of motor trim.

American plants

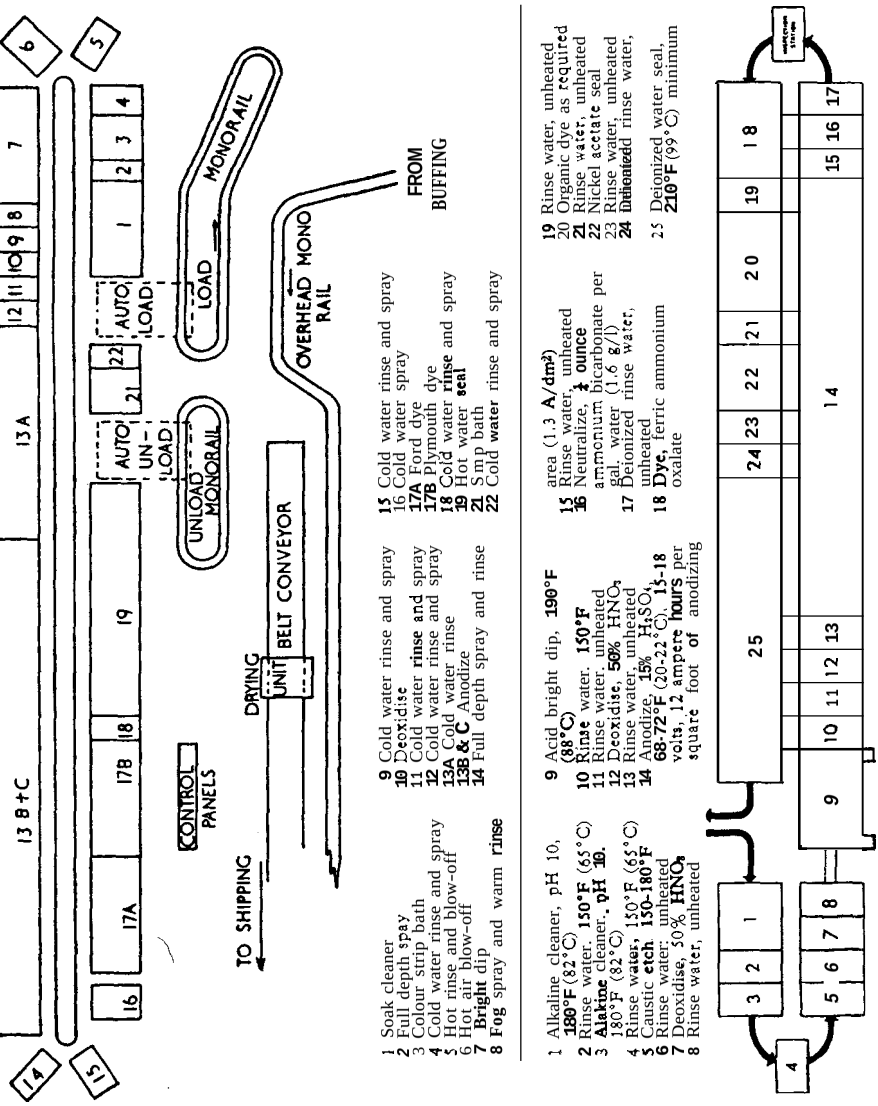
In these the chemical polishing solution employed was norinally of the phosphoric-nitric acid type and was normally preceded by a brief mechanical polishing stage, usually on automatic polishing machines. The layout of this type of automatic bright anodizing plant is illustrated in Figs. 7-72 and 7-73 and a typical sequence was:

Soak clean
Spray rinse
Rinse
Hot rinse
Air blow-off'
Chemical polish (phosphoric acid-type)
Fog spray and warm rinse
Deoxidize (nitric acid plus an inhibitor)
Cold rinse
Cold rinse
Cold rinse
Sulphuric acid anodize
Rinse and seal, etc.

Frequently two automatics were used in line, one for chemical brightening and anodizing, the other for dyeing and sealing the coating. A sequence of this type was used in the Cadillac Division of General Motors Corp.[542] Grille sections and other motor trim were loaded on to the first machine where they went through the sequence: alkaline clean, spray clean, cold rinse, soak clean, cold rinse, deoxidize in nitric acid solution containing an inhibitor, cold rinse with **air** blow off, bright dip, cold rinse, anodize, cold rinse, cold demineralised water rinse, unload. The bright dip was often of a phosphoric-nitric acid type and removed 25-50 μm (1-2 mil) of aluminium; the anodizing bath was 15% sulphuric acid (wt) and was operated at 21°C and 12 amp/sq ft (1.3 A/dm^2) to produce a 2.5-5 μm (0.1-0.2 mil) coating.

At the unloading station, the jigs were placed in boiling demineralised water at pH 6.7-7.0 for approximately 5 minutes and the parts were then transferred to different jigs for the gold dyeing machine in which the sequence was nitric acid (42" Be) dip for 53 seconds, two cold rinses, demineralised water rinse, first colouring dip (inorganic dye at pH 4.8-6.0), two cold rinses, second colouring dip (red dye at pH 5.3-5.7 for 3 minutes), two cold rinses, seal in $^1/_8$ oz/gallon (0.8 g/l) nickel acetate solution (pH 5.5-5.8, 98-100 "C), two cold rinses, final water seal in demineralised water (pH 6.7-7.0, 5 minutes, 98-100 °C). Jigs were of aluminium and were stripped in caustic solution after each completed sequence.

Other North American bright anodizing lines were U-shaped or H-shaped,[543] as shown in Figs. 7-76 and 7-77, and a long transfer tank was used to move work from one leg of the H to the other. These layouts allowed work to be loaded and unloaded at the same end of the line and made maximum use of the labour force available. They also avoided the need to carry empty flight bars back down the line.



Figs. 7-72 and 7-73. Layouts of two U.S. automatic chemical brightening and anodizing plants

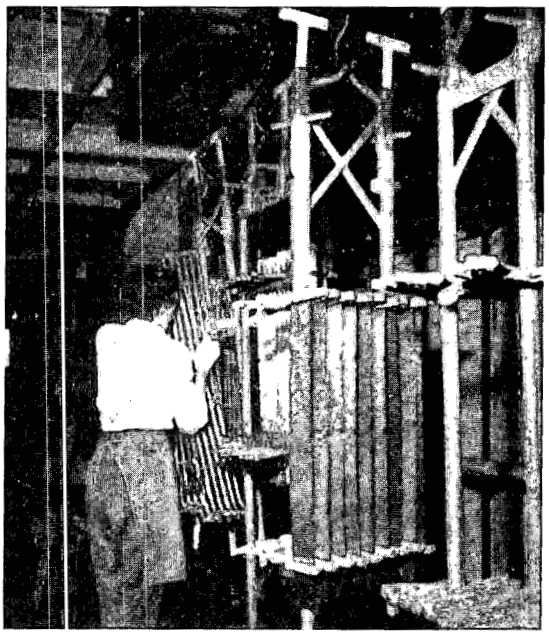


Fig. 7-71. Loading stage of an automatic chemical brightening and anodizing plant

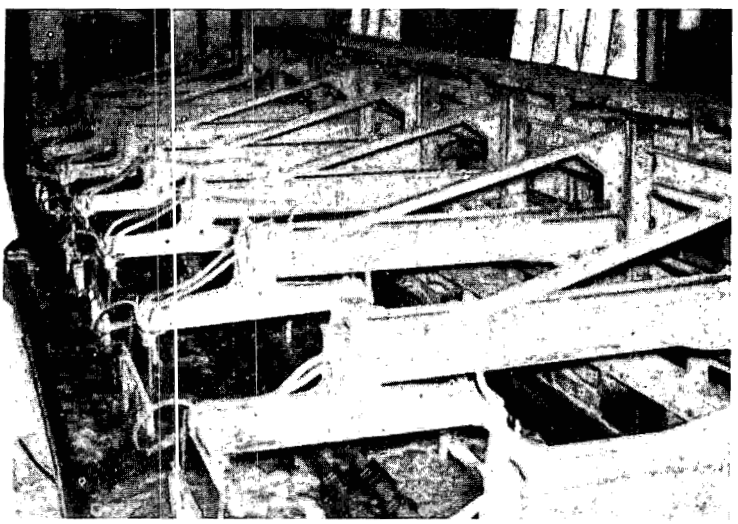


Fig. 7-75 Close-up of anodizing stage in a chemical brightening-anodizing automatic plantFig. 7-76. 'H' shaped tank arrangement for bright anodizing line[543]

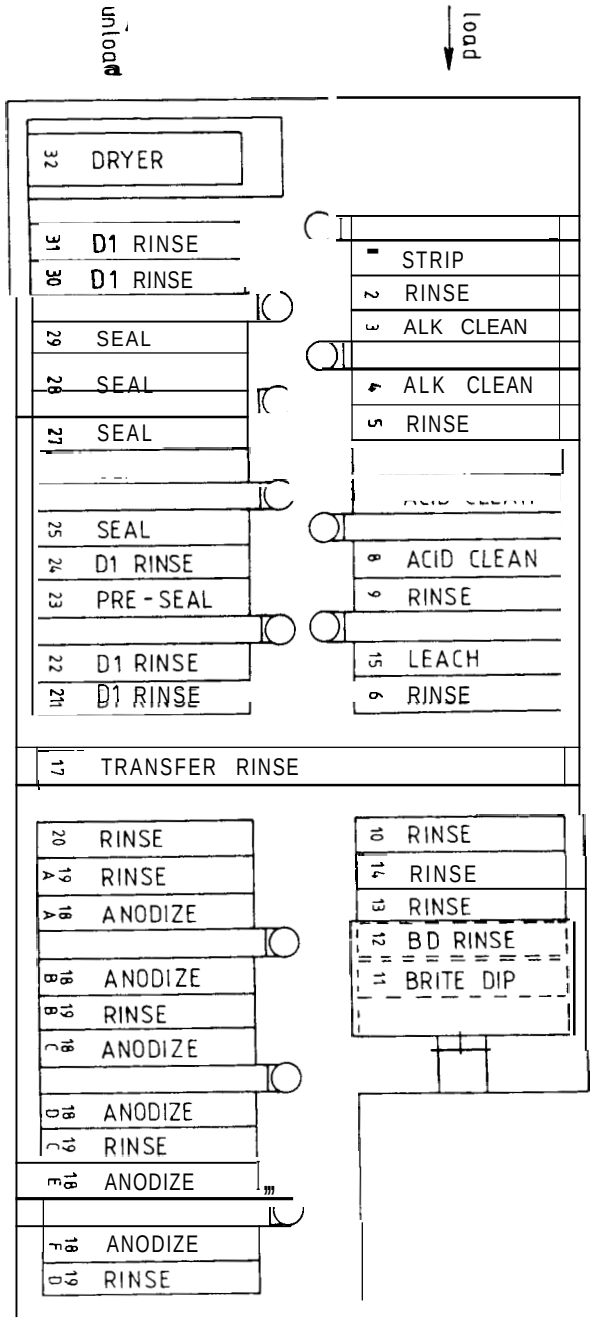


Fig. 7-76. 'H' shaped tank arrangement for bright anodizing line[543]

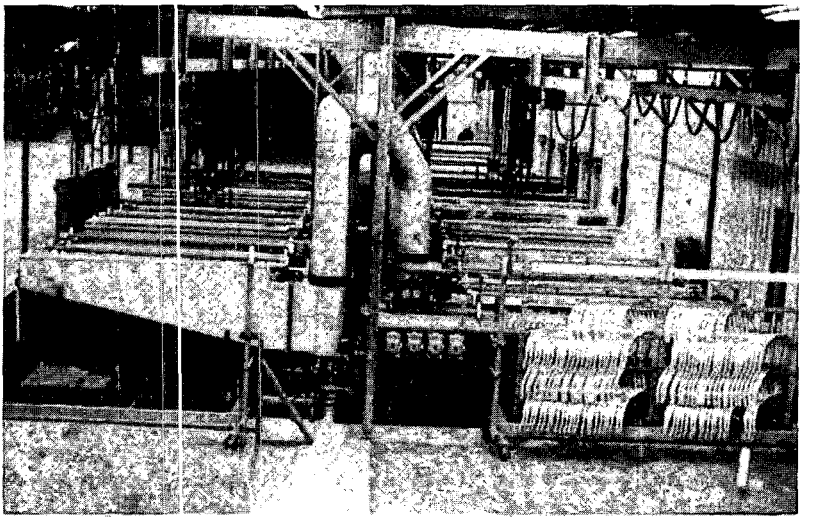


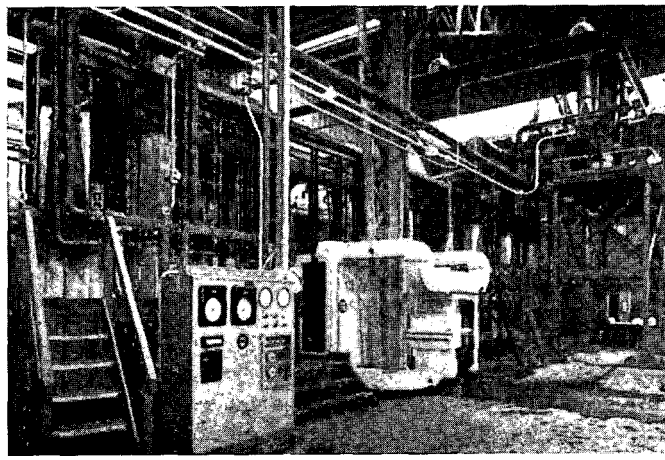
Fig. 7-77. 'H' shaped bright anodizing line at Autanodics: Michigan [courtesy of Walgren Co.]

European plants

While in the installations described above the aluminium was frequently buffed before transfer to the chemical brightening and anodizing automatics, this was not generally required with the Alupol V/Phosbrite 159 or Erftwerk chemical polishing solutions (see Chapter 3) which were used in some automatic bright anodizing plants in Europe.

Figs. 7-78 and 7-79 show a large British plant installed by the London Aluminium Co. for bright anodizing trim of both British and German cars.[544] The plant was 78 ft long and 12 ft 6 inches wide (24 x 3.8 m) and the process sequence is seen in Fig. 7-79. Treatment time in the Phosbrite 159 chemical polishing bath was varied by a delayed set-down mechanism. In the chemical polishing bath the parts could be mechanically oscillated and an air-operated temperature controller was fitted. The overall stage time could be varied from zero to 5 minutes. The temperature of the anodizing bath was maintained thermostatically within 3°C by regulation of the flow of chilled water through carbon block heat exchangers.

Fig. 7-80 shows a plant for the automatic chemical polishing and anodizing of radiator grilles and other car accessories designed and installed by Albright and Wilson (Mfg) Ltd. in the works of the Coventry Radiator Co. The illustration shows radiator grilles being processed.



Figs. 7-78 and 7-79. Automatic chemical polishing anodizing plant at London Aluminium Co. Ltd. (Above) General view of loading side of plant, showing plant control cabinet with recording and indicating instruments, rectifier controls and conveyor controls in inset panel, air drying oven (centre) and stainless steel side hoods on hot water seal tank leading via PVC ducting to extraction fans on platform.

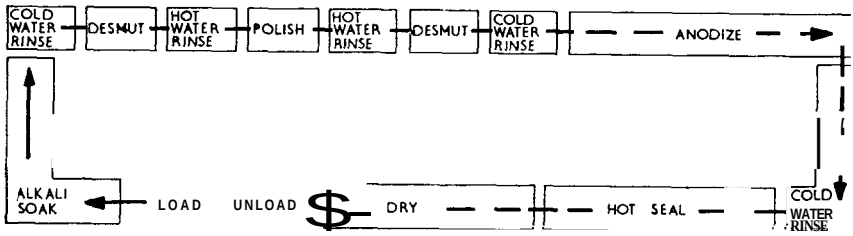


Fig. 7-79. Process sequence

Figs. 7-81, 7-82, and 7-83 show a large German automatic chemical polishing and anodizing plant[545] which produced 55 radiator grilles and 110 rear lamp fittings per hour at the Simca motor works in France. The sequence was: alkaline clean (35-40°C), hot rinse, cold rinse, chemical polish, spray rinse, cold rinse, nitric acid desmudge, cold rinse, anodize (22 minutes), cold rinse, colour (50-60°C, 4 minutes), spray rinse, cold rinse, seal (boiling water 20 minutes), nitric acid dip, cold rinse, hot rinse, dry, unload. The plant, which was of the return type with a central lifting frame, was almost 140 ft long, 13 ft 3 inches wide and 15 ft 3 inches high (42 x 4 x 4.6 m) and employed a phosphoric acid type chemical polishing bath on 99.99% Al-3% Mg alloy material. An interesting feature of this plant was the extremely rapid transfer arrangement which lifted the racks from the chemical polishing bath to the rinse in 5 seconds.

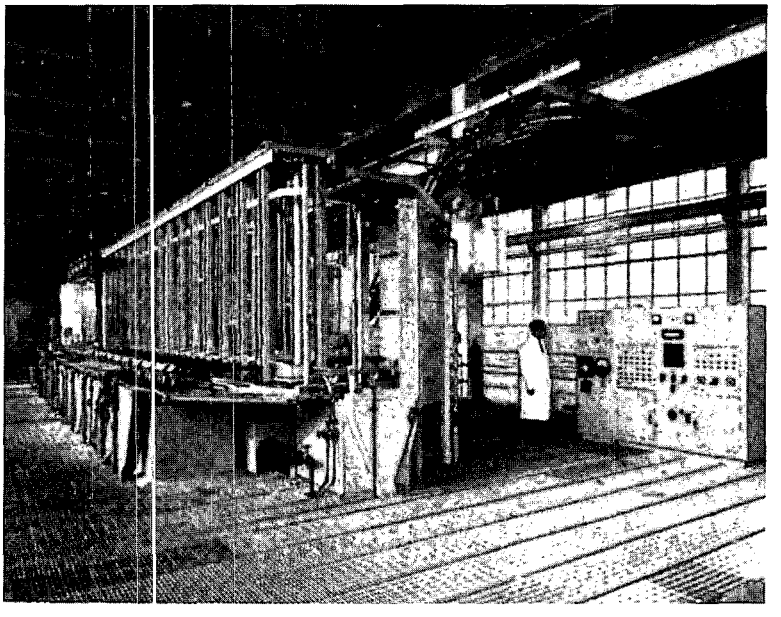
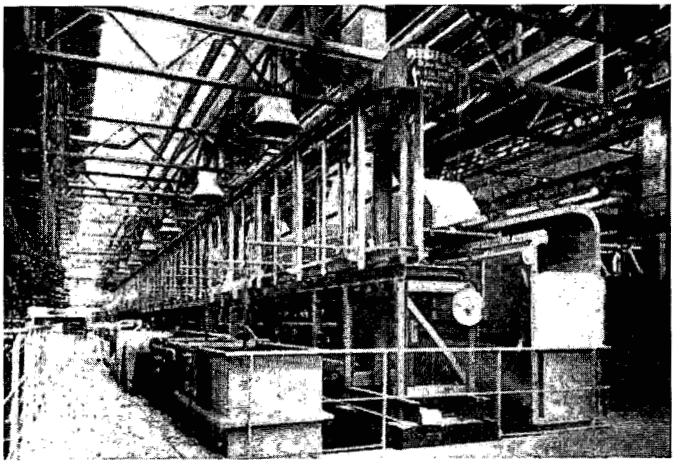


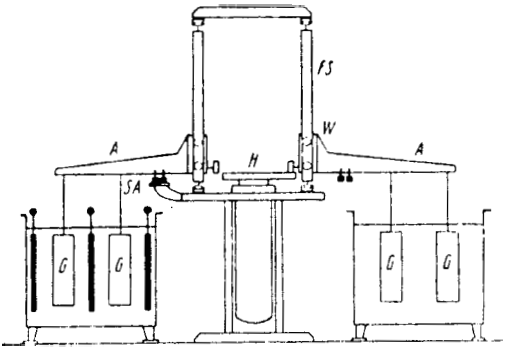
Fig. 7-80. Automatic chemical polishing and anodizing plant for radiator grilles and other car accessories designed and installed by Albright and Wilson (Mfg) Ltd. in the works of the Coventry Radiator Co. The illustration shows radiator grilles being processed

Automatic anodizing *of* small parts

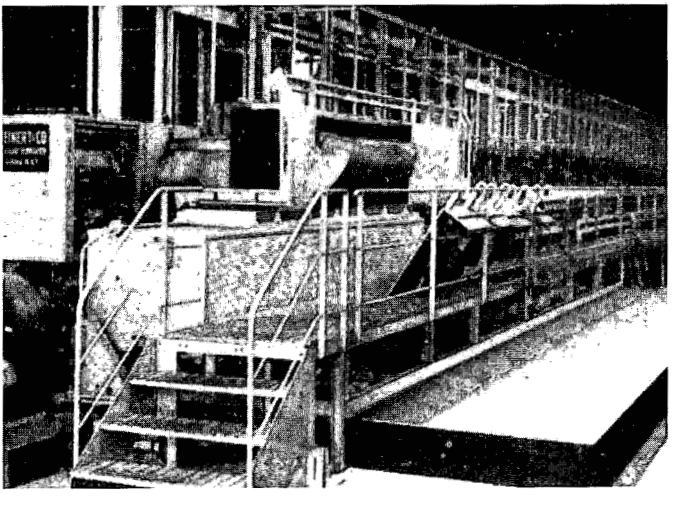
Continuous anodizing is normally associated with coils of rolled strip or long runs of comparatively large components. Indeed one of the main disadvantages of anodizing small parts is the high labour costs involved in handling which often makes anodizing uneconomic compared with alternative forms of finishing. The 'Anomatic' anodizing plants, patented and constructed by the Aluminum Coil Anodizing Corporation of Illinois, were designed to cater for the anodizing of large volumes of small stamped or machined aluminium parts. It consisted of an endless titanium strip which automatically carried small racked parts through a multi-tank system. The articles, ranging in variety from keys, knitting needles and lipstick cases to horn rings and 40 mm ammunition cases, were automatically clipped in groups at the exit. The plants were said to be suitable for clear anodizing or hard coating.[546]

Acorn Anodising Co. also suggest an automated system for small parts using an elongated electrically-conducting carrier provided with a series of resilient clips.[547]





Figs. 7-81–7-83.
Automatic chemical polishing anodizing plant at Simca, France



10. CHEMICAL CONTROL OF ANODIZING SOLUTIONS

Sulphuric acid processes

For routine control it is usual to determine the 'free' sulphuric acid, i.e., the sulphuric acid not neutralized by dissolved aluminium in the form of $Al_2(SO_4)_3$, the aluminium content, and the chloride content.

For this purpose SO ml of solution are diluted to 250 ml and this is used as stock solution.

Free sulphuric acid[1109]

Ten ml of the stock solution are pipetted into a conical flask and diluted to approximately 100 ml. 1 g of potassium fluoride and 1 ml of a 0.1% alcoholic solution of thymol blue are added and the acid titrated against N sodium hydroxide to a permanent blue end point.

$$1\ \text{ml N NaOH} = 1.33\%\ H_2SO_4\ (v/v)$$

Aluminium

Fig. 7-84 shows the solubility curve for aluminium against sulphuric acid concentration and, in practice, the aluminium content should not be allowed to exceed the value corresponding to the acid concentration used.

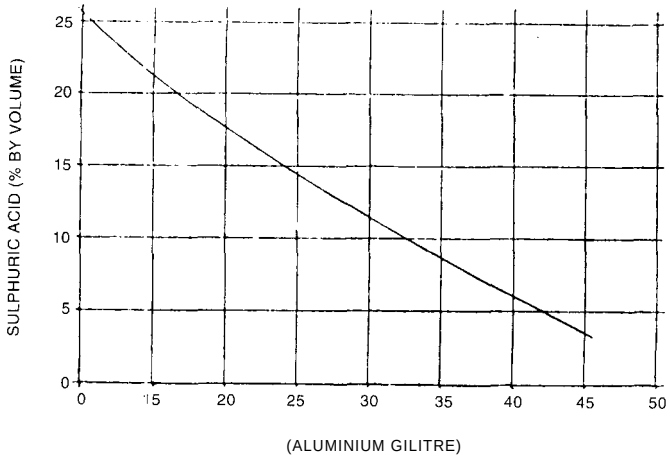


Fig. 7-84. Solubility of aluminium in sulphuric acid solutions at 15°C[""]

The following methods can be used to determine the aluminium content.

(1) Pipette 25 ml of the stock solution into a 250 ml flask containing excess N sodium hydroxide. Add 1 ml thymol blue solution and titrate against N nitric acid until the colour changes from blue to grey. This method determines the 'total' sulphuric acid and the aluminium is obtained by difference.

1.8 (ml N NaOH – ml N HNO_3) – 4.5 (ml N NaOH in 'free' sulphuric acid titration) = **Al** in g/l.

(2) Direct estimation.[4] Dilute 50 ml of anodizing solution to 500 ml. Heat to 70°C and slowly pass H_2S for 30 minutes. Filter through a glass filter and wash with dilute H_2S solution. Boil off H_2S from filtrate and add 2 ml of 3% hydrogen peroxide. Cool the solution, transfer to a 500 ml measuring flask and make up to the mark with distilled water. Pipette 25 ml of this solution into a 800 ml beaker, add a few drops of methyl orange and then 1:1 ammonia until the colour changes. Add 4 ml conc. hydrochloric acid, dilute to 400 ml and boil. To this solution add 20 ml of 25% sodium thiosulphate solution, 10 ml glacial acetic acid and 10 ml of a 10% solution of ammonium phosphate. Boil for 15 minutes. Allow the precipitate to settle, and filter through a fast filter paper. Wash well with hot water, transfer to a crucible and dry at 105-110°C. Then heat at 1,200-1,300°C to constant weight. The precipitate is $AlPO_4$ (1 g $AlPO_4$ = 0.22107 g Al).

Combined method for sulphuric acid and aluminium

Mohler described a double-indicator method for determining sulphuric acid and aluminium sulphate in sulphuric acid anodizing solution.[548] In this, 5 ml of the solution are placed in a 250 ml flask and 2 drops of methyl orange and 2 drops of phenolphthalein are added. The solution is then titrated to the orange end point (A mil; corresponding to pH 3.6) against N sodium hydroxide and then the pink end point (B ml; corresponding to pH 8.9).

The sulphuric acid concentration is given by

$$\text{g/l } H_2SO_4 = A \times 9.8$$
$$\text{g/l Al} = (B - A) \times 1.8$$

The same principles can also be applied in a potentiometric method.

Chloride

To 100 ml of the stock solution add 10 ml nitric acid (d. 1.42) and 50 ml 1% silver nitrate solution. Allow the precipitate to settle, filter through a weighed Gooch crucible, wash with 2% nitric acid, dry, and weigh as AgCl. Calculate to NaCl.

$$\text{AgCl (g)} \times 4.1 \equiv \text{NaCl (g/l of anodizing bath)}$$

Chromic acid processes

Total chromic acid[77]

Five ml of the anodizing solution are diluted to 250 ml with distilled water and 30 ml dilute sulphuric acid (d. 1.2) are added. The solution is boiled and 1% potassium permanganate solution is added until the pink colour or brown precipitate is permanent. Boil for 20 minutes. Allow to cool, and add 0.1 g manganous sulphate. Boil for 5 minutes, cool, filter, wash the precipitate, add 30 ml dilute sulphuric acid to the filtrate and titrate against N/10 ferrous ammonium sulphate and back titrate with N/10 potassium permanganate.

$$\text{F.A.S. (ml)} \times 0.0666 \equiv CrO_3 \text{ (g) per 100 ml solution}$$

Free chromic acid[109]

(1) On new solutions, 5 ml of anodizing solution are diluted to 250 ml. 30 ml dilute sulphuric acid (d. 1.2) are added and the solution titrated against N/10 ferrous ammonium sulphate and N/10 potassium permanganate, as in the total acid determination.

(2) This method is for used solutions only. 10 ml of the anodizing solution are diluted to 100 ml with distilled water and the solution titrated to permanent turbidity against N/2 sodium carbonate.

$$N/2\ Na_2CO_3 \text{ (ml)} \times 0.5 \equiv \text{free } CrO_3 \text{ (\%)}$$

In this method greater accuracy is obtained by using a Nessler tube with a standard.

(3)[79] The free chromic acid may also be obtained by pH measurement with the use of a glass electrode. The free CrO_3 content can then be calculated, or read off from a graph. This method is subject to some error, however. as the pH of the solution is affected by changes in composition of the bath during anodizing.

(4)[164] Free chromic acid can be determined by an electrometric titration against N or N/10 sodium hydroxide to pH 3.05. At this pH, half of the chromic acid is neutralized and metallic chromate begins to precipitate.

Aluminium

From the values for 'total' and 'free' acid, the aluminium content may be calculated.

Chloride[109]

Dilute 50 ml of the anodizing solution to 300 ml. Add 20 ml concentrated nitric acid and boil. Add 5 tnl of 3% silver nitrate solution and proceed as in the estimation of chloride in sulphuric acid solution (see above).

$$\text{g AgCl} \times 8.2 \equiv \text{g NaCl per litre.}$$

Oxalic acid processes

Total oxalic acid

Twenty-five ml anodizing solution are diluted to 250 ml in a measuring flask. To 25 ml of this solution add 25 ml 2N sulphuric acid, warm to 60-70°C and titrate against N/10 potassium permanganate to a permanent violet.

$$1\ \text{ml N/10 } KMnO_4 \equiv 0.0065\ \text{g } (COOH)_2.2H_2O$$

***Free** oxalic acid*

Dilute 250 ml anodizing solution to 100 ml, add 2-3 drops of a 1% solution of phenolphthalein in alcohol and titrate against N sodium hydroxide to a permanent pink end point.

$$1\ \text{ml N NaOH} \equiv 0.063\ \text{g } (COOH)_2.2H_2O$$

Aluminium and other metal ions

Calculate from combined acid value, i.e.,

(total acid – free acid) x 0.2 = Al (%)

An alternative method of controlling the solution is to base additions on values calculated from the amp-hours passed. Thus:

Oxalic acid lost per amp-hour	≈ 0.132 g
Aluminium dissolved per amp-hour	≈ 0.084 g

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