THE SURFACE TREATMENT AND FINISHING OF ALUMINUM AND ITS ALLOYS

by P. G. SHEASBY
and R. PINNER

SIXTH EDITION

VOLUME 2

ASM INTERNATIONAL

FINISHING PUBLICATIONS LTD.

19-2001

The Surface Treatment and Finishing of Aluminium and its Alloys

by

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SIXTH EDITION

Volume 2

ASM INTERNATIONAL,
Materials Park, Ohio 44073-0002 USA.

FINISHING PUBLICATIONS LTD.
105 Whitney Drive, Stevenage, Herts SG1 4BL, UK

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2001
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c.1

First edition 1956
Second edition 1959
Third edition 1964
Fourth edition 1971
Fifth edition 1987
Reprinted 1990
Sixth edition 2001

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Co-published in the United States
with ASM International

British Library Cataloguing in Publication Data

Sheasby, P.G.
The surface treatment and finishing of aluminium and its alloys. – 6th ed.
1. Aluminium – Finishing.
I. Title II. Pinner, Robert
673.7227 T.S.655

Volume 1 ISBN 0-904477-21-5
Volume 2 ISBN 0-904477-22-3
Volumes 1 & 2 ISBN 0-904477-23-1

Printed and bound in Great Britain by
Redwood Books, Trowbridge, Wilts BA14 8RB, UK

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 6th 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 8

Anodizing in Architecture

1. GENERAL

The greatest advance made in the use of anodized aluminium during the twentieth century has been the penetration into the architectural field, and today the use of anodized curtain walls,[1,2,3,4] panels, window frames and roofing materials for houses, offices, flats, factories and shop fronts accounts for a very significant part of the total area of aluminium which is treated, particularly in the U.S.A., Gt. Britain, Italy, Holland, Germany, Japan, South Africa and Switzerland.' As anodic coatings for these purposes are frequently exposed to severe conditions and are often not easily accessible for adequate cleaning, substantially thick coatings of good quality must be applied.

Most architectural work in Great Britain and elsewhere is anodized by the sulphuric acid process. In order to maintain the consistency of the anodized work and to meet the requirements of the various national standards, the large and often sophisticated plants: now customary for this class of work have facilities for controlling the acid temperature to within ±1°C or better, and provision for regulating the current, or current density, to a constant value in order to control the rate of film formation.

Although three or four organic dyestuffs have been approved for exterior work, most of the traditional dyestuffs are subject to some fading on long term exposure with the result that such coloured finishes as are accepted for this purpose are those based on inorganic pigments, which are few in number and of a very limited colour range. During the decade 1960-70 there was a very great increase in what are now termed the integral colour anodizing processes, that is, those based on the use of special electrolytes other than sulphuric acid which

provide a permanent and 'built-in' colour. The subsequent decades have shown a reversion to the sulphuric acid electrolyte followed by electrolytic colouring techniques for impregnating the coating with metallic particles. These developments are dealt with at length in the later pages of this chapter. The generally upward trend in the use of anodized aluminium in architecture was reversed in the 1980's by the introduction of powder paint systems with high durability. These offered a wide range of colour finishes, which were generally cheaper than colour anodized aluminium, and as a result several major architectural anodizing lines closed down. However in the 1990's this trend is again reversing, with the concern over filiform corrosion under paint coatings, and the desire of architects for the metallic appearance of anodizing, **but it** is unlikely that anodizing will ever regain the architectural dominance that it had in the 1960's and 70's. Interestingly recent figures (1996) from ESTAL[6] show that in the European market production of both anodizing and painted products is increasing, though the latter is increasing at a faster rate. These figures show a European market in 1996 of 476,000 tonnes for anodizing and 742,000 tonnes for painting.

The move in Great Britain towards home improvement, and the use of aluminium for replacement windows, patio doors and double glazing, has meant a significant increase in the demand for aluminium extrusions. However white painted extrusions are increasingly used for these applications in preference to anodizing, and plastic windows have taken a large slice of this market. Interestingly, the enormous market for aluminium extrusions in Japan, again mainly for domestic applications, is still largely satisfied by anodized aluminium, though this is normally sealed with an electrophoretically deposited clear lacquer coating. In Japan there is also a very large market for colour anodized aluminium, mainly the bronze finishes produced by electrolytic colouring, and similar markets occur in Australia and New Zealand. This type of finish has now come to Europe with the installation by Reynolds in Holland of a large vertical anodizing line, which includes electrophoretic lacquering as well as conventional sealing[7,8].

Coating thickness and standards

The question of what anodic coating thickness is appropriate in any particular situation has been a hotly debated topic because thickness is only one of the characteristics which determine film quality, and as has often been pointed out a 15 μm coating properly prepared and adequately sealed is to be preferred to a soft porous 35 μm coating with indifferent sealing. It must also be remembered that when this dialogue started scarcely any operator would have been in possession of the now ubiquitous eddy current meters to measure the film thickness accurately and quickly at any point, neither was there any quick and reliable method for estimating whether sealing had been properly carried out. Concomitant with penetration into the architectural field has been the development of test methods which have helped in no small measure to create confidence in the finish.

There are currently two anodizing standards operating in the United Kingdom. BS 3987:1991 deals specifically and only with anodized aluminium used for external architectural applications in Great Britain.[9] It specifies a minimum average coating thickness of 25 μm (1 mil; 0.001 inch) with a minimum local thickness of 20 μm anywhere on the significant surface. BS 1615:1987 is a general standard[10] covering all applications, so does not lay down any particular thickness standard but lists grades from AA5 to AA25 in steps of 5 μm, from which the purchaser may select the appropriate grade. An Appendix offers guidance on the choice as follows:

'The life of anodized aluminium in exterior applications depends not only on the coating thickness but also on the frequency with which atmospheric deposits are removed by washing. It is particularly important to remove atmospheric deposits regularly from surfaces that are not exposed to rain.

'Grade AA2.5 should be specified for static exterior applications in the U.K., e.g. windows and curtain walling.

'Grades AA20 and AA15 may be specified for static exterior applications in mild atmospheres or rural environments away from industrial pollution or marine influence, where long-term durability may not be important (e.g., shop fronts), or if frequent washing can be guaranteed.

'Grades AA10 and AA5 may be specified for exterior applications in special circumstances (e.g., if frequent maintenance can be guaranteed), if the installation is not permanent, or if some deterioration is acceptable.'

A note states that 'Many countries have national standards for anodized aluminium and, because other climates are generally less aggressive than in the U.K., the minimum coating thickness specified for static exterior use tends to vary from 10 to 20 microns'.

A significant difference between the 1987 version of BS 1615 and earlier versions is that it is now a 'method for specifying' and not a specification. This means that it tells the reader how to write a specification for an anodized product and what characteristics need to be specified, but it is not a specification in its own right. This means, for example, that it is no longer possible to claim that something is anodized to BS 1615 Grade AA15. A specification based on this can certainly be produced, but the specification must be developed by the purchaser or the anodizer. This is a general trend in standards production and is not restricted to BST or to anodizing, and the new European Standard, EN 12373:Part 1, which will eventually replace BS 1615 and all other European national standards, will also be a method for specifying.

Because of the relative aggressivity of U.K. exposure conditions, thickness grades up to 35 microns have been considered, and actually appeared in the 1961 edition of BS 1615. However it has been recognised that, under normal operating conditions. of temperature and current density, the coating produced by sulphuric acid anodizing begins to deteriorate when in excess of 30 μm, becoming progressively more soft and porous and of less protective value. Thicker coatings can be prepared by lowering the temperature and using a higher current density

but it is not believed that such coatings perform any better than a properly prepared 25 μm coating; neither is any better performance normally required. Even with 25 ym coatings, however, anodizing conditions must be carefully controlled and electrolyte temperatures below 21°C, sulphuric acid concentrations below 185 g/l and anodizing current densities above 1.4 A/dm^2 (13 A/ft^2), must always be used. If this is not done the outer parts of the coating can become relatively soft, and the coating will 'chalk' rapidly on outdoor exposure. This type of problem has led the British Anodizing Association to issue the architectural anodizing guidelines already described in Chapter 7.[11] This problem was recognised in the 1991 revision of BS 3987 with the need to evaluate the abrasion resistance of a coating as well as its thickness and sealing quality. **A** simple control method using abrasive papers (BS 6161:Part 18) was specified, and coatings produced by sulphuric acid anodizing should not be abraded by glass coated paper. Similarly coatings produced by integral colour anodizing should not be abraded by garnet coated paper.

Guidance notes in Appendix B on 'Properties affecting coating performance' recommend that coatings with a Wear Index greater than 1.4 when measured by BS 6161:Part 9 (Measurement of wear properties with an abrasive wheel wear test apparatus) are likely to be of unsatisfactory quality for external architectural applications.

Another difference with the new BS 3987 was the recognition of the great importance of sealing quality, and the inclusion, for the referee chromic acid / phosphoric acid dissolution test (BS 6161:Part 3), of a predip in nitric acid (10 min. in a 50% (vol) nitric acid solution at 18-22°C). This is also required in the latest Qualanod specification,'*and is included in the new European Standards, where EN12373:Parts 6 and 7 describe the use of the chromic acid/ phosphoric acid dissolution test without and with a nitric acid predip respectively. Part 7 (with the predip) is recommended for the evaluation of sealing quality of external architectural coatings.

The stipulation of a 25 ym coating is a more exacting requirement than any other country demands, and recognises the essentially aggressive nature of the U.K. climate due to extensive industrial areas, proximity to the sea and a high humidity coupled with relatively high and fluctuating winter temperatures which promote excessive condensation.

In the United States 18 μm is required for architectural work[13] and in much of Europe a 20 ym minimum is demanded,[12,14] but in the drier South a thickness of 15 ym is sometimes regarded as sufficient.[15] Several attempts have been made to combine these in some simple formula by assigning values to the climate or environmental pollution P, and the degree of moisture M. Thomas has suggested that the simple relationship:

$$\text{Film thickness in microns} = 5(M + P)$$

will cover most situations and generally comply with National Standards if the following values for M and P are used:

Indoors; external very mild and rural	P = 1
External marine	2
External industrial	2
Industrial + marine: very aggressive	3
Exceptionally severe local conditions	P = 4
Indoors heated; external very dry	M = 0
Indoors humid; ext. moderately wet	1
Heavy condensation; very wet (U.K.)	2

This indicates a minimum of 5 μm for the mildest of conditions, either 10 or 15 μm for use indoors, and 15, 20 or 25 μm for the progressive degrees of severity out of doors.

Basis metal

The materials mainly used for architectural applications in Great Britain are:

wrought alloys : 5251(N4), 5005(N41), 6063(HE9) and 6082(HE30)
cast alloys : LM5

Choice of material depends on the anodizing properties (see Chapter 7), on the colour required and on corrosion factors. Thus, atmospheric exposure tests on aluminium roofing materials[16] have shown that 99.5% aluminium and its alloys with magnesium or manganese have better corrosion resistance than Al-Mg-Si alloys but such differences tend to disappear when the materials are anodized to architectural standards. Al-5% silicon alloy has been used quite widely for producing a grey coating for architectural components, while aluminium-chromium alloy has been used to produce a yellow or gold finish after anodizing without the need for dyeing.[17] Particularly with sheet products used in prestige architectural applications, anodizing quality sheet of the 5005 type is usually used.

Choice of finish

A designation system for aluminium finishes has been adopted by the Aluminum Association,[18] and the main tables of designations are shown below. Mechanical finishes are designated by the letter M and are described in Table 8-1. Chemical finishes are designated by the letter C and are shown in Table 8-2 and the anodic finish itself is designated by A and is described in Table 8-3. Thus, as examples, an 18μm etched and anodized architectural finish produced by an integral colour anodizing process would be designated AA - M10C22A42, and a typical automotive trim designation might be AA - M11C12C31A213. Clearly this is a very precise but complicated system, and so far it has not been adopted outside the U.S.A.

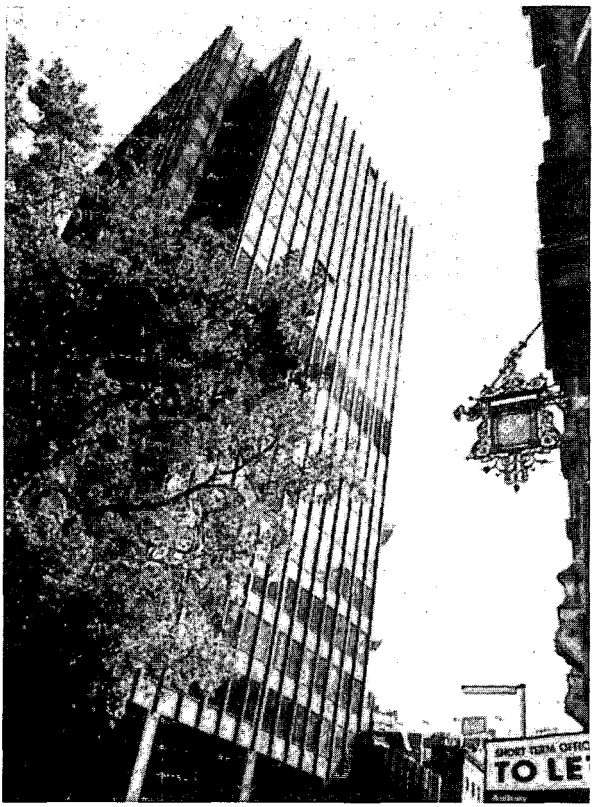


Fig. 8-1. Duranodic integral colour bronze finishes used on the Cedar Building, London

[Courtesy of Josef Gartner and Co. (U.K.) Ltd.]

Several methods are used to produce the various surface textures required for anodizing architectural components. Among mechanical treatments are polishing, abrasive blasting (with alumina or aluminium alloy shot or by vapour blasting) or scratch brushing with stainless steel or nickel-silver brushes. The lined finishes are produced as indicated in Table 8-1 by the use of endless belts of various grades, but they are also frequently produced by the use of non-woven nylon wheels impregnated with aluminium oxide, of the Bear-Tex or Scotchbrite type, as indicated in Chapter 2. Material of this type has also been formed into belts backed by a foam layer or air cushion which can follow the contours of extrusion profiles better than those backed with inflexible wheels. Alternatively the surface may be matt etched. Etching of architectural panels in sodium hydroxide based solutions provides a uniform matt finish. A slightly brighter finish can be obtained by adding 2% sodium fluoride.[19]

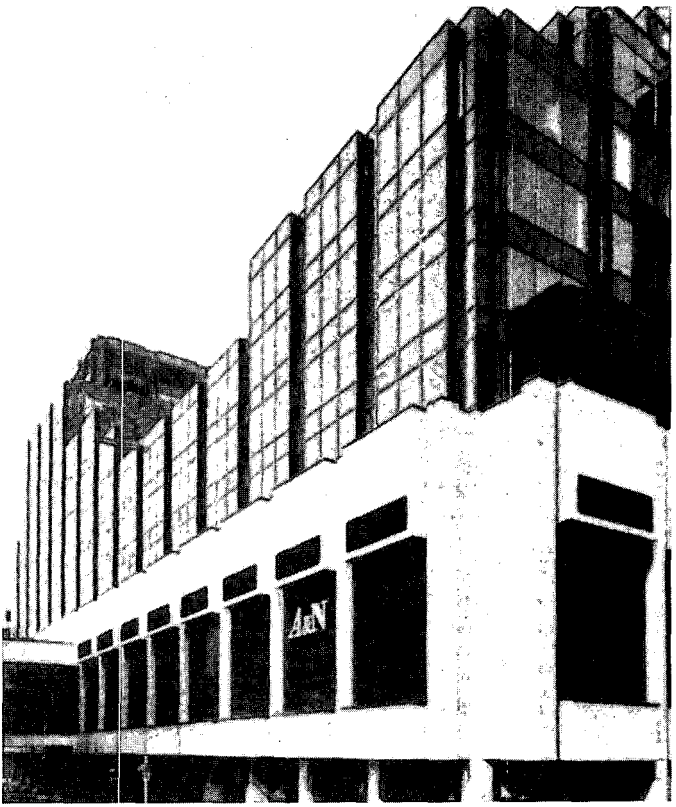


Fig. 8-2. Anolok electrolytic bronze finishes used on Army and Navy Stores Building, London

[Courtesy of LHT Anodisers Ltd.]

For a bright finish it is possible to polish electrolytically or chemically, though it must be remembered that specular reflectivity will be largely lost after anodizing to a thickness substantially higher than 10 μm (0.4 mil).

Most anodizing standards do not include designation systems, but the German Standards[14] include a single designation of E0 for non-pretreated and anodized material, E1-E5 for varying degrees of inechanical treatment followed by anodizing, and E6 for a chemically etched and anodized finish. A similar designation system is included in EN12373:Part 1.

Pre-anodizing

It can be said that aluminium entered the field of architecture through the window. Originally it was a replacement for steel, and frames were torch welded

in the time-honoured manner. Inevitably heat stains due to precipitation occurred, until, with the advent of flash butt welding techniques, machines were available which could produce neatly welded frames with no visible heat-affected zone. The advantages of being able to request almost any extrusion profile, however complicated, soon appealed to designers who were able to invent a range of knock-down frames which could be fixed with screws, cleats or snap-in fixings. This in turn enables the components to be anodized in straight lengths with better utilisation of tank space, since a large welded window frame tends to leave little room for anything else to be conveniently accommodated. The vast profusion of sizes and shapes is additionally an embarrassment to the anodizer, and also to the assembler, who must sort them out again and hope that the correct number of each is present.

It is not surprising therefore that for certain classes of work the advent of so-called pre-anodizing has simplified matters and effected great economies. In this situation, the metal proceeds directly from the factory to the anodizing plant in standard lengths (in many cases the anodizing is actually carried out at the extrusion plant), and the window manufacturer receives only anodized and inspected lengths which must be subsequently fabricated. Figs. 8-3 and 8-4 show one such plant built in the U.K. for this purpose which was also fully automated so that the whole treatment sequence could be pre-recorded on a punched card system which then proceeded as soon as the tanks became available without any intervention from the operators.[20,21] This plant used the Glydo automatic transfer system of W. Canning Ltd.[22]

TABLE 8-1

Mechanical finishes (M)

Type of finish	*Designation**	*Description*	*Examples of methods of finishing***
As Fabricated	M10	Unspecified	
	M11	Specular as fabricated	
	M12	Nonspecular as fabricated	
	M1X	Other	To be specified.
Buffed	M20	Unspecified	
	M21	Smooth specular	Polished with grits coarser than 320. Final polishing with a 320 grit using peripheral wheel speed of 30 m/s (6,000 feet per min.). Polishing followed by buffing, using tripoli based buffing compound and peripheral wheel speed of 36-41 m/s (7,000-8,000 feet per rnin.).

Type of finish	*Designation**	*Description*	*Examples of methods offinishing***
	M22	Specular	Buffed with tripoli compound using peripheral wheel speed 36-41 m/s (7,000-8,000 feet per min.).
	M2X	Other	To be specified.
Directional textured	M30	Unspecified	
	M31	Fine satin	Wheel or belt polished with aluminium oxide grit of 320-400 size; peripheral wheel speed 30 m/s (6,000 feet per min.).
	M32	Medium satin	Wheel or belt polished with aluminium oxide grit of 180-220 size; peripheral wheel speed 30 m/s (6,000 feet per min.).
	M33	Coarse satin	Wheel or belt polished with aluminium oxide grit of 80-100 size; peripheral wheel speed 30 m/s (6,000 feet per min.).
	M34	Hand rubbed	Hand rubbed with stainless steel wool lubricated with neutral soap solution. Final rubbing with No. 00 steel wool.
	M35	Brushed	Brushed with rotary stainless steel wire brush, wire diameter 0.24 mm (0.0095 in.); peripheral wheel speed 30 m/s (6,000 feet per min.); or various proprietary satin finishing wheels or satin finishing compounds with buffs.
	M3X	Other	To be specified
Non-directional textured	M40	Unspecified	
	M41	Extra fine matt	Air blasted with finer than 200 mesh washed silica or aluminium oxide. Air pressure 310 kPa (45 psi); gun distance 203-305 mm (8-12 inches) from work at 90° angle.
	M42	Fine matt	Air blasted with 100-200 mesh silica sand if darkening is not a problem; otherwise aluminium oxide type abrasive. Air pressure 207-621 kPa (30-90 psi) (depending upon thickness of material); gun distance 305 mm (12 inches) from work at angle of 60-90°.

Type of finish	*Desig-nation**	*Description*	*Examples of methods of finishing***
	M43	Medium matt	Air blasted with 40-50 mesh silica sand if darkening is not a problem; otherwise aluminium oxide type abrasive. Air pressure 207-621 kPa (30-90 psi) (depending upon thickness of material); gun distance 305 mm (12 inches) from work at angle of 60-90".
	M44	Coarse matt	Air blasted with 16-20 mesh silica sand if darkening is not a problem; otherwise aluminium oxide **type** abrasive. **Air** pressure 207-621 kPa (30-90 psi) (depending upon thickness of material); gun distance 305 mm (12 inches) from work at angle of 60-90".
	M45	Fine shot blast	Shot blasted with cast steel shot of ASTM size 70-170 applied by air blast or centrifugal force. To some degree, selection of shot size is dependent on thickness of material since warping can occur.
	M46	Medium shot blast	Shot blasted with cast steel shot of ASTM size 230-550 applied by air blast or centrifugal force. To some degree, selection of shot size is dependent on thickness of material since warping can occur.
	M47	Coarse shot blast	Shot blasted with cast steel shot of ASTM size 660-1320 applied by air blast or centrifugal force. To some degree, selection of shot size is dependent on thickness of material since warping can occur.
	M4X	Other	To be specified.

* The complete designation must be preceded by AA - signifying Aluminum Association
**Examples of methods of finishing are intended for illustrative purposes only

TABLE 8-2

Chemical finishes (C)

Type of finish	*Designation**	*Description*	*Examples of methods of finishing***
Non-etched cleaned	C10	Unspecified	
	C11	Degreased	Organic solvent treated
	C12	Inhibited chemical cleaned	Inhibited chemical type cleaner used.
	C1X	Other	To be specified.
Etched	c20	Unspecified	
	c21	Fine matt	Trisodium phosphate, 22-45 g/l (3-6 oz per gal) used at 60-71°C for 3-5 min.
	c22	Medium matt	Sodium hydroxide, 30-45 g/l (4-6 oz per gal) used at 49-66°C for 5-10 min.
	C23	Coarse matt	Sodium fluoride, 11 g/l (1.5 oz) plus sodium hydroxide 30-45 g/l (4-6 oz per gal) used at 54-66°C for 5-10 min.
	c2x	Other	To be specified.
Brightened	C30	Unspecified	
	C31	Highly specular	Chemical bright dip solution of the proprietary phosphoric-nitric acid type used, or proprietary electrobrightening or electropolishing treatment.
	C32	Diffuse bright	Etched finish C22 followed by brightened finish C31.
	c3x	Other	To be specified.
Chemical Coatings†	C40	Unspecified	
	C41	Acid chromate-fluoride	Proprietary chemical treatments used producing clear to typically yellow coloured surfaces.
	C42	Acid chromate-fluoride-phosphate	Proprietary chemical treatments used producing clear to typically green coloured surfaces.
	C43	Alkaline chromate	Proprietary chemical treatments, used producing clear to typically grey coloured surfaces.
	C44	Non-chromate	Proprietary chemical treatment employing no chromates.
	C45	Non-rinsed chromate	Proprietary chemical coating treatment in which coating liquid is dried on the work with no subsequent water rinsing.
	C4X	Other	To be specified.

* The complete designation must be preceded by **AA -** signifying Aluminum Association.
**Examples of methods of finishing are intended for illustrative purposes only.
† Aluminum Association Standards for Anodized Architectural Aluminium.

TABLE a-3

Anodic coatings (A)

Type of finish	*Designation**	*Description*	*Examples of methods of finishing***
General	A10	Unspecified	
	A11	Preparation for other applied coatings	3 μm (0.1 mil) anodic coating produced in 15% H_2SO_4 at 21 ± 1°C at 129 A/m^2 (12 A/ft^2) for 7 min. **or** equivalent.
	A12	Chromic acid anodic coatings	To be specified.
	A13	Hard, wear and abrasion resistant coatings	To be specified.
	A1X	Other	To be specified
Protective & decorative coatings less than 10 μm (0.4 mil) thick	A21	Clear coating	Coating thickness to be specified. 15% H_2SO_4 used at 21 ± 1°C at 129 A/m^2 (12 A/ft^2).
	A211	Clear coating	Coating thickness - 3 μm (0.1 mil) minimum. Coating weight - 6.2 g/m^2 (4 mg/in^2) minimum.
	A212	Clear coating	Coating thickness - 5 μm (0.2 mil) minimum. Coating weight - 12.4 g/m^2 (8 mg/in^2) minimum.
	A213	Clear coating	Coating thickness - **8** μm (0.3 mil) minimum. Coating weight - 18.6 g/m^2 (12 mg/in^2) minimum.
	A22	Coating with integral colour	Coating thickness to be specified. Colour dependent on alloy and process methods.
	A221	Coating with integral colour	Coating thickness - 3 μm (0.1 mil) minimum. Coating weight - 6.2 g/m^2 (4 mg/in^2) minimum.
	A222	Coating with integral colour	Coating thickness - 5 μm (0.2 mil) minimum. Coating weight - 12.4 g/m^2 (8 mg/in^2) minimum.
	A223	Coating with integral colour	Coating thickness - **8** μm (0.3 mil) minimum. Coating weight - 18.6 g/m^2 (12 mg/in^2) minimum.
	A23	Coating with impregnated colour	Coating thickness to be specified. 15% H_2SO_4 used at 27 ± 1°C at 129 A/m^2 (12 A/ft^2) followed by dyeing with organic or inorganic colours.

Type of finish	*Designation**	*Description*	***Examples** of methods of finishing***
	A231	Coating with impregnated colour	Coating thickness - 3 μm (0 1 mil) minimum. Coating weight - 6.2 g/m^2 (4 mg/in^2) minimum.
	A232	Coating with impregnated colour	Coating thickness - 5 μm (0 2 mil) minimum. Coating weight - 12.4 g/m^2 (8 mg/in^2) minimum.
	A233	Coating with impregnated colour	Coating thickness - 8 μm (0.3 mil) minimum. Coating weight - 18.6 g/m^2 (12 mg/in^2) minimum.
	A23	Coating with electrolytically deposited colour	Coating thickness to be specified. Application of the anodic coating, followed by electrolytic deposition of inorganic pigment in the coating.
	A2X	Other	To be specified.
Architectural Class II† 10-18 μm (0.4-0.7 mil) coating	A31	Clear coating	15% H_2SO_4 used at 21 ± 1°C at 129 A/m^2 (12 A/ft^2) for 30 min. or equivalent.
	A32	Coating with integral colour	Colour dependent on alloy end anodic process.
	A33	Coating with impregnated colour	15% H_2SO_4 used at 21 ± 1°C at 129 A/m^2 (12 A/ft^2) for 30 min. followed by dyeing with organic or inorganic colours.
	A34	Coating with electrolytically deposited colour	Application of the anodic coating followed by electrolytic deposition of inorganic pigment in the coating.
	A3X	Other	To be specified.
Architectural Class I† 18 μm (0.7 mil) and thicker coatings	A11	Clear coating	15% H_2SO_4 used at 21 ± 1 °C at 129 A/m^2 (12 A/ft^2) for 60 min. or equivalent.
	A42	Coating with integral colour	Colour dependent on alloy and anodic process.
	A43	Coating with impregnated colour	15% H_2SO_4 used at 21 ± 1 °C at 129 A/m^2 (12 A/ft^2) for 60 min., followed by dyeing with organic or inorganic colours, or equivalent.
	A44	Coating with electrolytically deposited colour	Application of the anodic coating followed by electrolytic deposition of inorganic pigment in the coating.
	A4X	Other	To be specified.

* The complete designation must be preceded by AA - signifying Aluminum Association.
**Examples of methods of finishing are intended for illustrative purposes only.
† Aluminium Association Standards for Anodized Architectural Aluminium.

Plant layout and practices

A typical installation for anodizing aluminium window and shop front sections is shown in Figs. 8-5–8-8.[23] The process tanks were 7.6 m long (25 ft) and 2.5 m deep (8 ft), except for the anodizing tanks which were 2.75 m (9 ft) deep to allow for extra clearance and solution circulation. The second anodizing tank was added later and the dye tanks (9 and 10a) were replaced by electrolytic colouring processes. The tanks were positioned side by side with a raised operating platform running along the control side of the plant at working height. Traverse of the work carriers was by an overhead remotely controlled crane powered by a fluid drive motor to give snatch-free movement. This plant was typical of an in-line architectural plant with steel tank construction, the tanks being raised on plinths above the general floor level.

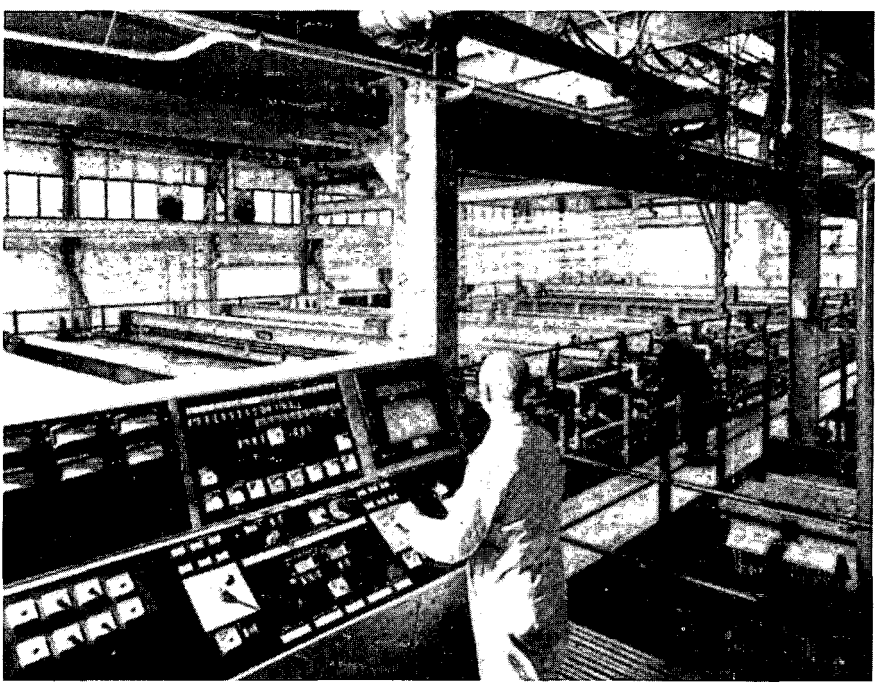


Fig. 8-3. General view of the Warrington, Lancs., pre-anodizing plant of the British Aluminium Co. Ltd. In the foreground is the master console for the automated anodizing plant while the cleaning, etching, washing, anodizing and sealing tanks are in the background

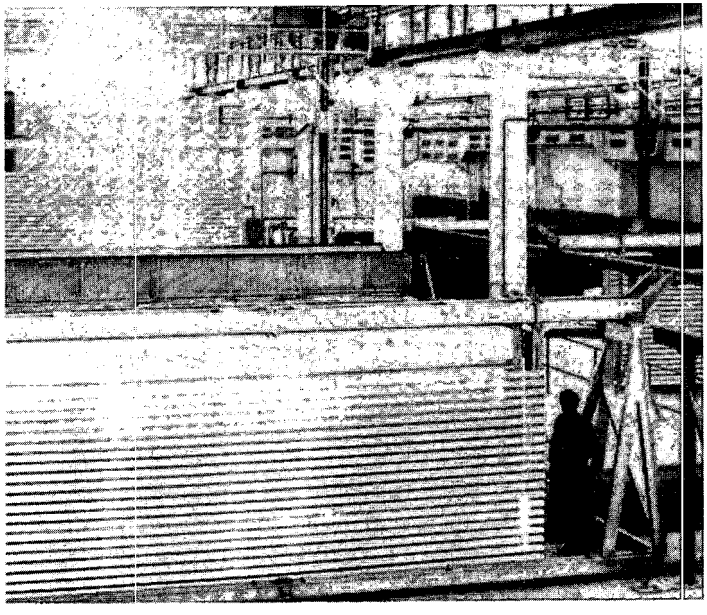


Fig. 8-4. Architectural anodizing line for lineal extrusions at Alcan Aluminiumwerke: Uphusen, W. Germany

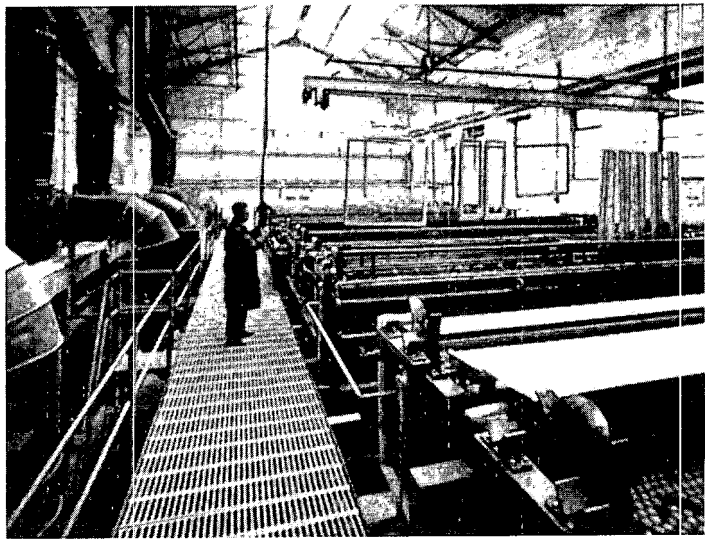


Fig. 8-5. General view of anodizing plant for shop front sections, etc.[23] The extraction ducting passes under the walkway and up on the left of the picture

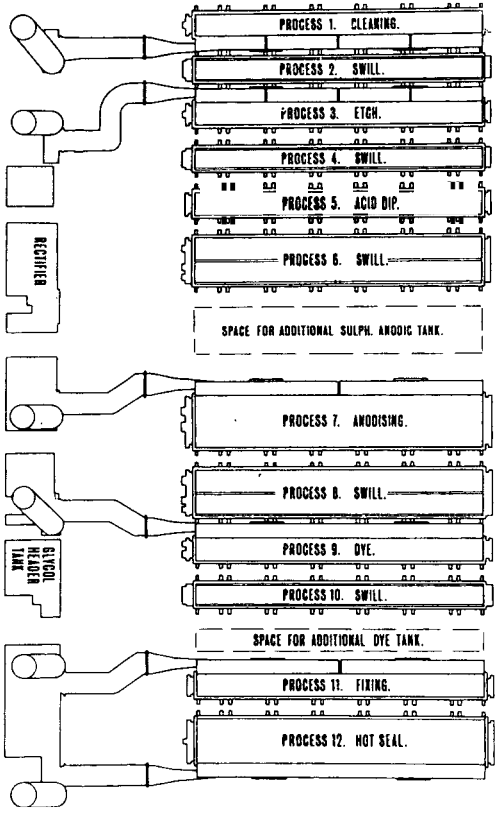


Fig. 8-6. Layout of the plant shown in Fig. 8-5

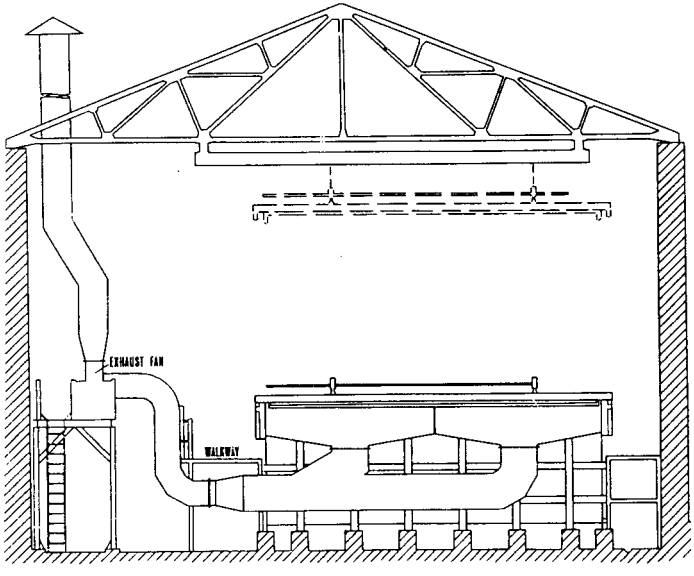


Fig. 8-7. Section of the plant illustrated in Fig. 8-5 showing typical arrangement of the tanks on short plinths with hoist above

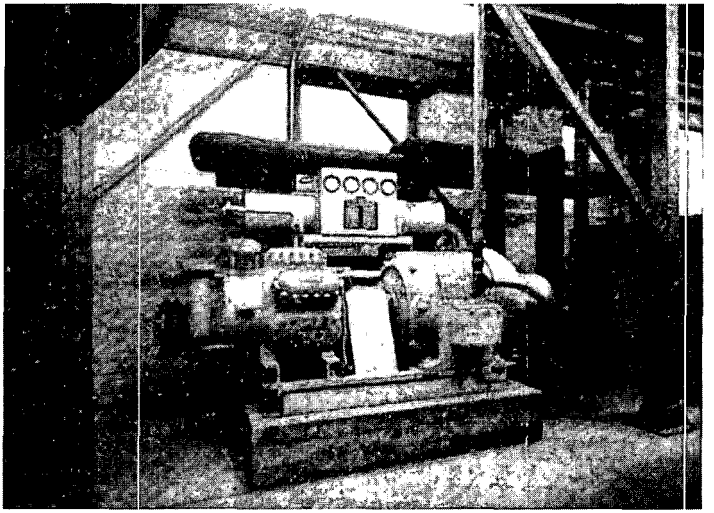


Fig. 8-8. Refrigeration unit of the plant shown in Fig. 8-5. This is placed at ground level below the extraction system

However many architectural plants are now being designed as 'U'-shaped lines, in order to make most effective use of the jigging and de-jigging labour force, and to prevent flight-bars having to be carried back to the start cf the line over the process tanks. Such a line arrangement is shown in Fig. 8-9. One leg of the 'U' contains the pretreatment part of the process, and the other the anodizing. colouring and sealing operations. A double-length water rinse forms the transfer tank from one leg of the line to the other (Fig. 8-10). At the other end of the line a wheeled transfer trolley moves the used flight-bar across to the jigging area for re-jigging. Lines of this sort are often built of concrete (appropriately lined) with the tanks sunk below floor level. Such a line would have tanks 8-9 m long, 2.5-3 m deep and 1- 1.2 m wide, and with three anodizing baths it would have a typical current capacity of 30,000 amps (3 x 10,000) and a production capacity of perhaps 2,000-3,500 tonnes/year of anodized extrusions. **A** typical process sequence would be:

1. Jig.
2. Alkali clean (10 min. at 70°C).
3. Cold water rinse.
4. Etch (sodium hydroxide based solution at 55-60°C for 10-15 min).
5. Cold water rinse.
6. Cold water rinse.
7. Desmut (30% (vol) nitric acid at room temperature).
8. Cold water rinse.

9. Transfer rinse.
10. Anodizing to 25 microns (50-60 min in 165 g/l H_2SO_4 at 20 ± 1°C and 1.5 A/dm^2).
11. Cold water rinse.
12. Cold water rinse.
13. Electrolytic colour (if required).
14. Cold water rinse.
15. Cold water rinse (sometimes deionised water).
16. Seal (40-60 min in deionised water with 1 g/l ammonium acetate at pH 5.5-6.5 and temperature 97-99°C.)
17. Dejig.

The water rinses are generally flowing rather than static and they are appropriately counter-flowed to minimise water usage. In addition, the process sequence is usually arranged to allow double rinsing between major process stages, with one rinse (e.g., rinses 4 and 11 in Fig. 8-9) acting as a 'dirty' rinse and the other as a subsequent 'clean' rinse.

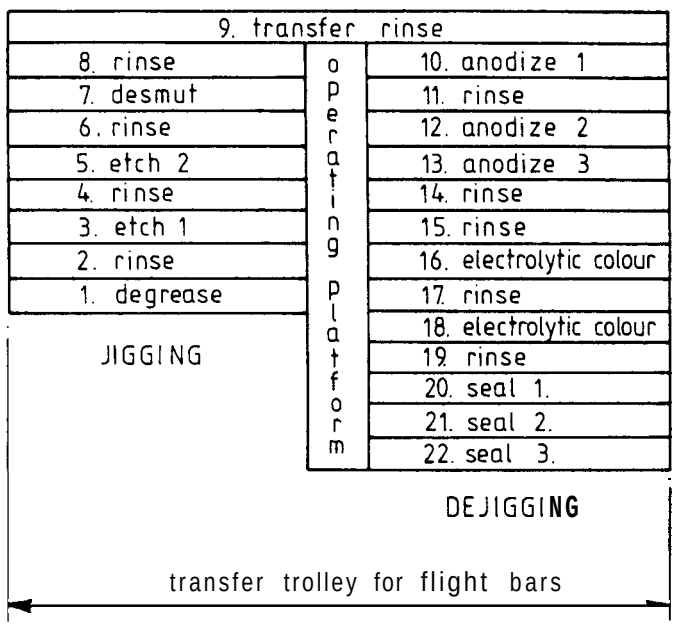


Fig. 8-9. Typical tank arrangement for 'U' shaped architectural anodizing line

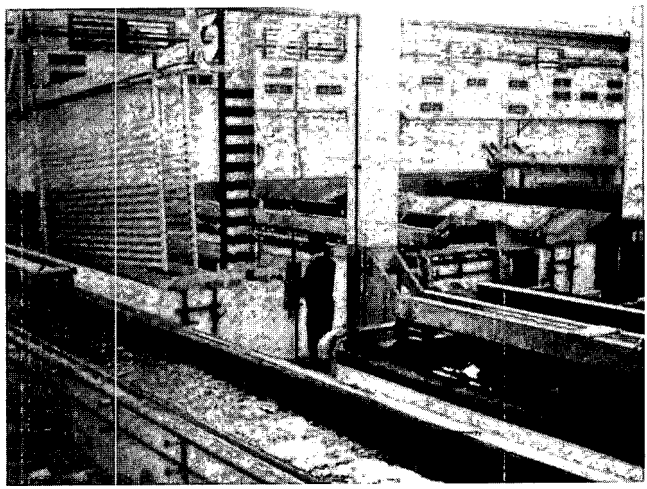


Fig. 8-10. 'U'-shaped anodizing line at Alcan Aluminiumwerke: Uphusen, W. Germany. The pretreatment leg of the line can be seen in the right foreground, the transfer rinse tank in the left foreground, and the anodizing leg of the line in the background

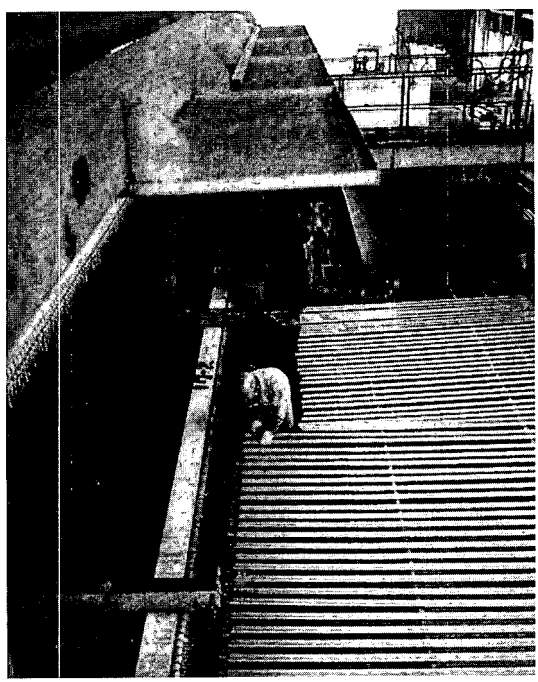


Fig. 8-11. Horizontal jigging of sections for vertical anodizing. (Courtesy of Nippon Light Metal Co. Ltd., Tokyo]

Effluent treatment, recycling and minimising waste are increasingly important factors in anodizing plant design, and a plant in Holland[24] has set out to minimise these problems. This plant has tried to minimise water usage by counterflow and spray rinsing, to reduce drag-over of process chemicals, to improve electrolyte agitation and to recover process solutions wherever possible.

In most European and North American plants the work is essentially jigged horizontally and the longest tank dimension is its length. In Japan, however, many modem anodizing lines carry extrusions vertically, rather than horizontally through the line. Such lines have been described by Patrie,[25] and a comparison between horizontal and vertical anodizing has been made by Shibata.[26] Such a vertical line is shown in Figs. 8-11–8-13. The extruded sections (up to 5 m in length) are jigged on a horizontal table and are then raised to a vertical position for transfer through the line. They are held at one end only, from a clamp that never enters the solution (Figs. 8-11 and 8-14), and the sections essentially hang from the clamps during processing. Only one worker per shift is said to be required to jig work for a line with a capacity of 2,000 tonnes/month. Such a system also lends itself to automatic handling of the sections in the jigging and dejigging areas. Clearly the equipment for such vertical anodizing lines is more complicated than that for a conventional line, and much higher and more expensive buildings are required (typical height 18 m). However such lines have enormous production capacity, and a typical line capable of producing about 24,000 tonnes/year of anodized extrusions has four anodizing baths each with a rectifier capacity of 24,000 A. With a market of over 500,000 tonnes/year of anodized extrusions in Japan, many such lines are now in use.

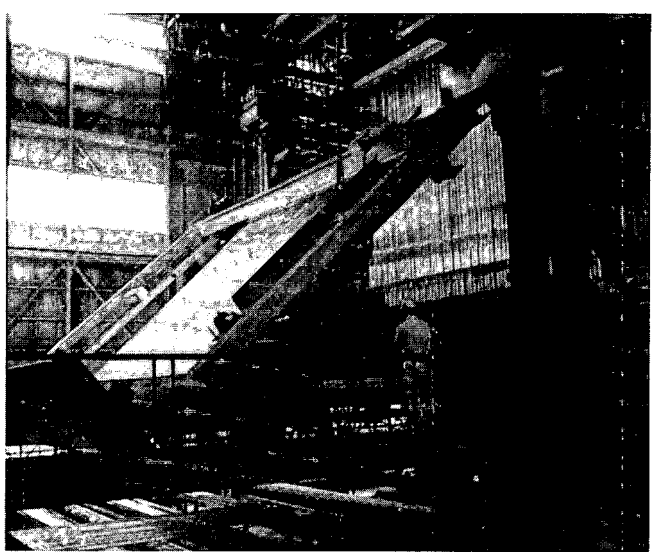


Fig. 8-12. Raising the sections to a vertical position for carrying through the line [Courtesy of Nippon Light Metal Co. Ltd., Tokyo]

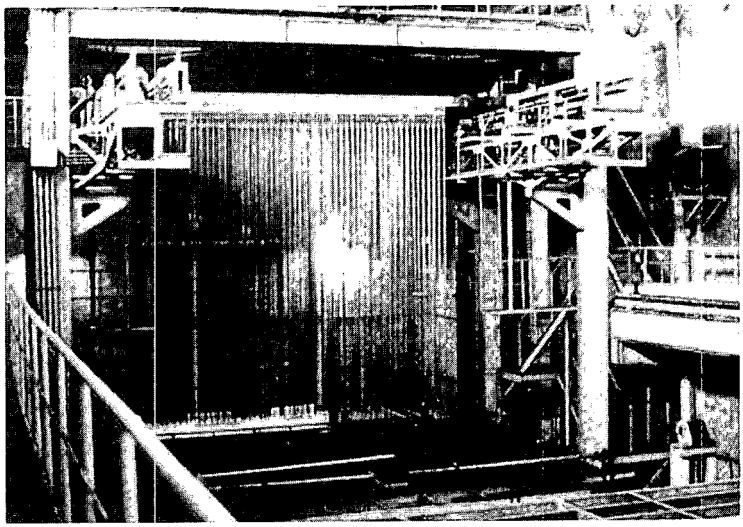


Fig. 8-13. Sections being carried through the vertical line
[Courtesy of Nippon Light Metal Co. Ltd., Tokyo]

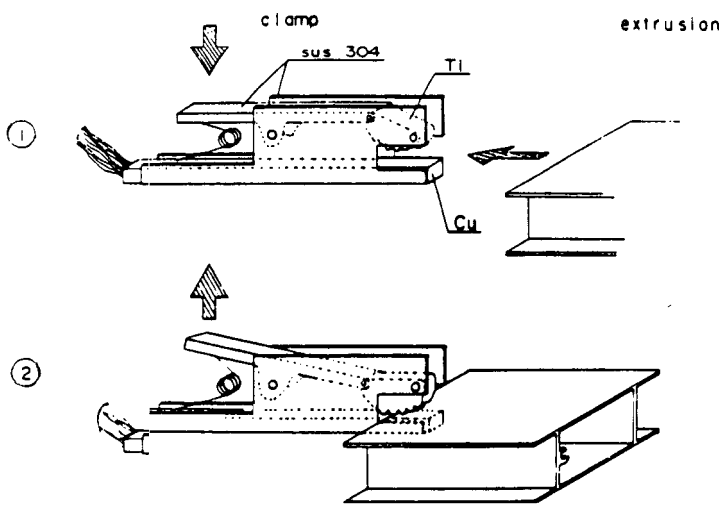


Fig. 8-14. The mechanism of clamping. The clamp is open before an extrusion comes and it closes firmly when inserted. The upper **5** cm of the extrusion always stays out of the (finishing) solutions. Thus, the clamps can be used again after a simple showering of water. The rate of fall-off accident is only 1/100,000[26]

The process sequence in such lines is similar to that in horizontal lines, and all the normal processes can be carried out vertically. The lines usually include electrolytic colouring processes and a large proportion (more than 50%) of the extrusions produced are coloured. The lines do not normally include conventional sealing, as the market demand in the domestic field is for a product that is electrophoretically coated with a stoved clear lacquer coating after anodizing and colouring. With this extra protection the anodic coating thickness can be reduced and is typically about 8 microns. Such a coating operation may originally have been a major reason for the development of vertical anodizing systems, as it is much more difficult to carry out in a conventional line. Current practices in such lines, which now apply a range of electrodeposited organic coatings, have been described by Sato ***et al.***[27]

Another process which becomes possible with vertical anodizing is a differential anodizing process known as 'Stannite', which gives a 'wood-grain' pattern on the anodized extrusions. This process[28] involves a multistage anodizing treatment in which the work is first degreased and etched normally. It is then a.c. anodized in an alkaline electrolyte, which often contains a weak acid capable of barrier layer formation, such as boric acid or tartaric acid. Conductivity of this electrolyte is important and it should be between 1 and 100 m ohms/cm. Such an electrolyte might, for example, contain 0.2 mol/1 sodium metaborate and 3 g/l boric acid, and anodizing would be carried out, using a stainless steel counterelectrode, at a current density of 2 A/dm^2 for 15 minutes. During this treatment a 'wood-grain' pattern develops on the extrusion surface. This is apparently caused by gassing effects which influence the rate of anodizing in different areas, so in order to produce the effect along the length of the extrusions they must be processed vertically. Having produced the wood-grain effect, the sections are etched briefly in caustic soda, presumably to remove the barrier layer of oxide, and then anodized conventionally in a sulphuric acid electrolyte. They are then usually coloured, either electrolytically or using conventional dyeing methods, and in Japan are finally lacquer sealed as already described. Typical effects produced are shown in Fig. 8-15.

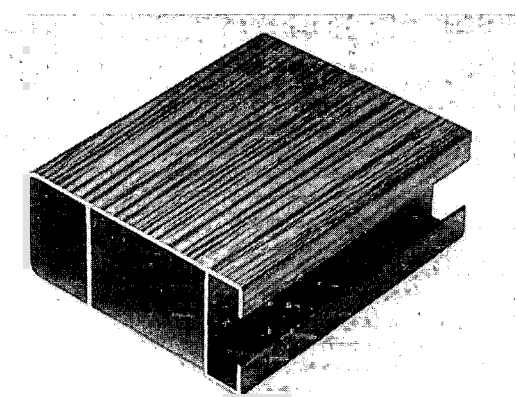
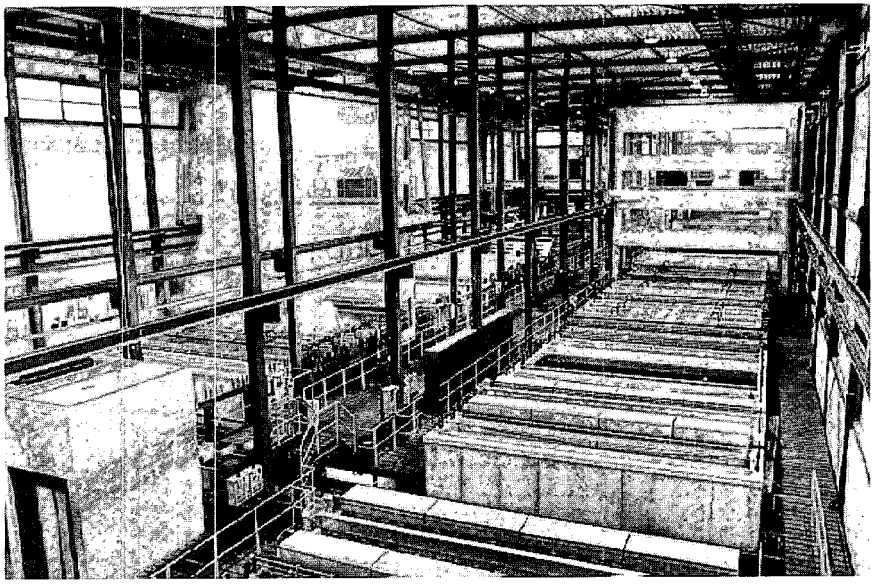
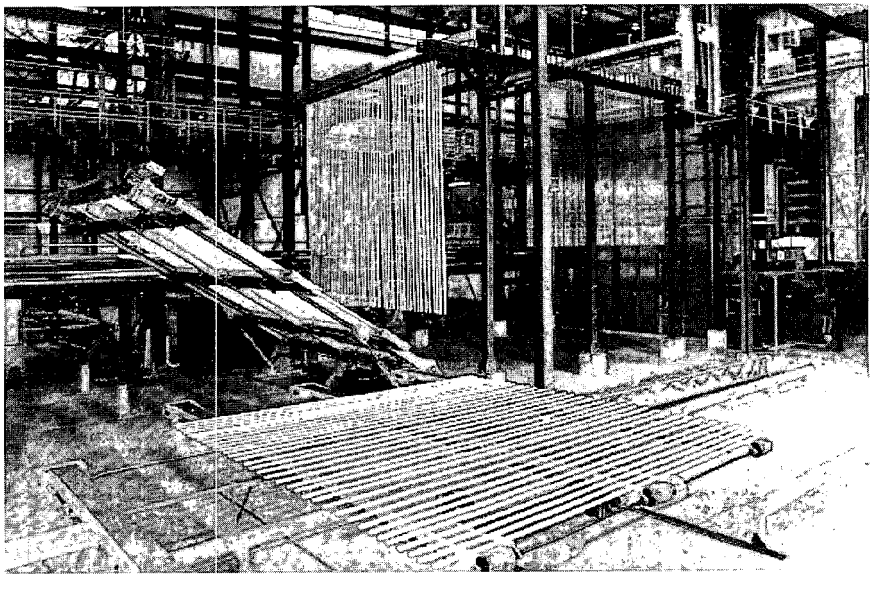


Fig. 8-15. 'Wood-grain' effects produced on extruded section in Japan[28]





Figs. 8-16 and 8-17. Vertical anodizing line at Reynolds Aluminium Holland[7.8]

More recent information" confirms the process parameters but also describes the achievement of these woodgrain finishes by laminating with a printed pvc film. Such vertical anodizing lines have also been installed in Europe in recent times, notably that in Germany at Joseph Gartner and at Reynolds Aluminium in Holland.[7,8] The latter plant, which is illustrated in Figs. 8-16 and 8-17, has a 160,000A capacity and is capable of producing 2,000 tonnes per month of architectural products. The plant uses programmed pulsed rectifiers to ease the problems of uneven current distribution and agitation with deep tanks, and it is capable of electrophoretic clear and white coating as well as conventional sealing. This plant suffered a major fire in 1996[30] just as it was starting production, and it was rebuilt to come into operation in 1998.

However one of the differences between vertical anodizing in Japan and Europe is that the finishes accepted in the market are different. In Japan the vertical lines use a relatively dilute etch for shorter times and at lower temperatures than is usual in Europe, and they rely on the electrophoretic lacquer for the finished appearance. They also use etch recovery systems, which means that they cannot use additives in the etch or go to high aluminium contents. In contrast, in Europe strong etching is used to produce more matt finishes. The degree of etching required presents serious problems with vertical lines, particularly when processing hollow sections. Caustic etching is an exothermic process and the problem is often how to keep the temperature down rather than up! The etching solution contained within a hollow section will get very hot, and in the case of a vertical line it may actually boil out of the end. This means that the etch tank has to be covered to prevent solution escaping, but in doing so the hydrogen evolved is also contained and may give rise to an explosion hazard. For these reasons at least one plant has adopted a spray etching process for a vertical line.

Changing practices in the European architectural market can also cause problems for anodizers and this has been true of the move towards double glazed windows with a 'thermal break' between the outer and inner sections of the window. In some cases this break is provided by a hard polyurethane foam which must be put in place before the finishing operation. The anodizing of such foam-filled sections has been described by Stuckart.[31] He stresses the need for careful design of such systems, the choice of suitable plastics and the careful jigging and handling of such sections. The sealing operation represents the most critical process stage, owing to the high temperatures involved, but very thorough rinsing is also required to minimise solution carry-over.

Other features of plant design

(See also Chapter 7, Section **3)**

A large anodizing plant is a vastly complicated piece of chemical, mechanical and electrical engineering: the following few comments are no doubt obvious to those familiar with the procedures, but nevertheless are worth emphasising.

One of the greatest operational costs is in loading and unloading the jigs, which makes anodizing a labour-intensive process: skill and experience here can make all the difference between profit and loss, and no degree of automation can adequately offset the costs here. The rate determining factor in the whole process is of course the fact that 25 μm coatings require 1 hour at 1.5 A/dm^2. It is necessary therefore to ensure a supply of fully loaded jigs ready to fill the anodizing tanks. The jigs carry both a high current and a heavy load; they must be affixed to non-significant areas or make contact at very small points only. A variety of spring clips and fastenings is used but bolted or clamped (contactsare the favourite means with many operators.

The maximum throughput of a plant is determined by the installed rectifier capacity. A 24 volt silicon rectifier is the most common power source. It is most advantageous to have on-load stepless voltage control from zero to maximum, a constant current control device and automatic provision to return the voltage to zero after completing a treatment cycle but many rectifiers are now computer controlled. Maximum utilisation means that the surface area of each jig load must be calculated in advance to ensure that most of the capacity is employed; it is essential in this respect for the anodizer to have a record of the periphery of the various profiles with which he is concerned. The charge for anodizing will be based on the surface area anyway."

The next point to ensure is that the rectifier output can be handled on a continuous basis. A typical load taking 6000 amperes at 20 volts will represent a heat input of more than 120 kilowatts or 409,920 Btu/hour, all of which has to be removed by the refrigeration system. The latter can be one of the most expensive items in the capital cost of a plant and under-designing can restrict the plant output or cause quality to suffer. The heat taken from the system must be eliminated elsewhere requiring about 85 gallons (380 litres) of water per minute.

Contacts between the bus bars and flight bars need careful design and attention, and flexibly mounted contact pads at the ends of the anodizing tanks are often desirable; flat copper pads attached to the tank and aluminium flight bars are usually used. Contacts between the flight bar and the vertical jig splines must be well maintained, and the splines must have an adequate cross-section to carry the current. Contacts between the cathodes and bus bar also need frequent maintenance, particularly when aluminium cathodes are used. Lead lined tanks are still used occasionally in architectural lines, with the lead acting as the cathode, but shielding of the bottom, ends and part of the side walls is alrnost always necessary, as it is important to ensure that the coating formed is uniformly distributed over the load, and the disposition of the cathodes can play an important part. Aluminium cathodes are widely used, and some plants have central cathode systems, as well as side cathodes, to improve film thickness uniformity.

Dyed coatings

For architectural applications the durability and light-fastness of coloured coatings is of great importance, and early experience of dyed finishes showed that there was a very limited range that were sufficiently light-fast to be used for this purpose. However Sandoz carried out long-term exposure tests on dyed finishes at 13 sites around the world and showed that a limited range, designated as 'Sanodal' colours, could be recommended.[33,34] These included Sanodal Gold 4N, Sanodal Red B3LW, Sanodal Yellow 3GL, Sanodal Turquoise PLW, and Sanodal Deep Black MLW. Such finishes have been used in Europe and other areas. In order to obtain optimum lightfastness, as much dye as possible needs to be absorbed in the film, so the use of 25 micron films and slightly higher anodizing temperatures and sulphuric acid concentrations is often recommended. However care must be taken to avoid producing 'soft' films.

Another general aspect of the use of coloured coatings for architectural purposes is colour matching, and this can be a difficult problem, as not only differences in colouring conditions, but also variation in metallurgical structure or composition of the basis metal, pretreatment conditions, and anodizing conditions can all affect the uniformity of the final result. Building design is also important and large areas of flat panels which are required to match closely need very strict process control to achieve a satisfactory result. In general some colour variation must be accepted and upper and lower limits indicating the extent of this variation need to be agreed between the architect, the fabricator and the anodizer before work commences.

It is true, of course, that the quality of the finish required varies with the distance at which it is seen. Thus, aluminium on an upper storey of a large office building need not present such a flawless surface as on the ground floor. On the other hand, architectural aluminium is required to have a life of many decades and consistency of colour and superior light-fastness are essential requirements.

Sealing

The sealing operation is as important in the service performance of anodized aluminium as the film thickness. The methods of sealing and tests for sealing are discussed in detail in Chapter 11.

Most plants in Europe use deionised water at a temperature of 95-100°C and a pH of 5.5-6.5 for a period of 30-60 minutes. Low pH is particularly detrimental to seal quality and Sheasby[35] has shown that addition of 1 g/l of ammonium acetate as a buffering agent is beneficial in terms of seal bath control and life. Additives are frequently used to eliminate sealing smut formation,[36,37] but they can adversely affect seal quality and they must be used

under careful control. The high cost of energy for sealing has encouraged the development of shorter time or lower temperature seal systems, and these are discussed in Chapter 11. Sealing baths containing nickel or cobalt acetate or sulphate are also used at a temperature below boiling point, and these are particularly useful for dyed work which is subject to leaching at boiling point or, for installations where the latter is difficult to attain, and it is a method more tolerant of impurities in the water. Nickel acetate sealing (or 'fixing') at about 85°C is usually followed by boiling water at 100°C, and is particularly economic. By using plastic balls on a sealing tank as a steam blanket it is found possible to hold the temperature much more easily and with must less power consumption than when the tank top is open, and evaporation losses are very much reduced..

An alternative sealing method is in steam which is also extremely effective provided that the enclosure containing the work is filled with steam under a slightly positive pressure; purity of the water is automatically ensured. The procedure is normally to bring a tightly fitting dome or lid over the sealing tank and fill with steam, a cooling coil being provided for condensation before the tank is opened. In some installations steam is blown into an inverted metal dome which functions like the conventional vapour degreaser used upside down, and the work is lifted into this on a hydraulic platform. Very little steam escapes from the open bottom and it is said to be an effective method.

Organic coatings

Either wax or lacquer is frequently applied to the anodic oxide coating to prevent damage during erection or by contact with plaster or cement.

Wax may be applied by hand wiping, dipping or spraying; electrostatic spray application has been used in large installations.

The best protection is probably given by clear methacrylate or cellulose acetate-butyrate lacquers,[38] but vinyl copolymers have also been used with success in coatings about 0.7-1.2 mil (18-30 μm) thick.[16]

In a method designed to test the efficiency of lacquers for protection against building materials,[38] a blob of wet cement mixture made of 5 parts by weight sand, 2 parts by weight cement and 1 part water is placed on the lacquered surface and examined after seven days.

More positive protection than is afforded by either wax or methyl methacrylate is often given (and paid for) by applying low-tack adhesive tape to all significant surfaces, and these are not removed until erection is complete. Tapes must be tested however to ensure that they remain strippable.

A further useful procedure with assembled and glazed window frames is to encase the whole assembly in a large polythene bag where it remains until the building is complete, when the bag can be cut away but still leaving the built-in faces with the protection of a layer of polythene for the rest of their life.

Assembling anodized architectural parts

Window frames fitted into masonry, metal or wood surrounds are commonly protected by alkali-resistant bituminous paint. In contact with wood, creosote or zinc naphthenate may be safely used as preservative.[39] Sodium silicate or phosphate may be used to give water proofing, though preservatives containing copper, and lead primers, must be avoided. Putties of the whiting/linseed oil type are satisfactory when applied to anodized aluminium or to metal which has been coated with an etch- or zinc chromate primer.

Steel in contact with aluminium may be sprayed with aluminium or painted with a zinc chromate primer. Alternatively, neoprene washers or strip may be used to separate the metals.[40] Screws, nuts or bolts when they are not of aluminium may be of stainless steel or of mild steel plated with chromium or cadmium. Stainless steel screws, coloured to match bronze or black finishes produced by electrolytic colouring or integral colour anodizing, are available in some countries.[41]

Anodizing does not always give satisfactory protection for aluminium which is in direct contact with zinc, steel, concrete[42] or oak or chestnut timbers[5] in buildings.

While it is often possible to assemble architectural aluminium panels after anodizing, there are some instances in which welded components must be used. Satisfactory joints are possible by flash welding with carefully designed electrodes. Where this is not possible, 'back' welding may be used and the thin dark line at the weld may frequently be worked into the finished design.

Maintenance cleaning

Cleaning of anodized architectural aluminium is very important if the finish is to be preserved. Fox-Williams and Watts believe that dirt which settles on the surface holds moisture and forms corrosion cells if allowed to remain,[43] and it is certain that anodized finishes on accessible surfaces, e.g. shop fronts, window frames, etc., have an appreciably longer life than surfaces which are cleaned infrequently. This effect is so pronounced that areas which are frequently cleaned may be anodized with thinner coatings, e.g., 15 μm (0.6 mil), without suffering undue deterioration. Equally it means that areas that are exposed to pollution but are not accessible to rain washing, such as the underside of a canopy, need particular attention and maintenance.

Cleaning compositions using anything but very mild abrasives are unsuitable for anodized aluminium as they may damage the coating. Hiibner and Schiltknecht[44] give the following formula for 'Lumiclean', a mild polishing and cleaning composition for anodized aluminium which is used once or twice a year for cleaning architectural anodized material:

bentonite	6.0%
liquid paraffin	8.0%
slaked lime	10.0%
wetting agent	0.5%
oil of wintergreen	0.05%
water	75.45%

To prepare this compound, the bentonite is mixed into four fifths of the water and allowed to stand with periodic stirring for about 5 days. The slaked lime is stirred into a paste with the remainder of the water and this and the other ingredients are added to the bentonite paste with stirring for 10-20 minutes. The cleaning compound is wiped on to the surface with a soft cloth, allowed to dry on the work and wiped off with a clean cloth.

Much work on the cleaning of anodized aluminium has been carried out in Germany in recent years,[45] and special cleaning formulations have been developed.[46,47] Whilst the benefit of suitable abrasive cleaning treatments is recognised, the high cost and labour involved in such cleaning methods has led workers to seek alternatives. These take the form of acid-based cleaners using acids such as tartaric acid, citric acid, acetic acid, lactic acid, certain esters of phosphoric acid and in some cases nitric acid. Stronger acids such as hydrofluoric acid, hydrochloric acid, sulphuric acid and phosphoric acid have been shown to cause serious film damage.[47] A test, in which the anodized aluminium is immersed in the cleaner for 8 hours at 20-22°C, has been developed,[45] and after drying no visible colour change, no surface dulling, no loss of anodic film thickness and no change in admittance value on the tested samples are acceptable. The formulations developed are said to have equal cleaning effect to abrasive cleaning in most circumstances.

These investigations have also led to general cleaning recommendations being produced by Aluminium Zentrale in conjunction with the German anodizing industry.[48] This covers vitreous enamelled and painted aluminium surfaces as well as anodized aluminium. For the **latter** it recommends that the initial cleaning treatment, at the time of completion of the building, should be an abrasive clean using materials such as pumice powder or fine grades of Scotchbrite. After thorough rinsing with water containing a neutral wetting agent, a preservative which leaves a water repellent film on the cleaned surface should be used. Subsequent cleaning at regular intervals is required to maintain appearance, but the severity of this and the intervals between cleaning will depend on the pollution and aggressivity of the atmosphere at the site.

The British Standard BS 3987 : 1991[9] gives similar general recommendations in an Appendix on maintenance which offers the following advice:

'Regular cleaning is essential if the finish of anodized aluminium is to be preserved over the years. Deterioration of the anodic coating can occur mainly as a result of grime deposition and subsequent attack by moisture, particularly when it is contaminated with sulphur compounds. Deposited grime retains the contaminated moisture on the anodized surface, permitting attack to proceed and thereby damaging the anodic oxide coating which cannot be renewed! *in situ*.

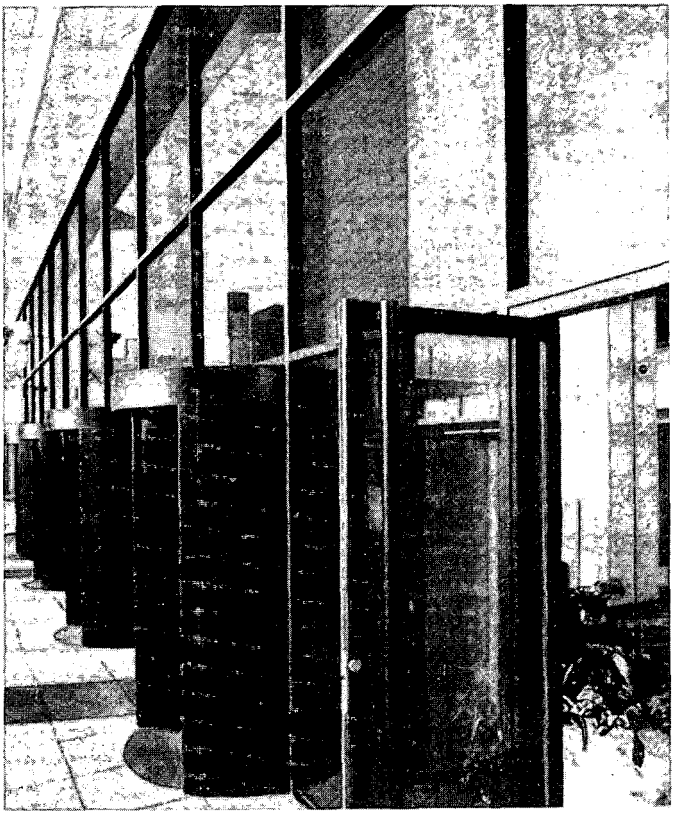


Fig. 8-18. Black Anolok electrolytic finishes used on American Express Building, Brighton, U.K.
[Courtesy of British Alcan Aluminium Limited]

'The frequency with which cleaning should be carried out will range from monthly to six monthly intervals according to the degree of contamination of the service environment. The aim of the cleaning operation should be the removal of grime deposited on the surface without damage to the anodic oxide coating.

'The cleaning method to be adopted depends on the degree of deterioration that may already have occurred and by the scale of the operation. Hand rubbing is often used for small work, but large expanses, as in multi-storey buildings, call for carefully controlled methods of loosening adherent deposits.

'The anodized aluminium should be washed down with warm water containing a suitable wetting agent or with a mild soap solution. Fibre brushes may be used to loosen attached grime but the use of emery, sand paper, steel wool or other

abrasive materials, and acid or alkaline cleaners should not be permitted as they damage the anodic oxide coating. It is essential to rinse thoroughly after cleaning using copious applications of clean water, particularly where crevices are present. Where greasy deposits are concerned, cleaning may be by means of a soft cloth dipped in white spirit. After cleaning, the anodized aluminium may be treated with a good quality wax polish.

'Since emulsion cleaners or proprietary chemical agents may attack the anodic oxide coating, they should never be used except in consultation with companies specialising in the cleaning of anodized aluminium.'

The European Standard EN 12373 : Part 1 recommends in Annex E that only cleaning agents with a pH in the range of 5-8 should be used, and that they should be tested in contact with anodized aluminium before use. In terms of abrasion, only cleaning materials which have been found not to scratch or otherwise damage the anodic coating should be used.

In considering the behaviour of anodized aluminium installations in principally industrial urban atmospheres, such as in Paris, Darnault[49] has distinguished four stages. In the first the deposits of grime can be readily removed by washing with a sponge and water containing a wetting agent, which is the case where maintenance is carried out more than once a year. In the second stage the grime deposits yield less readily and require a very fine abrasive powder for restoring the surface, which is the case when cleaning is carried out less than once a year. In the third stage where the surfaces are not cleaned for four or five years a more vigorous action is required where an abrasive pad must be applied. The fourth stage is reached when the surface has received no maintenance for a period of about ten years when the grime has become so ingrained in the surface that the original appearance can only be restored by the use of mechanical cleaning appliances.

Quality schemes

It was originally intended that the BS 3987 should form the basis of a Kite Mark scheme administered by the British Standards Institution, which would give assurance that the goods complied with the British Standard under a system of supervision, control and testing operated during manufacture, and including periodical inspection at the manufacturer's works in accordance with the certification mark of B.S.I. This intention was overtaken by the establishment in 1974 of an European quality labelling scheme for architectural anodizing under the name Qualanod. This scheme was established jointly by the European Wrought Aluminium Association and the European Anodizers Association, with the headquarters of Qualanod International in Zurich. This scheme now covers 127 anodizers in 18 countries in Europe.

Each country has its own national Qualanod organisation which is responsible for administering the scheme in that country, and independent inspectors are used

to visit licensees to check that plants are capable of producing the required quality and that satisfactory quality is being maintained. After appropriate examination of an anodizer's facilities and satisfactory testing of the quality of his architectural products, the anodizer is licensed to use the registered Qualanod quality label. Rules for the granting of the Qualanod licence and subsequent quality inspection are laid down in a specification document." This specification details minimum requirements for properties such as anodic film thickness and seal quality and uses the appropriate I.S.O. and CEN standards to evaluate these. It gives guidance on plant and process parameters needed to ensure adequate product quality and lays down rules for the independent Qualanod inspectors.

For example in the initial granting of a Qualanod licence the following conditions must be met:

1. Two inspections are carried out and these are made at the request of the anodizer but without prior notice being given to him of when the inspections will take place.

2. The testing apparatus in the plant is checked to see that at least two instruments for thickness measurement (using the eddy current principle) and at least one apparatus for admittance measurement, is available and functional. An analytical balance is also required so that acid dissolution tests of seal quality can be carried out.

   Finished architectural products which have been tested and released by the internal plant inspectors are then examined for quality. Sampling is carried out on a statistical basis (Table 8-4), but at least half a shift's production must be available and at least 30 pieces must be checked. Thickness is checked in accordance with the required thickness grade using ISO 2360 (eddy current method), and sealing quality by means of ISO 2143 (dye stain test) or 2931 (admittance test). At least one sample, however, must be checked for seal quality using the referee acid dissolution test, ISO 3210 (chromic acid-phosphoric acid dissolution test). Limit values for all these tests are laid down in the specification.

4. The inspector then reports the results of the inspections to the committee responsible for granting the licence and if the results of both inspections were satisfactory the licence to use the quality sign will be granted.

If the result of either inspection does not meet the requirements, the anodizer may apply for further inspection of his plant. This inspection covers the examination of the whole plant facilities and operating procedures employed, and again these must satisfy the Qualanod specification requirements. If they do, further satisfactory inspection of the apparatus and finished product quality will allow the granting of a licence.

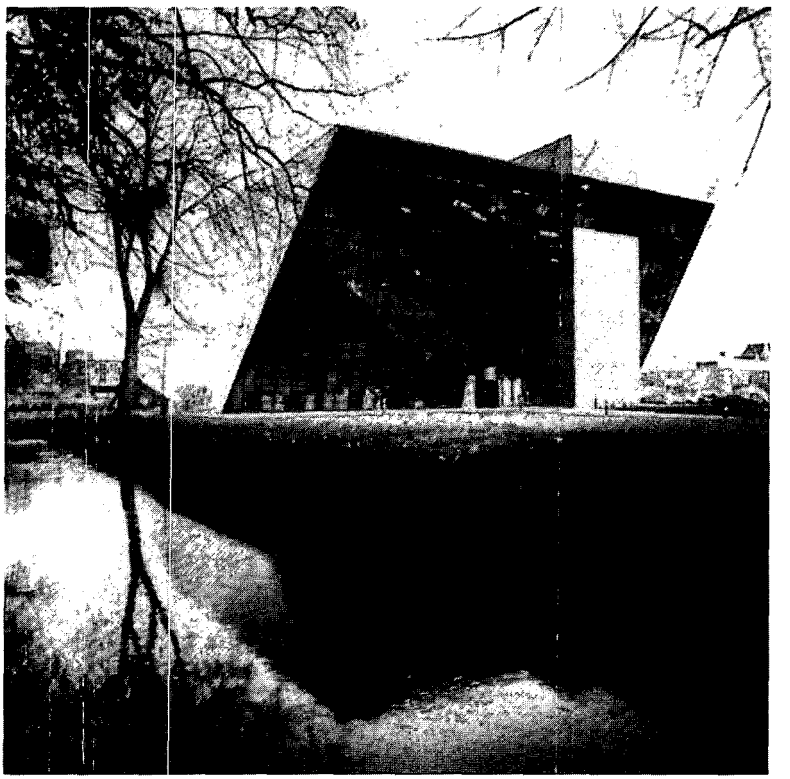


Fig. 8-19. Sandalor blue finishes used on the Equitable Life Assurance Building, Aylesbury, U.K.
[Courtesy of Josef Gartner and Co. (U.K.) Ltd.]

In the plant inspection, factors such as tank design, refrigeration capacity, heating capacity, power supplies, electrolyte, agitation, cross section of jigs and jig contacts are taken into account. Limits on anodizing electrolyte composition and temperature and sealing conditions are also specified.

Routine inspections, of which there must be at least two per year, proceed along similar lines. If results of product and subsequent plant inspections are both unsatisfactory, two further product and plant inspections are carried out within the following two months, and if any of these subsequent inspections are unsatisfactory, the authority to use the quality label is withdrawn.

TABLE 8-4

Number of samples to be inspected according to lot size[12]

* *Lot size*	*Number of samples to be inspected (random selections)*	*Acceptance limit for substandard samples*
1 - 10	all	*0*
11 - 200	10	1
201 - 300	15	1
301 - 500	20	2
501 - 800	30	3
801 - 1300	40	3
1301 - 3200	55	4
3201 - 8000	75	6
8001 - 22,000	115	8
22,001 - 110,000	150	11

* **A** lot is defined as a complete order of a customer or the part of it which is in the works.

The scheme allows thickness classes of 5, 10, 15, 20 and 25 microns (minimum average thickness) of which classes 5 and 10 are for internal applications and 15, 20 and 25 for external applications. The choice of thickness class to be used is dependent on the relevant national standards.

The Qualanod regulations are under constant review and international committees amend both the technical and commercial aspects of the regulations when necessary.

Coloured finishes in architecture

While sulphuric acid coatings on Al-Mg-Si extrusions and Al-Mg sheets are the principal materials which find their way into large buildings, there has been an increasing interest in coloured finishes which are permanent and lightfast. In 1970 something like 10,000 tons of anodized aluminium were used in building projects in Britain, and about 10% of this would have been finished by some colour process. In 1983 the figure was nearer to 40,000 tons, but still only about 10% was coloured. In the U.S.A., Japan and several European countries there is a considerably greater consumption of aluminium extrusions and sheet in architectural work. Japan, in particular, uses enormous quantities of aluminium for both domestic and monumental architectural projects and, as with some countries such as Germany and Italy, the proportion of coloured work is very much higher than in the U.K.

Coloured finishes for architectural work can be produced in one of the following ways:

1. By integral colour anodizing using special electrolytes containing organic acids in which the coating becomes coloured by incorporation of metal or intermetallics from the alloy or anode decomposition of the electrolyte.

2. By anodizing in sulphuric acid and subsequently colouring by:
   A. Organic dyestuff
   B. Inorganic pigments
   C. Double decomposition to form inorganic pigment *in situ*
   D. Electrolytic decomposition from an electrolyte containing metallic salts *to* form coloured deposits.

3. By the use of special alloy compositions which either yield a coloured finish with sulphuric acid anodizing or enhance the colour in the case of the processes used in Group 1.

If 1950-1960 was the decade of chemical brighteners then the subsequent decade spawned integral colour anodizing processes in like profusion, to be followed in the 1970s by electrolytic colouring procedures, which have now largely taken over the architectural colour anodizing market. These developments will be briefly surveyed in the following pages.

2. INTEGRAL COLOUR PROCESSES

Early processes

The origin of the term integral colour is uncertain but it is the sort of phrase invented *to* give a new look to an old idea. It is old of course because the use of oxalic acid dates back to the Japanese patents of 1923,[50,51] which under appropriate treatment conditions give a very hard anodic coating which is coloured from pale yellow to deep bronze. The colour however was always one of its least predictable features because it required a thick coating for its full development, was much better when alternating current was employed, and the requirements for producing a consistent colour were not understood. The process was used in Britain before the war and the British Aluminium Company have had samples exposed out of doors without significant deterioration for 45 years.

In the 1930s also, the sulphonic group of acids, which play a very prominent role in current integral colour processes, were investigated by Schering in Germany, more for the valuable film properties that could be

obtained than for the colour effects. Their patents relate to anodizing with the sulphonation products of organic compounds containing oxo- or oxy- groups, such as aromatic phenols, cresols and thymols, naphthols, anthraquinone and sulphobenzoic acid, alone or preferably with the addition of sulphuric acid or sulphates. Sulphosalicyclic acid is specifically mentioned.

Kalcolor process (U.S.A.)

The name that has become principally connected with integral colour or 'hardcolour' anodizing processes has been the Kalcolor process of Kaiser Aluminum. The main constituent of the electrolyte is sulphosalicylic acid to which is added a small proportion of sulphuric acid or metal sulphates.[54,55,56,57,58,59,60,61,62]

Table 8-5 gives the preferred operating conditions as disclosed in the patents, the sulphuric content requiring to be less than 1% for coloured films; and Table 8-6 gives examples of the colours produced on various alloys under specified operating conditions.

TABLE 8-5

The Kalcolor process[55,56,60]

		Preferred composition	*Examples*	
			A	B
Sulphosalicylic acid	g/l	70-150	100	100
Sulphuric acid **(or** metal sulphates)	g/l	3-40	5	5
Temperature	°C	22	22	25
Current density	A/dm^2	2-3	2.9	2.6
Voltage		25-70	25-60	50-60
Time	minutes	20-45		

For coloured films the sulphuric acid content should be less than 10 g/l.

TABLE 8-6

Colours obtained with the Kalcolor process[56]

Alloy	Colour	Initial current density (amp/ft²)	Time to maximum volts (minutes)	Maximum volts	Total anodizing rime (minutes)
5005 clad with 5005 (sheet)	Amber grey	24	20	50	30
5005 clad with 5005 (sheet)	Charcoal brown	24	35	60	45
3003 clad with 3003 (sheet)	Dove grey	24	10	50	20
3003 clad with 3003 (sheet)	Charcoal grey	24	20	65	40
5085 (sheet)	Black	24	25	65	40
5086 (sheet)	Grey	24	15	50	20
5357 (sheet)	Light brown	24	20	50	30
5357 (sheet)	Brown	24	30	60	45
6063-T5 (extrusion)	Amber	24	20	50	30
6063-T5 (extrusion)	Light brown	24	35	60	45

The colours obtained with the Kalcolor process depend on the basis metal composition, current 'density, voltage, film thickness and electrolyte composition, particularly the sulphate and aluminium contents. It is necessary therefore to control all these factors carefully in order to obtain a consistent colour in the finished product. Example **A** in Table 8-5[55] is processed at constant current density involving a voltage rise to 60, while in Example B[56] the current density is held constant until some prearranged voltage between 50 and 65 is reached, and thereafter the voltage is held constant and the current allowed to decline naturally. The time of treatment is varied according to the colour desired.

It is clear therefore from the high current densities and the high voltages used that the equipment required is considerably more expensive than for the sulphuric acid process, and the heat to be removed is four or five times as great so that refrigeration must also be on a much larger scale. This begins to explain why integral colour anodizing processes of this type are considerably more expensive than sulphuric acid anodizing.

A further feature which distinguishes the Kalcolor, in common with other similar processes, from the sulphuric acid process is the necessity to maintain the aluminium content not only at fairly low level but also within close limits, or **it** becomes difficult to obtain reproducible results, particularly with respect to uniformity of colour and thickness of the anodic coating. The aluminium content[57] should be held within 0.5 g/l of some predetermined value between 0.1 and 13 g/

1, but within these broad limits it is desirable that the aluminium content be held between 1.5 and 3 g/l and within ±0.25 g/l of the selected value. This control is effected by means of a cation exchange resin such as the hydrogen form of a strongly acidic sulphonated copolymer of styrene and divinylbenzene with 8% divinylbenzene cross-linking (e.g. Dowex 50W-X8). The resin is contained in a stainless steel tower and after about 12 hours use the electrolyte is passed through the resin at 4.5 1 per minute for 60-90 minutes when each 0.08 m^3 will remove about 1 kg of aluminium. After rinsing the resin is reconstituted with sulphuric acid, about 450 1 of 10% acid removing 1 kg of aluminium from 0.08 m^3 of resin.

Kalcolor finishes were available in gold, light amber, amber, statuary bronze, light grey, medium grey, dark grey and black on sheets and extrusions, and Kalcolor casting alloys were available for the gold, bronze and black colours. Whilst the colour range could be achieved using two standard alloys for extrusions and three for sheet products, special sheet, extrusion and casting alloys were developed for use with the process. These were designed either to give faster production of the darker end of the colour range or to give specific colours such as grey or black, and they are described in section 3 of this chapter.

With any colour anodized finish it is essential to establish acceptable top and bottom limits as some degree of variability is inevitable with all anodizing processes.

The Kalcolor coatings were extremely dense and abrasion resistant, comparable with hard anodized finishes produced in sulphuric electrolytes at low temperatures. Depending on colour, the thickness varied from 0.72 to 1.25 mil (18-31 μm), the coating weights from 32 to 59 mg/in^2 (5.0-9.1 mg/cm^2), and the apparent density from 2.72 to 2.93 g/cm^3.

In one variation of the process it was proposed to obtain a brighter and more lustrous finish by first anodizing for a short time in sulphuric acid before Kalcolor treatment.[59] The initial anodizing could be for one minute or less, or the preformed sulphuric coating could be up to 8 μm thick. The same idea has been claimed by Vereinigte Aluminium Werke[81] and also by Reynolds Metals Company[63] who have referred to it in a patent which predates both the other two.

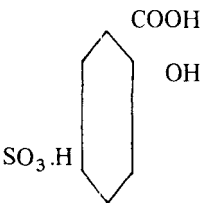
Integral colour anodizing is essentially a much more difficult proposition than ordinary anodizing but there is no doubt that the Kalcolor process was highly successful because of the immense research effort put into it, as hundreds of buildings over the whole world testify. It was also the first to be commercially launched and it was only to be expected that it would be followed by a large number of comparable processes.

Duranodic-300 process (U.S.A.)

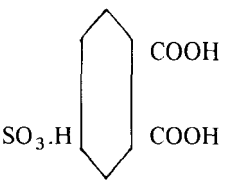
First and principal among the successors to the Kalcolor process was the Duranodic-300 process developed by the Aluminum Company of America, which followed it chronologically by an interval of 2-3 years. It was based on a similar type of electrolyte, utilised very similar principles of operation and yielded products which were practically impossible to distinguish from Kalcolor by

observation. The main electrolyte component was sulphophthalic acid which, like sulphosalicylic acid, is a derivative of sulphuric acid or a sulphonated acid having a higher solubility and conductivity than the organic acid from which it is prepared, but it could equally be another sulphonic acid covered by a group of closely related patents.

sulphosalicylic acid



sulphophthalic acid



The preferred electrolyte composition range as disclosed in the relevant patent specification[64] is shown in Table 8-7, and Table 8-8 gives specific examples.

It will be seen that the presence of a small and controlled proportion of sulphuric acid is necessary for the operation, and that in nearly all respects the Kaiser and Alcoa processes are closely comparable. The coatings produced are coloured and have an extremely high abrasion resistance. Electrolytes A and D are preferred for producing coloured coatings of high abrasion resistance at room temperature., but E and F, where the proportion of sulphuric acid is much higher, give light coloured coatings unless the temperature is lowered to 10°C. Using example A at 24°C and 24 amp/sq ft (2.59 A/dm^2) a coating of 25 μm is built **up** in 30 minutes during which time the voltage increases from 32-70 volts. The colours vary from dull gold on pure metal, through bronze on 6063 alloy to black on 7075 alloy. (Table 8-9).

TABLE *8-7*

Operating limits in the Duranodic-300 process[64]

4-sulphophthalic acid or 5-sulphophthalic acid	70-130 g/l
sulphuric acid	3-10 g/l
temperature	15.6-32.2°C
current density	12-36 amp/sq ft (1.3-3.9 A/dm^2)

TABLE 8-8

Examples of the Duranodic-300 process[64]

Electrolytes		*A*	*B*	*C*	*D*	*E*	*F*
4-sulphophthalic acid	g/l	100	–	10	75	50	75
5-sulphophthalic acid		–	88	–	–	–	–
sulphuric acid	g/l	8	7	1	10	100	65
water		balance					

TABLE 8-9

Colours obtained with the Duranodic-300 process

Alloy designation	*Nominal constituents (%)*	
1100	normal impurities	dull gold
5052-H34	2.6 Mg, 0.25 Cr	pale yellow
6061-T6	0.6 Si, 0.3 Cu, 1 Mg, 0.25 Cr	black
6063-T5	0.4 Si, 0.7 Mg	bronzes
7075-T6	1.6 Cu, 2.5 Mg, 0.3 Cr, 5.6 Zn	black
8013	0.35 Cr	gold bronze

It is difficult to make comparisons between the Kalcolor and Duranodic processes as they are basically so similar, but over a period of time it seems that the use of sulphophthalic acid, rather than the use of sulphosalicylic acid, has become dominant in both processes. This seems largely to be because it makes production of the darker bronze finishes easier and makes the process less dependent on the use of special alloys, particularly in the case of extrusions. Special alloys are, of course, still required to produce the grey finishes. The Duranodic process has not been operated in Britain, but it has been used in Europe and there are many examples of prestige buildings produced using this finish.

Other integral colour processes

Succeeding years saw the introduction of a number of integral anodizing processes, most of which emerged from the research laboratories of the major aluminium producing companies. The following names have been associated with some of these commercial processes:

Kaiser Aluminum and Chemical Corporation	Kalcolor
Aluminum Company of America	Duranodic-300
Vereinigte Aluminium Werke	Veroxal
Swiss Aluminium Company	Permalux
Istituto Sperimentale Metalli Leggeri	Acadai
Péchiney Cie	Eurocolor 100
Hungarian Light Metals Institute	Autocolor - HSH
Reynolds Metals Company	Reynocolor
Sumitorno Chemical Industries Co. Ltd.	Sumitone
Kawneer	Permanodic
Aluminium Laboratories Ltd. (Alcan)	Alcanodox

Features common to integral colour processes

It will be appropriate next to consider what the various colour anodizing processes based on special electrolytes have in common. It will emerge in fact that sulphuric acid is the unique electrolyte in that it produces, at low voltage, transparent coatings, the properties of which can be varied widely from extreme hardness to a soft powder by adjusting the conditions; no other anodizing system possesses this versatility.

In order to produce hard compact coatings it is necessary to reduce the capacity of the electrolyte for attacking the anodic film; this is most readily done by reducing the temperature, but it is found that in order to maintain the current density the operatin;; voltage has to be raised. and when this is done, yellow, brown or grey colour effects start to appear in the coating. By lifting the current density further these effects become enhanced so that deep black coatings can be produced even on 99.99% purity aluminium. Now, while this has been done frequently in order to obtain hard coatings, as explained in Chapter 9, the colour effects in these cases have always been regarded as quite incidental or even a nuisance, and little thought has been given to securing uniformity of colour or exploiting the feature. Scott'" has investigated the effect of various operating conditions on the appearance, coating thickness and abrasion resistance of films produced on 99.0% aluminium sheet. Table 8-10 gives the colours obtained by Scott, those in italics requiring conditions which he considered could be used for decorative work. Those marked with an asterisk had a mottled appearance to varying degrees, consisting of a silver background with islands of thicker dark brown oxide, which is quite a familiar phenomenon according to the literature on integral colour anodizing.

The activity of the sulphuric acid can also be reduced by lowering the concentrations, and Csokán[66] has investigated the use of dilute sulphuric acid at 1% concentration. He reports a similar type of film formation, namely, an initial light coloured film followed by a secondary growth of darker film starting at isolated centres and spreading out radially with more and more centres appearing

TABLE 8-10

Self colour of hard anodic oxide films on 99% aluminium[65]

Electrolyte temperature	*0°C*			[redacted]			*+10°C*			
Anodizing time (minutes)	*20*	*40*	*80*	*20*	*40*	SO	*20*	*40*	*80*	
Current density (A/ft^2)										
20	brown*	brown*	*brown†*	brown*	brown*	dark grey	grey*	grey*	brown*	2½% H_2SO_4
40	*grey brown*	*brown*	*black*	light brown	*brown*	*black*	brown*	brown*	*brown black*	
80	*brown*	*black*	*grey black*	*brown*	*black*	*grey black*	*brown*	*brown black*	*grey black*	
20	silver* grey	*brown grey*	*brown*	light grey*	grey	*grey brown*	silver*	silver grey	*light grey*	5% H_2SO_4
40	brown grey	*brown*	*brown black*	*yellowish grey*	*brown grey*	*brown black*	*light yellowish grey*	*grey brown*	*dark brown*	
80	*brown*	*brown black*	*grey black*	*dark brown*	*black*	*grey black*	*grey brown*	*dark brown*	grey black	
20	silver* grey	*light yellowish grey*	*light grey*	silver grey*	*silver grey*	*light grey*	silver*	*silver*	*light grey*	10% H_2SO_4
40	*yellowish grey*	*light grey brown*	*brown black*	*light yellowish grey*	*lightgrey*	*brown black*	*light yellowish grey*	*yellowish grey*	*dark brown*	
80	*light grey brown*	*warm black*	*black*	*bronze*	*brown black*	*grey black*	*yellowish grey*	*dark brown*	grey black (patchy)	

* Mottled.

† Italics indicate that the process **is** considered to be suitable for decorative work.

until the whole surface is eventually covered with the darker secondary growth. Japanese workers[67] have produced amber coloured films in sulphuric acid by using pulsed currents, and Alcoa[68] have used low voltage anodizing in sulphuric acid to give bronze or grey coloured finishes. This latter work has already been referred to in Chapter 7 (page 490).

A similar idea prompted the study, by Herenguel, in France[hy], of weaker electrolytes based on sodium bisulphate for the formation of hard coatings at high speed, while the Schering patents,''[53] as already mentioned, were designed to reduce the activity of sulphuric acid by sulphonation. However none of these studies was concerned principally with colour. Oxalic acid seems to have the right anodizing characteristics when used alone for producing coatings at once thick, hard and coloured but not coloured quite deeply enough.

Now, when the integral colour systems are examined they can nearly all be regarded as methods of anodizing in very dilute sulphuric acid since a small amount is essential for the correct operation of most, or they can be regarded as systems where the aggressive sulphuric acid is modified by sulphonation. The carboxylic acids feature prominently but hardly ever without the presence of sulphate.

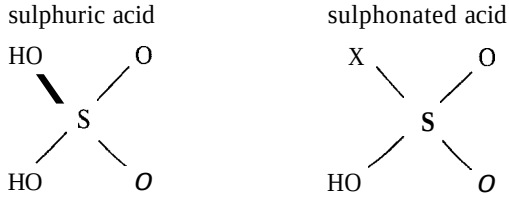
The integral colour processes all operate at current densities which are two or three times higher than is normally used in sulphuric acid anodizing; they all require high voltages up to about 80V; they operate at temperatures of 25-30°C, requiring good refrigeration to extract the high heat output; they require very careful control of the electrolyte composition; and finally the colours which they produce are restricted to the greys, browns and yellows, through deep bronze to black.

Acids used in integral colour processes

The following acids have been noted as appearing in the integral colour anodizing systems that have been proposed or operated:

- oxalic acid
- sulphosalicylic acids
- sulphophthalic acids
- sulphoresorcinol
- chromotropic acid
- naphthalenedisulphonic acids
- sulphamic acid
- cresolsulphonic acid
- sulphomaleic acid
- glycollic acid
- maleic acid
- succinic acid
- citric acid
- propionic acid
- tartaric acid
- formic acid
- substituted succinic acids
- sulphoanthranilic acid
- malonic acid

The list may not of course be complete. It includes a number of dibasic carboxylic acids (including formic acid if one may allow for a hydrogen bond between two molecules) and sulphonated acids of the general formula $SO_3H.X$ where X is an aromatic acid radical:



The aromatic acids such as salicylic, phthalic, resorcinol, anthranilic, chromotropic, etc. have a low solubility and a low conductivity, but sulphonation renders them much more suitable for anodizing systems. Sulphamic acid has the similar formula $SO_3H.NH_2$ and the substituted succinic acids are hybrid specimens.

The traditional anodizing acids, chromic, sulphuric and phosphoric acids, have a considerable solvent power for aluminium oxide (i.e. field-assisted), with the result that the useful coating thickness that can be formed is limited to 6 microns in the case of chromic acid, about 3 microns for phosphoric acid and 35 microns for sulphuric acid unless the normal conditions are departed from. Oxalic acid is better in that 100 microns or more may be reached, and this must be regarded as the original integral colour process. The organic electrolytes are formulated into balanced mixtures which have just the correct properties for forming hard porous coatings, normally with a rising voltage characteristic, which are also coloured. We will refer to the various processes that have been mentioned in the literature, but the proliferation of electrolyte types seems to have been motivated by commercial rather than technical reasons.

Oxalic-sulphuric acid electrolytes[70]

Given the general proposition that most electrolytes function better with a small amount of sulphuric acid, it is logical to extend this principle to oxalic acid, and this has been done by the Aluminum Company of America who claim that a lower voltage and therefore less cooling can be used.

An essential part of the process is to control the ratio of oxalic acid to sulphuric acid at a high value. If $R = (COOH)_2.2H_2O/H_2SO_4$, then the minimum value of R is related to the temperature in °F by the formula $R = 21 - (2T/15)$ so that at 90°F, R should be greater than 9, at 75°F it should be greater than 11, and at 60°F it should exceed 13. If the sulphuric acid content is too high the films become non-uniform, and at higher levels still they are colourless, resembling sulphuric acid films.

TABLE 8-11

Operating conditions for oxalic/sulphuric acid processes[70]

				Examples		
		Range	*Preferred*	*A*	*B*	C
Oxalic acid ($2H_2O$)	g/l	> 20	45-70	60	20	50
Sulphuric acid	g/l	> 1.5	2-5	4.5	1.5	2.5
Temperature	°F	> 55	55-90		60-75	
Current density	A/ft^2	12-144	18-48		24-36	

The anodizing voltage starts at 40 to 55, according to temperature, and generally ends at about 40 to 85 for times of 20 to 45 minutes. The lower values of the range 45-70 g/l for oxalic acid produce darker coatings but require somewhat higher anodizing voltages, while higher oxalic acid contents produce lighter coatings although lower anodizing voltages are required.

The colours obtained for 20-25 μm coatings were:

	Alloy	*Colour*
1100		grey-brown
6061	0.6 Si, 0.3 Cu, 1 Mg, 0.25 Cr	dark brown, black at 37 μm
6063	0.4 Si, 0.7 Mg	grey-brown
6351	1 Si, 0.6 Mn, *0.6* Mg, *0.25* Cr	dark grey
6463	0.4 Si, 0.7 Mg	metallic light bronze

Sulphoresorcinol[71]

Sulphoresorcinol is the sulphonation product of resorcinol or 1,3-dihydroxy benzene sulphonic acid, $HO_3S.C_6H_3.(OH)_2$.

It must be used with the correct proportion of sulphuric acid, the minimum value for R, the ratio of organic to inorganic acid, being given by:

$$R = 4.5 + S/20$$

where

R = ratio of 4-sulphoresorcinol/H_2SO_4
S = g/l of 4-sulphoresorcinol

The preferred operating conditions for the process are:

4-sulphoresorcinol	50-125 g/l
sulphuric acid	2-10 g/l
temperature	15-32°C
current density	12-36 amp/sq ft (1.2-3.6 A/dm^2)

Examples of the electrolyte composition are:

	A	*B*	*C*	*D*	*E*	*F*
4-sulphoresorcinol, g/l	75	10	50	100	35	80
sulphuric acid, g/l	6	1	5	6	100	50

A typical electrolyte A used at 75°F for 30 minutes at 24 A/ft^2 gives a 25 μm film and the voltage rises from 31 to 80 volts. Electrolytes E and F give colourless coatings only.

Colours produced on 25 μm coatings are:

1100 (pure aluminium)	dull **tan**
6061	dark grey-bronze
6063	medium dull bronze
6463 (higher purity 6063)	light metallic bronze

Sulphoanthranilic acid[72]

There are two isomers of sulphoanthranilic acid ($SO_3H{\cdot}C_6H_3{\cdot}NH_2{\cdot}COOH$) which may be used along with an addition of sulphuric acid or sulphate for integral colour anodizing. The ratio of the organic acid to the inorganic acid must be greater than 6:1 by weight. Operating conditions (preferred) and examples are:

	Preferred	*A*	*B*
5-sulphoanthranilic acid g/l	>50	63	–
4-sulphoanthranilic acid g/l		–	13
sulphuric acid g/l	2-8	2	2.5
temperature °C	15-32	24	24
current density A/ft^2	12-36	24	24

In the first example the starting voltage is 38 and it increases moderately over a 30 minute period to give a dark bronze coating on 6063 alloy. In the second example a tan-bronze is obtained on the same alloy in 10 minutes. High sulphate contents reduce the depth of colour and the preferred range is determined from this point of view.

Sulphoanthranilic acid may be used in baths of high sulphuric acid content to produce hard coatings, with the advantage that the temperatures need not be as low as when sulphuric acid is used alone.

Substituted succinic acid[73]

Mixtures of sulphuric acid with the substituted succinic acid

$$HOOC - \underset{\displaystyle SO3H}{\underset{|}{CH}} - CH_2 - COOH$$

will, according to this patent, produce a versatile electrolyte suitable for a variety of purposes, but for the production of self-coloured films the sulphuric acid content must be low and the organic acid more than eight times the sulphuric acid content by weight. Operating conditions quoted are:

		Range	*Preferred*	*Example*
SO_3H-succinic acid	g/l	>5	35-100	70
sulphuric acid	g/l	>0.5	2-12.5	5
temperature	°F	40-100	60-90	75
	°C	5-40		
current density	A/ft^2	12-64		24
alurninium content	g/l	2.5	0.1-1	

The following colours were obtained in an electrolyte of the composition quoted in the example:

Time	*Voltage*	*Film*	*Pure Al*	*1%Mg_2Si*	*1¼% Mn*
20 min	35-50	13 μm	light yellow	light brown	
30	35-70	20	medium yellow	medium brown	dark grey
40	35-85	27	dark yellow	near black	
50		33		black	

Aluminium dissolves in the electrolyte at the rate of approximately 0.08-0.09g per amp-hour of anodizing, and the effect of 1 g/l in solution on the conductivity is equivalent to a lowering of the succinic acid content by 20 g/l; this also affects the performance. While additions may be made to make good the loss it is better that only a low, substantially constant, level of aluminium is permitted to accumulate and remain in the electrolyte, and this is best achieved by controlled batch or continuous by-pass ion exchange procedures to maintain the aluminium between 0.1 and 1 g/l.[73]

Lignosulphonic acid[74]

A further patent by Alcoa proposes the use of a by-product of wood pulping for anodizing. Lignosulphonic acid is not a material capable of precise definition but the process resembles others in that the sulphonated acid prepared from spent sulphite liquor may be used for integral colour anodizing when sulphuric acid or sulphate is present in an amount less than one tenth that of the organic acid.

Lignin is a water insoluble polymer the complex organic structure of which is not completely known. It is considered as made up of a group of high molecular amorphous compounds which are chemically very closely related, but of somewhat varying molecular weight. The monomeric lignin building unit is reported to be a substituted phenyl propane, with a methoxyl group meta to the side chain, this

hydroxyl group providing a point of linkage to the next monomer unit in a lignin molecule.

Lignin is readily sulphonated as in the sulphite pulping process, and the solids in the spent liquor contain nearly 70% of sulphonated lignin products which can be converted to the acid forms by ion-exchange treatment. The products are available in America in various forms, crude, refined or fractionated (Norlig MC, Marasperse C, Maracarb NC, Goulac, etc.) or as an acid product 'Norlig 10% solids' which can be used directly without any ion-exchange procedure.

The following operating conditions are quoted for the lignosulphonic acid/ sulphuric acid process:

		Range	*Preferred*	*Example*
lignosulphonic acid	g/l	>25	60-500	185
sulphuric acid	g/l	3-13	4-13	11
temperature	°C	5-45	24	15-32
current density	A/ft^2	9-I44	12-36	24

In an example a 25 μm coating is formed in 30 minutes with a voltage rising from 30 to 75. and the resulting colour is dull yellow-tan on pure aluminium and medium bronze on 6063 alloy.

Sulphamic acid/sulphuric acid process[75]

The use of sulphamic acid for anodizing has been referred to in Chapter 7. It has been the experience of several experimenters that the commercial product functions quite differently from the recrystallized acid from which sulphate is the main impurity removed, and also that the behaviour varies due to production of sulphuric acid during electrolysis, but it has taken quite a time to realise that the importance of sulphuric acid is part of a general pattern.

Michelson, Murphy and Montgomery of Olin Mathieson have patented a sulphamic/sulphuric acid process for colour anodizing in which sulphophthalic acid may be added as an optional extra to enhance the depth of colour. The operating conditions are:[75]

		Range	*Preferred*	*Examples*	
sulphamic acid	g/l	>30	50-150	80	100
sulphuric acid	g/l	1-10	2%-7%	2%	2%
4-sulphophthalic acid	g/l	1-100	10-30	20	–
temperature	°C	10-90	15-30	25	25
current density	A/ft^2	10-110	16-33	24	24
voltage		10-90	25-70		

Basically therefore the process requires the ratio of sulphamic to sulphuric acid to be controlled at a high value. The importance of sulphuric acid content is

illustrated in Table 8-12 where the total retlectivity was measured with a photovolt meter on specimens of 6061-T6 alloy (0.6 Si, 0.3 Cu, 1 Mg, 0.25 Cr) which were anodized in the various electrolyte compositions at 24 amp/ft^2 until 50 volts was reached and treatment continued at 50 volts for a further 30 minutes.

TABLE 8-12

Effect of sulphuric acid content of sulphamic acid on colour[75]

Electrolyte			*Photovolt reading*
165 g/l sulphuric acid			53
5% sulphamic acid	– 0%	H_2SO_4	37
5% sulphamic acid	– 0.25%	H_2SO_4	20
5% sulphamic acid	– 0.50%	H_2SO_4	13
5% sulphainic acid	– 0.75%	H_2SO_4	15
5% sulpharnic acid	– 2.0%	H_2SO_4	38
10% sulphamic acid	– 0%	H_2SO_4	40
10% sulphamic acid	– 0.25%	H_2SO_4	18
10% sulphamic acid	– 0.50%	H_2SO_4	20
10% sulphamic acid	– 0.75%	H_2SO_4	23
10% sulphainic acid	– 2.0%	H_2SO_4	37
10% sulphainic acid	– 0%	H_2SO_4	40
10% sulphaniic acid	– 0.25%	H_2SO_4	22
10% sulphamic acid	– 0.50%	H_2SO_4	21
10% sulphamic acid	– 0 75%	H_2SO_4	27
10% sulphamic acid	– 2.0%	H_2SO_4	44

The reflectivity falls rapidly as the sulphuric acid level increases from zero to 0.25% and at over 0.75% it begins to become lighter again.

In a later patent a more general ternary composition is covered:[76]

sulphamic acid	30	g/l - saturation
sulphuric acid	2 - 20	g/l
lower aliphatic dibasic acid	5 - 30	g/l

Allowing for the 'difficulties in giving a good verbal description of some of the colour effects obtainable with anodized aluminium, the Olin Mathieson process would appear from the claims made to be a little unusual in its scope, as indicated in Table 8-13.

The foregoing sections have dealt with processes originating in the U.S.A. from whence the impetus given spread around the world. It is simpler to deal with

subsequent developments country by country since the ideas so frequently overlap, and the electrolyte types involve so many permutations that they cannot be neatly classified into a system. The main source of information has been the patent literature; the named processes are liable to change (and sometimes decay) with research and development so that a close connection with any particular patent specification cannot be inferred with any certainty.

TABLE 8-13

Colours obtainable with the Olin Mathieson process[75]

Alloy designation	*Maximum volts*	*Time (minutes)*	*Current density ut maximum volts (A/ft²)*	*Colour*
6061	55	20	24	brown
	70	40	24	black
3003	65	20	24	grey
	70	40	24	dark grey
5457	50	30	24	brownish green
5005	65	30	24	grey
	75	45	24	grey green
5052	50	30	24	bronze
2024	50	30	12	bluish grey
1100	65	30	24	dark olive green

Veroxal process (Germany)

The Veroxal process was an integral colour anodizing method developed by Vereinigte Aluminium-Werke A.G., from which the name is derived. It was in use commercially from 1966 for architectural work in both large and small installations. There were originally five colours, later increased to six, and described by the numbers VX1 to VX6. These were:

1.	Silver grey	AlMg 1 sheet
2.	Light brown	AlMgSi 0.5, extrusions
3.	Medium brown	
4.	Dark brown	
5.	Anthracite	AlMn sheet
6.	Black	AlMgSi or AlZnMg extrusions

The electrolyte contained maleic acid, oxalic acid and sulphuric acid. Sautter[77] indicated that the light colours may be obtained at 2 A/dm² (20 amp/sq ft) and the dark brown at 3 A/dm² with the voltage rising to just over 40 in the first case and to close on 80 at the higher current density (see Fig. 8-20).

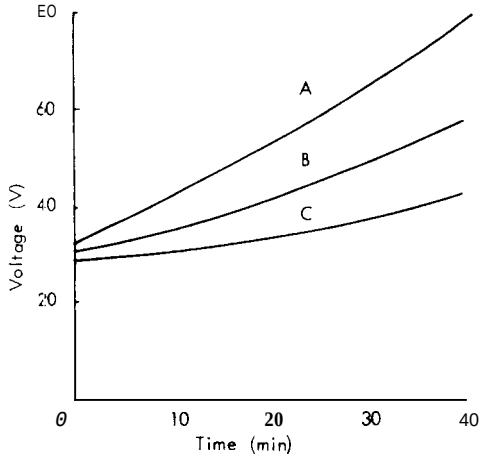


Fig. 8-20. Voltage increase during Veroxal treatment of AlMg1 alloy at various current densities at 23°C[77]

A. 3 A/dm², dark brown
B. 2.5 A/dm², medium brown
C. 2 A/dm², light brown

Neunzig and Röhrig[78] refer to a Veroxal process for producing very hard self-coloured films which were light- and weather-resistant, in an article dealing with electrolytes in which the sulphuric acid content was reduced and small amounts of oxalic acid added. An early VAW process[79] contained sulphosalicylic acid 30-50 g/l, sulphuric acid 5 g/l and maleic acid 10 g/l used at 1.5-3 A/dm², but this application was abandoned.

A subsequent process based on the maleic/oxalic/sulphuric mixture is described in a patent[80] which is a model of brevity, the composition and operating conditions quoted being as follows:

		Range	*Preferred*	*Example*
maleic acid	g/l	30-400	100-300	20
oxalic acid	g/l	5-50	10-30	15
sulphuric acid	g/l	1-10	*3*	3
current density	A/dm²	1-5	1.5-3	
temperature	°C	10-30	15-25	

Very deep colours could be readily obtained with this electrolyte at a film thickness of only 20-30 μm. Anodic treatment could be preceded by anodizing in sulphuric acid.[81]

Careful control of the electrolyte composition was important, as in the case of other processes, including a limit to the amount of aluminium which was allowed to build up in the solution. A process has been described[82] in which dissolved aluminium can be precipitated by the addition of sodium or potassium fluoride in order to regenerate the electrolyte.

Immel and Läser[83] have investigated electrolytes containing maleic acid and shown that in the course of anodizing substantial quantities of its stereoisomer fumaric acid can be formed; this has a low solubility and will precipitate on the cathode. Also, lesser amounts of succinic acid and malic acid can be formed. They have used paper chromatography to separate the various constituents and identified them by their infrared spectrograms. It seems that in practice it is the production of succinic acid rather than fumaric acid that is the problem and increasing attention has been paid to this. The first suggestion was to limit the cathode area to between 10% and 50% of the area of the anode.[84] The cathodes could be of graphite or aluminium alloys containing high proportions of zinc (10-40%),[84] or of silicon (8-30%) or magnesium or tin.[85] Later developments,[86] describe a porous cathode container to separate the cathodes from the remainder of the electrolyte. The production of succinic acid occurs by reduction of maleic acid by the hydrogen produced at the cathode, so separation of the cathode system allows the use of an electrolyte containing no maleic acid in the cathode box and hence no production of succinic acid. The electrolyte in the cathode box is preferably a mixture of an organic acid, such as oxalic acid, and a small amount of sulphuric acid, and suitable material for the porous wall of the box is said to be a mixture of alumina silicates with a pore size of about I micron. A further refinement[87] is the use of a cation exchanger diaphragm, such that the aluminium dissolved during anodizing is concentrated in the catholyte, and hence can be relatively easily removed. For this system catholytes of dilute sulphuric acid or ammonium sulphate are suggested.

Immel and Laser have also described the 'Colodur' process for integral colour anodizing,[88] which will give bronze or black colours when used at 16-30°C and 0.7-3.0 A/dm^2 for 40-70 minutes to give coatings of 18-40 microns.

Permalux process (Switzerland)

The Permalux process for integral colour anodizing was introduced in Switzerland in 1968 and was described by Bloch and Endtinger.[89] It was based on an electrolyte containing maleic acid and was sometimes known as the MS-process. It operated at 20-30°C and 1-3 A/dm^2 to give coatings that were usually about 20 μm thick for external architectural work. It provided a range of five colours from silver through bronze to black, and these were numbered from 1 to 5 with the prefix Permalux, the following alloys being used:

Colour	***Sheets***	*Extrusions*
1. Silver	Peraluman-15	Extrudal
2. Light bronze	Peraluman-15	Extrudal
3. Medium bronze	Peraluman-15	Extrudal

Colour	*Sheets*	*Extrusions*
4. Dark bronze	Peraluman-15	Extrudal
5. Black	Aluman	Anticorodal

Peraluman-15	Al-Mg 1.5
Extrudal	Al-MgSi 0.5
Aluman	AI-Mn
Anticorodal	Al-MgSi 1

The coating produced was extremely hard and abrasion resistant, and it might be inferred therefore that the process was very similar in characteristics to other integral colour processes and that the operating conditions and plant requirements would be very similar, making it a relatively expensive process in comparison with sulphuric acid anodizing but similar to Kalcolor. Maleic acid was, however, a much cheaper product than sulphosalicylic acid.

Maleic acid-sulphuric acid process (Switzerland)[90]

The electrolyte composition covered in this Swiss process is

maleic acid	100-400 g/l
sulphuric acid	1-10 g/l

The problem of obtaining non-uniform films with 'islands of dark oxide' which one gets when working with maleic acid at low concentrations is overcome by using the acid at more than 100 g/l. An essential feature of the process, as in the case of most other processes, is that the content of sulphuric acid should be related to the maleic acid concentration in order to obtain dark uniform coatings, the following limits being observed:

maleic acid	100	150	200	250 g/l
sulphuric acid	1	1-3	1-5	2-4 g/l

When sulphuric acid is increased beyond the optimum level it leads to the spotted appearance due to islands of thick oxide, as described by Scott[''] and also by Csokán[66] when working with sulphuric acid coatings. At higher levels still, only colourless coatings are obtained. At 250 g/l the non-uniform film formation is no longer obtained and the sulphuric acid range given is determined only by the need to obtain coloured coatings.

Using 300 g/l maleic acid with 3 g/l sulphuric acid at 25°C and 2 A/dm^2 for 30 minutes gives a 20 μm film which is medium bronze on AlMgSi-0.5 and dark brown on AlMgSi-1, the final voltages being 65 and 63 respectively.

Tartaric acid-sulphuric acid process (Switzerland)[91]

A further Swiss process covers the use of tartaric acid at 50-100 g/l to which sulphuric acid 2-5 g/l is added. The electrolyte of this composition may also

contain 50-150 g/l sulphamic acid, 10-50 g/l sulphosalicylic acid or 10-50 g/l sulphophthalic acid. The sulphate may be present as a metal sulphate. The following are four examples:

	A	*B*	*C*	*D*
tartaric acid g/l	50	50	40	80
sulphosalicylic acid	45	–	–	–
sulphophthalicacid	–	25	–	–
sulphamic acid	–	–	100	10
sulphuric acid	3	4	–	3
sodium bisulphate	–	–	6	–

Anodizing at 25-30°C to give a 20 μm film produces dark, medium and light bronze colours with the first three respectively, using a 6063-type alloy, and dark brown-grey with the fourth electrolyte when anodizing a 6063-type extrusion.

It is interesting to note that Kamiyama and Osuga in Japan studied an electrolyte containing tartaric acid 25-30 g/l, sulphamic acid 100-110 g/l, and sulphuric acid 5-6 g/l.[127]

A process proposed by Aluminium-Walzwerke Singen in Germany used an electrolyte containing tartaric acid 10-200 g/l, sulphonic acid 10-150 g/l and sulphuric acid or sulphate 1-10 g/l.[92]

Control of sulphate content

During integral colour anodizing the sulphate content of the electrolyte may decrease by becoming incorporated into the coating, or it may increase in certain electrolytes containing sulphonic or sulphamic acids due to decomposition. The latter case is not easy to deal with since the colour produced during treatment depends on maintaining the sulphate at a closely controlled value. Swiss Aluminium have proposed doing this by the addition of calculated amounts of oxides, hydroxides or weak acids of calcium, strontium or barium.[93,94]

In an electrolyte containing sulphamic acid 100 g/l, tartaric acid 80 g/l, and sulphuric acid 3 g/l, the sulphate increases to 5 g/l during use and the original bronze of 13-15% reflectivity becomes lighter with 25% reflectivity. This may be corrected by adding 6 g/l of barium hydroxide $Ba(OH)_2.8H_2O$.

In an electrolyte containing maleic acid 300 g/l and sulphuric acid 3 g/l the 'old silver' colour can be altered to bronze by adding quicklime. The reflectivity may be changed in the following manner:

lime added (g/l)	*reflectivity* (%)	
0	41	—— old silver
1.5	34	
3	27	
4.5	18	
6	13.5	
7.5	13	—— bronze

Further additions of lime have no effect since the minimum sulphate level has been reached.

Anodizing at resonant frequencies[95]

In an unusual procedure which is claimed to introduce substantial economies into anodizing and assist in the achievement of reproducible colours, it has been proposed to superimpose alternating onto direct current and at the same time introduce inductances or capacitor banks into the circuitry so that the total inductance and capacitance of the whole set-up is within 5%, if possible, of the frequency given by the well-known relationship for tuned circuits, $f = 1/2\pi\sqrt{LC}$.

When this is aclhieved there is a reduced expenditure of electrical energy, lower cooling requirements and a better control of colour.

Using the electrolyte

sulphamic acid	100 g/l
tartaric acid	80 g/l
sulphuric acid	3 g/l

to form a 27 μm coating, the use of mixed a.c./d.c. in a resonant circuit with 41% modulation reduced the total power requirements from 60 to 26 Wh/dm^2 which represents an economy of over 50% and an 18%reduction in voltage.

Acadai process (Italy)

An integral colour anodizing process which was named the 'Acadai' process was developed in Italy by ISML (Istituto Sperimentale dei Metalli Leggeri) and was in commercial use in 1968. It was briefly referred to by Paolini[96] and said to contain tartaric or citric acid, oxalic acid and sulphuric acid; he also referred to the Swiss Permalux process based on maleic acid as being known as the Acadai process in Italy (also in[89]). Later the Acadai-MS process was referred to."

Paolini and Sacchi[98] carried out studies in Italy in 1963on the use of electrolytes containing sulphosalicylic acid for obtaining hard coloured coatings, and in later papers they described the effects of operating conditions and sulphate content on the colours obtained, as well as discussing the costs of processing and capital installation.[96,99] Using 100 g/l sulphosalicylic acid a deep bronze colour was obtained with 0.25% sulphuric acid, a light grey colour with 0.5%and an uncoloured film with 1.0% sulphuric acid. The sulphonic acids were relatively strong from the chemical point of view but had a low solvent capacity, so that the addition of a small amount of sulphuric acid was necessary to decrease the voltage of the working process and permit the formation of uniform films. The sulphonic acid systems function as binary ones, but in the case of acids like tartaric or citric which are both chemically weak and have a low solvent power, the same addition of sulphuric acid leads only to a high working voltage and burning of the film; it is

necessary in this case to add a third component such as oxalic acid or maleic acid which, in Paolini's view, acts as a 'bridge' between the strong sulphuric acid and the very weak tartaric or citric acid.[96]

Tartaric/oxalic/sulphuric acid process (Italy)[100]

The above ideas are no doubt embodied in the ISML process of Sacchi and Paolini where a ternary electrolyte was proposed. This was composed of an aliphatic dicarboxylic acid of dissociation constant from 10^{3} to 10^{-5} at 50 to 300 g/l (preferably tartaric or citric); an acid of much higher dissociation constant at 5-30 g/l (preferably oxalic or maleic); and a smaller addition from 0.1-2 g/l of a stronger acid of greater solvent power such as sulphuric acid. An example is:

	Range	*Example*
tartaric acid	50-300	150 g/l
oxalic acid	5-30	15
sulphuric acid	0.1-2	0.5
temperature	15-50°C	30°C
current density	1-3 A/dm^2	2 A/dm^2

A gold colour was obtained on pure aluminium, a bronze colour on Mg or MgSi alloys, and a neutral grey colour under the same conditions on Mn-containing alloys. These colours may be intensified when small amounts of Cu or Cr are also in the alloys.

Maleic/oxalic/sulphuric acid process (Italy)[100]

As time has gone on it has become clear that the main Italian process used was also maleic acid based and a typical electrolyte composition is given as:

maleic acid	300 g/l
oxalic acid	15 g/l
sulphuric acid	3 g/l

This was used under similar conditions to other maleic acid based electrolytes and suffered from the same problems of decomposition products produced at the cathode. Again the problem was tackled by cathode separation from the main electrolyte and in one improvement of this process[""] a porous screen of polyethylene, glass or ceramic with pore size of 3-8 microns was used. The cathode solution was preferably either sodium, lithium or potassium hydroxide in 0.1-IN solution, or it could contain sulphuric acid or an alkali sulphate with a sulphate content between 0.1 and 10 g/l, preferably about 3 g/l.

Yet another suggestion was to use a cathode which was cooled to a temperature below that of the anodizing electrolyte,[""?] and this apparently reduced the formation of precipitates without requiring complicated cathode shields. Hollow cathodes in

stainless steel, graphite or aluminium were suggested, with a refrigerated liquid circulating in them.

Autocolor-HSH process (Hungary)

A short note on an integral colour anodizing process developed in Hungary first appeared in the British press at the end of 1967.[103] The inventors were Csokán and Szontagh of the Hungarian Light Metals Research Institute and a variety of colours and shades were obtainable. The process had been described previously in mote detail in Hungary"" and seemed to have a number of features which were unusual for integral colour processes. The electrolyte was said to be a cheap one, readily available and did not contain any sulphuric acid or sulphate. It worked equally well with alternating or direct current. The colour range varied from yellow to deep bronze with a.c., and from ochre-yellow to near-black with d.c. current, the former being quite bright and the latter matt in appearance. The colours could be obtained on quite thin coatings of 5 μm or so.

The Autocolor process was voltage controlled. The voltage was selected according to the colour required and applied at full value, the current being allowed to decline naturally; about 2 A/dm^2 was obtained with d.c., while a.c. operation seemed to proceed at a faster rate. This type of operation must make it more difficult to predict the exact coating thickness which is being obtained under any given conditions, but this is apparently not a very important point since the Autocolor coat was so hard and dense that it did not require the normal sealing operation and its corrosion resistance was superior to the coatings produced in Western countries although an application of lacquer was recommended for exposure to aggressive atmospheres. The electrolyte contained three components, a 1-1 aliphatic acid, an aromatic acid and an organic stabiliser, all in low concentrations, and control was simply carried out by infrequent additions of 'intensifying chemical'. The treatment costs were comparable with normal anodizing and dyeing, which is again an unusual feature in processes which are generally noted for their complexity and expense.[105]

Sulphosalicylic acid/formic acid (Hungary)[106]

The Hungarian patent ascribed to Csokan (70%) and Szontagh (30%) proposed an electrolyte containing formic acid and sulphosalicylic acid with a small addition of hydroquinone as the 'stabilising agent'. The limits quoted were:

	Range	*Example*
formic acid	10-80 g/l	30 g/l
sulphosalicylic acid	10-80 g/l	50 g/l
hydroquinone	40-100	5 g/l
voltage	5-20	50-80

Colours obtained were:[104]

		Voltage				
Alloy type	*Current*	*40*	**50**	60	70	*80*
Al-Mg	d.c.	light bluish	medium bluish	dark bluish	coffee brown	matt dark brown
	a.c.	–	old gold	light bronze	red brown	chocolate brown
Al-MgSi	d.c.	–	light blue grey	dark bluish grey	dark grey with bluish shade	dark olive green
	a.c.	–	golden yellow	bronze	tobacco brown	chocolate brown
Al-Cu-Mg	d.c.	–	–	golden yellow	greyish brown	dark bluish grey
	a.c.	–	–	dark beige	coffee brown	–

The Autocolor-HSH process resembled oxalic acid anodizing more than it did the other integral colour anodizing processes in the type of film, the ability to use alternating or direct current and the deep colours available, but these were much more readily available. Szontagh and Dencz[107] have contended that the depth of colour is proportional to the current-time integral or coulomb rating, which determines the thickness of anodic coating, rather than the voltage.

Eurocolor 100 process (France)

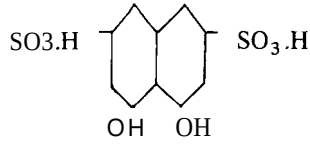
The designation 'Eurocolor' was used by Compagnie Péchiney in France to denote a series of colour anodizing processes, of which Eurocolor 100 was an integral colour anodizing process. This was based on the sulphomaleic acid based electrolyte described later and gave the following four designated colours:

105 – light bronze
106 – medium bronze
107 – dark bronze
108 – black.

Specially controlled alloy compositions were used in order to obtain the colours, and the coatings were extremely hard and abrasion resistant so the process was also suitable for hard anodizing requirements.

Chromotropic acid (France)[108]

A process invented by Chrétien and Richaud used an electrolyte based on chromotropic acid, or to give it its full title, 1:8 dihydroxynaphthalene-3:6-disulphonic acid:



As is usually the case a small proportion of sulphuric acid had to be present. The following conditions are quoted:

			Examples		
		Range	*A*	*B*	*C*
Chromotropic acid	g/l	1-100	5	20	100
sulphuric acid	g/l	1-100	5	5	5
temperature	°C	10-70	–	–	–
current density	A/dm^2	1-10	2.5	2.5	2.5
voltage		–	60	60	60

The method of operation was to hold the current density constant until 60 volts was reached after which the voltage was held constant, the film thicknesses being 5-8 ym in 20 minutes, 12-15 μm in 30 minutes and 20-30 ym in 45 minutes. The colour depended on the composition of the basis metal and became deeper as the film thickness increased. In the three examples given the concentration of chromotropic acid was said not to be important since the same colour was obtained in each case, which would appear to be of considerable advantage in control; the more readily available sodium salt of the acid could also be used.

The following colours could be obtained:

99.99% AI	pale gold
99.5% AI	beige-grey
A-GS (AlMgSi 0.5)	bronze
A-SG (AlMgSi 1)	bronze-grey
A-G3 (3% Mg)	grey
A-Z4G (3% Zn, 2% Mg)	near-black
A-S5G (5% Si)	grey-black
A-U4G (4% Cu)	grey-bronze

This process was modified later[109] to include a ternary addition of a carboxylic acid, so that shades from light gold to black could be produced in electrolytes containing a naphthalene sulphonic acid (e.g. chromotropic acid), an acyclic aliphatic acid (e.g. acetic, oxalic or succinic acid) and sulphuric acid.

Sulphonic acid-propionic acid (France)[110]

In a further development of the integral colour anodizing process the range of electrolytes was extended to include a ternary system with the following components:

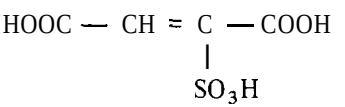
10-200 g/l	derivative of a sulphonated aromatic compound with at least one hydroxyl group
10-300 g/l	derivative of a sulphonated aliphatic compound will less than 5 carbon atoms
not more than 10 g/l	sulphuric acid.

As an example, a bronze colour could be obtained on Al-MgSi alloys in 30 minutes at 2.5 A/dm^2 and 20°C in

10 g/l	l-naphthol 8-amino 3,6-sulphonic acid
100 g/l	propionic acid
6 g/l	sulphuric acid

Sulphomaleic acid (France)[111]

One of the advantages of sulphomaleic acid was that it was considerably cheaper than some of the acids that were suggested for integral colour anodizing, and in addition it appeared to yield brown or black shades more readily than other organic acids of similar formula such as sulphosuccinic acid. The electrolyte contained from 10-300 g/l of sulphomaleic acid



with not more than 1.5 g/l sulphuric acid, and preferably in the absence of sulphonated aromatic acids. The preferred conditions were: 50-200 g/l sulphomaleic acid; 0.5-8 g/l sulphuric acid; 1-4 A/dm^2; 15-30°C. Examples are:

Alloy		MgSi	MgSi	AlMg	MgSiMn
sulphomaleic acid	g/l	100	150	80	120
sulphuric acid	g/l	5	3	6	4
temperature	°C	20	20	21	20
current density	A/dm^2	1.5	2.5	1.5	2.5
time	min	40	30	40	60
film thickness	µm	18	20	18	30
colour		light bronze	dark bronze	light bronze	black

One unusual feature of this process was that either alternating or direct current could be used.

Sulphoitaconic and sulphocitraconic acids (France)[112]

In a subsequent process patented by Péchiney the range of treatment conditions was identical with the sulphomaleic acid process above, but the electrolyte contained in its place either sulphoitaconic acid or sulphocitraconic acid or a mixture of both of them at a concentration which could be between 10 g/l and saturation at the temperature of operation, along with the usual amount of sulphuric acid which could be up to 1.5 g/l. The electrolyte could be employed at temperatures from −10°C to +50°C but the preferred range was 1.5-30°C.

As in the case of the sulphomaleic process either alternating or direct current could be used.

Carboxylic acids-acid sulphates (France)[69]

Reference must be made again to early work of Herenguel in France on mixed acid systems which, although the intention was to overcome the limitations of sulphuric acid in speed of film formation, approached the subject in the same manner as for integral colour anodizing and provided electrolytes which could be used for this purpose. Instead of sulphuric acid the very much weaker acid sulphate of sodium or potassium was used, and the solution was made to function at very high speed (providing 25 μm in 1 minute if necessary) by adding either formic, citric or tartaric acid. **A** formic-oxalic mixture was also very successful.

Some examples of Herenguel's electrolytes are given in Table 8-14.

TABLE 8-14

Electrolytes used by Herenguel for high speed film formation[69]

		A	*B*	*C*	*D*	
MHSO,	g/l	167	167	167	–	
Formic acid	g/l	80	–	–	55	
Citric acid	g/l	–	100	–	–	
Tartaric acid	g/l	–	–	100	–	
Oxalic acid	g/l	–	–	–	80	
Temperature	°C	30	40	40	25	
Current density	A/dm²	6	7	8	20	20
Time	minutes	45	45	45	45	2
Filtn thickness	microns	75	115	140	200	24

Alcanodox process (U.K.)[113]

The Alcanodox process for architectural anodizing was introduced by Aluminium Laboratories in 1902 and operated with an oxalic acid electrolyte to give gold colours on pure metal or Mg-Si alloys and deeper shades with some alloys, but generally less deeply coloured than the Kalcolor process which was operating at the same time.

Oxalic acid anodizing has of course been practised continuously in various parts of the world since the Japanese patents of 1923.[51] However in those days the gold shades produced were undesirable and conditions producing the minimum of colour were favoured. In the more recent form the concentration was increased

from 3-5% to near saturation and the temperature lowered from 25-35°C to 15-25°C. Operating conditions quoted were:

Oxalic acid ($2H_2O$)	80 g/l to saturation
temperature	15-25°C
current density	12-15 A/ft^2
time	50-90 minutes
voltage	34-67

The commercial process was used in the U.K. and Sweden in the 1960's and several important buildings were finished in this way.

In one variation of the oxalic acid process molybdic acid was added to produce bluish-white coatings.'''

Oxalic acid anodizing with pulsed current (U.K.)[115]

In order to obtain deeper colours with the oxalic acid process it was proposed to superimpose substantially square pulses of current at a relatively high current density on to d.c. anodizing. The pulse frequency was in the range 1%-20 with peak current reaching 20 A/dm^2 and from 3-6 times the mean anode current density of 1-3.6 A/dm^2. The electrolytes used were:

oxalic acid	80 g/l
oxalic acid	27 g/l + sulphuric acid 0.23 g/l
oxalic acid	80 g/l + formic acid 5.5 g/l

this last, incidentally, having been used by Herenguel.

The colour is said to increase in depth as the ratio of peak to mean current increases. It is suggested that the colour effects are due to particles of carbon from decomposed carboxyl radicals and that high current densities favour their formation, while the device of pulsed current enables this to take place without 'burning' of the film. This patent also claims the use of slightly over-aged Al-Mg-Si alloys (9-10 hours at 220°C) to enhance the depth of colour obtainable on anodizing.

The use of pulsed current was also claimed at about the same time by Fair[116] who proposed current pulses of 6-100 msecs at 20-200 volts followed by intervals five times as long as when steady direct current was flowing.

Acorn Anodizing Co. process (U.K.)[117]

Anodizing in an electrolyte of malonic acid was investigated by Kape[118] and has been described in Chapter 7. Malonic acid mixed with a small proportion of either oxalic or glyoxylic acid forms two of a group of binary electrolytes proposed by Acorn Anodising Company which produced anodic oxide coatings that were phenomenally hard as well as achieving a variety of colours that included yellow-brown, dark brown, greenish-yellow and others. The electrolytes

did not contain sulphuric acid or sulphates, they generally operated at very high voltages and the colour effects were reminiscent of those of the Autocolor-HSH process.

The two electrolyte components were the following:

1. Glyoxylic acid; any dibasic or polybasic organic acid excepting oxalic acid, maleic acid, any acid which liberates nitrate or chloride ions. Concentration from 10 g/l to saturation (malonic, tartaric, citric, diglycollic, malic, succinic, glutaric, itaconic, pyromellitic, trimellitic, citraconic, thiomalic, thiodiglycollic, acetylene dicarboxylic, aconitic, glyoxylic, phthalic acids).

2. Oxalic acid or glyoxylic acid; concentration from 1-100 g/l.

Table 8-15 lists a number of examples of this procedure where coatings have been formed to architectural specifications, for which the operating voltage range and colour obtained is given, the basis metal being Al-Mg-Si alloy to 6063 specification. An unusual feature of this table is the inclusion of the results for specific abrasion resistance as measured by the abrasive jet method described in Chapter 12. This is essentially a comparative method but results for a normal sulphuric acid coating are given, and also a sample produced in 10% sulphosalicylic acid-0.5% sulphuric acid at 25°C which had a specific abrasion value of 4.0, so that it will be appreciated that some of the values given must represent an extreme degree of hardness that would not readily be emulated by most of the processes so far described.

TABLE 8-15

Results obtained with mixed organic electrolytes"'

Electrolyte	*Voltage range*	*Colour of coating*	*Thickness of coating (microns)*	*Specific abrasion resistance**
8% sulphuric acid	19-20	silver	25-35	2.0
6% tartaric + 1.5% oxalic	too-I30	brown-grey	20	7.5
5% tartaric + 0.3% oxalic	110-130	medium grey	20	*6.15*
5% citric + 1.5% oxalic	85-104	greenish yellow	25	6.9
5% citric + 0.3% oxalic	110-180	grey-brown	15	8.3
5% itaconic + 1.5% oxalic	120-150	grey	25	6.9
5% malic + 1.5% oxalic	180-200	dark grey	25	1.45
5% diglycollic + 1.5% (oxalic	100-130	yellow grey	25	7.25
5% diglycollic + 1.2% (oxalic	100-140	yellow-brown	30	10.5
5% thiomalic + 1.5% oxalic	88-162	grey-bronze	25	7.6

* After sealing for 5 minutes in nickel acetate 8 g/l, 80°C. plus 60 minutes in hot water at 95°C.

Phenolsulphonic acid (Japan)[119]

Sumitomo Light Metal Industries patented a process in Japan based on phenolsulphonic acid to which small quantities of sulphuric acid were added, and this was operated under the name of the Sumitone process. It has been described by Terai, Suzuki and Hayashi[120] and was particularly aimed at reducing the cost of integral colour anodizing. This was done by using a relatively inexpensive electrolyte (12½% (wt) p-phenolsulphuric acid, 1% (wt) sulphuric acid), continuously regenerating this by ion-exchange, and lowering the operating voltages by using a.c. superimposed on d.c. As with most integral anodizing electrolytes, the presence of sulphuric acid reduces the operating voltages significantly and **the** effect of different concentrations is shown in Fig. 8-21. In practice starting voltages of 25 to 28 volts, giving a current density of about 2.5 A/dm^2, were used, and raised gradually to 45 to 65 volts. The superimposition of the a.c. component was designed to allow the use of higher d.c. current densities without burning problems, as it reduces the sharp voltage rise that normally occurs as the film is formed. The ion-exchange resin used for regenerating the electrolyte was similar to that already described in relation to the Kalcolor process

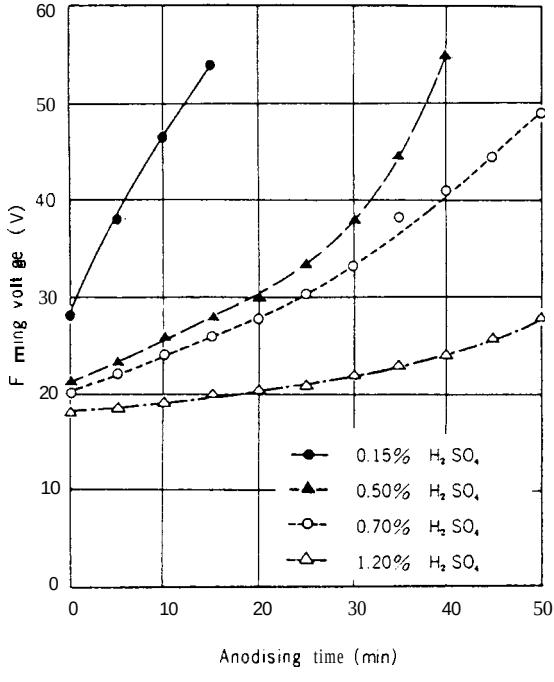
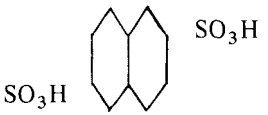


Fig. 8-21. Effect of addition of sulphuric acid on forming voltage""

Naphthalenedisulphonic acid (Japan)

A later patent by Sumitomo[121] covered the use of any isomers of naphthalene disulphonic acid, but the 1-5 type was preferred.



The electrolyte composition was:

		Range	*Preferred*	*Examples* (A)	(B)
1.5-naphthalenedisulphonic acid	g/l	15-400	50-200	90	90
sulphuric acid	g/l	1-30	3-15	6	6

The temperature was 20-30°C and the current density 1-3A/dm^2 requiring voltages from 20-80 which needed to be progressively increased during treatment, but with some alloys the voltage was held constant after 60 was reached. The examples given quote a black finish on AI-Mg-I-Si alloy containing 0.48% manganese, and a bronze finish on AI-Mg, 0.5-Si alloy, in both cases with a 35 μm film.

Coatings were said to be non-uniform if the sulphuric acid was below 1 g/l or if the organic acid was below 15 g/l. When the organic acid was lowered the colour of the work processed became darker but required a higher voltage, and *vice versa*. Colourless coatings resembling those produced in sulphuric acid could be produced in 100-200 g/l sulphuric acid with 50-250 g/l naphthalene-disulphonic acid, but much higher current densities could be employed.

A similar Japanese process was based on 2-naphthol 3-6 disulphonic acid (10-100 g/l) and sulphuric acid (1-10 ml/l).[122]

Cresolsulphonic acid (Japan)[123]

Cresolsulphonic acid as an integral colour anodizing electrolyte is another possibility which the Riken Denka Co. Ltd. of Japan added to the list, to be used in a concentration of 24-400 g/l with sulphuric acid 0.5-3.0 g/l.

Oxalic acid-sulphuric acid (Japan)[124,125]

Riken Light Metal Industries were also concerned by the high cost of integral colour anodizing and suggested modified conditions in sulphuric acid-oxalic acid electrolytes to give colour.[124] The preferred electrolyte and operating conditions were:

2.5-2.7% (wt) oxalic acid
0.15-0.17% (wt) sulphuric acid
1.8-2.0 g/l aluminium ions
25-40°C
20-55 V
0.5-2.5 A/dm^2

An earlier patent[125] also suggested the use of oxalic acid-sulphuric acid mixtures but with the optional additions of small quantities of nitric acid and boric acid.

Oxalic acid-citric acid (Japan)[126]

Okubo[126] investigated the anodic treatment of aluminium in mixtures of oxalic acid and citric acid with the addition of relatively smaller quantities of sulphuric acid, but his main concern was with the degree of hardness and wear resistance of thick coatings that could be obtained with this electrolyte. He viewed the procedure as a means of anodizing in dilute sulphuric acid while still obtaining uniform coatings.

Tartaric acid-sulphamic acid (Japan)[127]

In studies published in Japan"' Kamiyama and Osuga used the composition:

tartaric acid	25-30 g/l
sulphamic acid	100-110 g/l
sulphuric acid	5-6 g/l

They produced gold, amber, bronze and black colours according to the treatment conditions and alloy selected, but at lower cost than was possible when using aromatic acids. Dissolved aluminium in the bath affected the colour of the coatings obtained and it was necessary to maintain the aluminium in the range 0-1 g/l. In general a temperature of a little over 20°C was recommended, but the solution worked satisfactorily at up to 30-35°C. The composition used was only slightly outside the range quoted in a similar Swiss patent,[91] the tartaric acid content being lower and the sulphuric acid content a little higher.

Sulphofumaric acid (Japan)[128]

Other Japanese workers used an electrolyte based on about 70 g/l sulphofumaric acid and 0.5-2 g/l sulphuric acid[128] at a relatively low current density of 1 A/dm^2 and voltages of about 70 V. Apart from the use of lower current densities, the process was also claimed to simplify effluent treatment processes, as it gave a much lower biochemical oxygen demand (B.O.D.)in the effluent.

Sulphosalicylic acid-formic acid (Japan)[129]

Fujisash exploited mixtures of sulphosalicylic acid, formic acid and sulphuric acid[129] with a typical composition and operating conditions as follows:

sulphosalicylic acid	70 g/l
formic acid	15-18 g/l
sulphuric acid	1.2 g/l
current density	1-3 A/dm^2
voltage	45-80 V
temperature	20°C

Oxalic acid-sulphosalicylic acid (Russia)[130,131]

The main interest in Russia in the use of a sulphosalicylic acid electrolyte was in the rapid formation of thick and hard coatings. Vol'fson improved this electrolyte by introducing 30-50 g/l oxalic acid, and obtained good results with sulphosalicylic acid 100 g/l, oxalic acid 30 g/l, sulphuric acid 3 g/l.[130,131]

Oxalic acid-citric acid-boric acid (Russia)[132]

The production of opaque coloured coatings was investigated in Russia with a ternary system without sulphuric acid, containing oxalic acid 40-60 g/l, citric acid 10-30 g/l and boric acid 3-10 g/l, operated at 1-4 A/dm^2 and 50-90 volts. The coatings produced at 10-20°C were darker than those produced at 25-35°C and they became darker with increasing time of treatment.

Oxalic acid-chromic acid (Holland)[133]

An integral colour process was proposed by Philips of Holland which used more common acid:; to produce a grey or black finish, the electrolyte being considerably cheaper and not subject to the decomposition which affected other processes based on organic acids. The composition quoted was:

	Range	*Example*
oxalic acid	50-200 g/l	100 g/l
chromic acid	5-40 g/l	20 g/l
sulphuric acid	2.5-20 g/l	5 g/l

It was used between 15 and 30°C, the initial voltage of 30 being raised to 60-100 as treatment proceeded. **A** dense, hard and black coloured coating was obtained in 40 minutes on an Al-Mg-SiMn alloy at 1.5 A/dm^2 and 20°C, the voltage being raised from 30-60.

Investigations of integral colour anodizing

It will be appreciated from the foregoing lengthy survey of integral colour anodizing that it was largely an empirical art and that very little appeared in written form outside the range of commercial and patent literature, or technical literature with a strong commercial flavour. The developments were in the nature of prospecting and staking out of territorial claims and one might usefully ponder, though this is not the correct place to do so, on the multiplication of effort around the world in studying virtually the same problems, finding the same solutions, and as often as not abartdoning the territory. Basic investigations of the colouring mechanism have been much less evident.

As early as 1944, Fischer and Budiloff[134] investigated the cause of colour formation with oxalic acid anodizing, and they concluded that the basic gold

colour was due to colloidal carbon in the film. They recognised the importance of the oxalate anion in the film, and showed that coloured films could be produced even with super purity aluminium. Kape[135] looked at a whole series of organic electrolytes (see Chapter 7) and was able to postulate the requirements which a practicable integral anodizing electrolyte should meet and successfully forecast suitable acid mixtures. Tajima, Baba and Muramaki[136] found that no visible oxide films were formed in monobasic acids (formic, acetic or benzoic), whereas in the dibasic acids (malonic and succinic) a barrier or semi-barrier oxide layer was formed.

Many authors have recognised that several mechanisms were involved in integral colour anodizing, and that significant factors were the incorporation of intermetallic particles from the alloy being anodized, and the incorporation of colour active ions such as Cr, Cu or Mn, which can be present in solid solution in the aluminium matrix. However neither of these mechanisms explained the colouring that occurs with super purity aluminium. Endtinger and Zoller[137] ruled out organic compounds of carbon, as with the better analytical techniques now available they could not be detected in typical integral colour films. This was confirmed by Sautter,[138] who, like Raub *et al.*,[139] found that typical integral colour films contained almost as much sulphate as those produced in sulphuric acid (10-15%), with no sign of products of the organic acid present. Thus the nominal composition of the integral finishes was similar to that of normal sulphuric acid films, but with very different colouring effects.

Endtinger[137] and Sautter[138] considered that incorporation of fine particles of aluminium might be responsible for colour formation and might act as a finely dispersed pigment, the role of carbon in the work of Fischer and Budiloff. Equally Woodman[''"] attributed the colour of films grown in oxalic acid to scattering of light by the parallel pore texture, but many other integral colour films have similar parallel pores and yet give quite different colours. Many other studies have taken place including those by Tagai *et al.*[141] on sulphosalicylic acid based electrolytes, Takako and Baba[142] on oxalic and malonic acid films, Takahashi *et al.*[143] on a range of films and Shimura[144.145] on oxalic acid and maleic acid films. Many different conclusions are drawn, but the work of Takahashi[143] points to the mechanism now generally accepted.

They found that the AlKα line of a sulphosalicylic acid based film showed a chemical shift when examined by electron diffraction, indicating a different chemical bonding or valency of the aluminium. They attributed this to the heat produced by the electron beam, but another possibility suggested by Wefers and Evans[146] is that the displacement is caused by the presence of free metallic aluminium, Al°. This is perhaps the most acceptable explanation of the basic integral colouring mechanism and Wefers and Evans have proved the presence of Al° by mass spectrometry techniques. This has allowed them to measure the Al° level in the Al_2O_3 matrix in Duranodic type films, and to relate it to their reflectivity characteristics (Fig. 8-22). They showed that an equation could be derived which describes the correlation between the total reflectivity of the films and the concentration of free aluminium. The free aluminium originates in the

barrier layer and conditions favouring its formation are a high rate of oxidation at a low rate of field assisted dissolution of the oxide. Thus high anodizing current densities, high voltages and electrolytes with a low attacking power will favour colour production. In addition, of course, the incorporation of intermetallic particles from the alloy being anodized is a major factor in colour development.

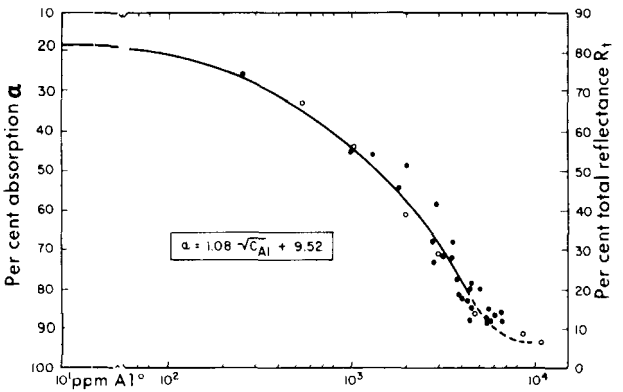


Fig. 8-22. Light absorption vs. concentration of Al^0 in D300 films on **Al** 99.99%[146]

Further work to elucidate the mechanism by which metallic aluminium is formed has been described by Wefers and Wallace.[147] The conclusions are illustrated schematically in Fig. 8-23. Wefers and Wallace indicate that:[147]

'The conditions prevailing during the growth of a colourless coating are represented in the upper part of the figure. Here temperature and concentration are sufficiently high to maintain a high rate of dissolution. Therefore the barrier layer remains thin and the field strength high. **A** significant concentration gradient does not develop due to the rapid interdiffusion of positive and negative ions across the thin barrier layer. Moreover, a negative space charge at the solid/solution interface, which would constitute an activation barrier for the injection of anions into the solid, is compensated by S^{6+} ions occupying most cation vacancies. In addition, protons released by the reaction of HSO_4^- and OH- ions with Al^{3+} constantly migrate through the solid/liquid interface, thus contributing to the balancing of any excess negative charge. Aluminium ions entering the electrolyte are tied up by the organic acid of the mixed acid electrolyte and in part by HSO_4^- ions. As long as the concentration of sulphuric acid is sufficiently high or the current density remains low, the accumulation of aluminium ions resulting from oxide dissolution will not significantly influence the pH of the electrolyte in the pore.

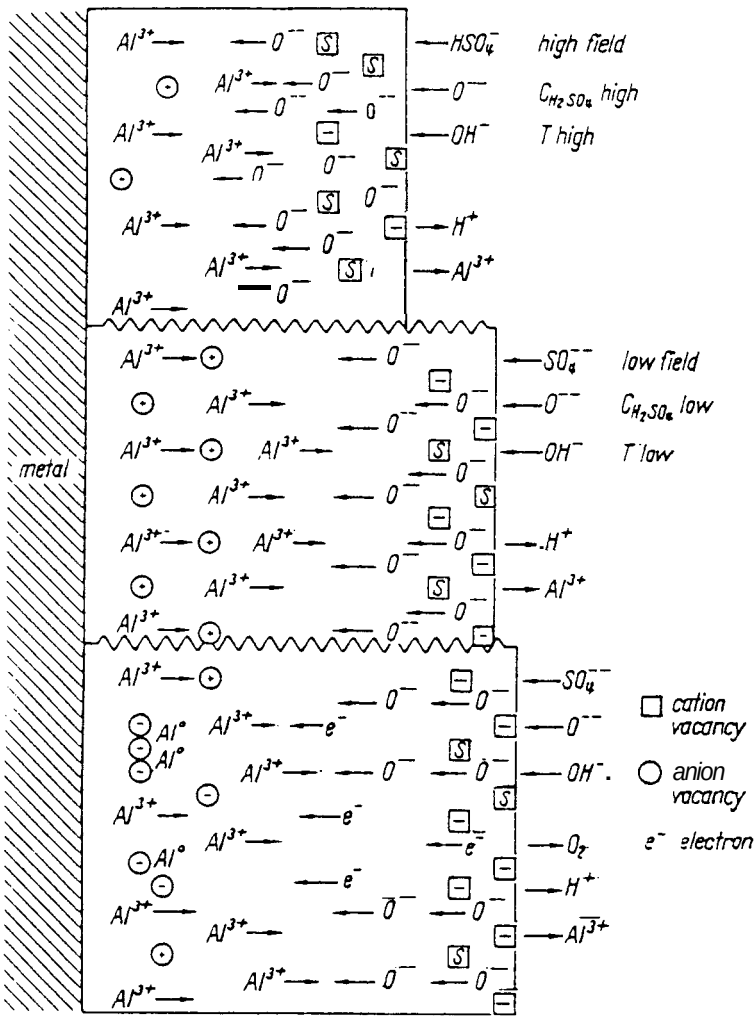


Fig. 8-23. Formation of colour centres in anodic oxide (schematic)[147]

'This situation changes when the concentration of free sulphuric acid decreases. **A** progressively increasing portion of the HSO_4^- ions will be bound by Al^{3+}. Since protons have a 5-10 times higher mobility in solution than sulphate ions, the pH near the oxide/electrolyte interface will increase, and

SO_4^{2-} ions become the predominant species. The rising pH has several consequences: dissolution of oxide decreases and the barrier layer thickness increases. Low concentration of available sulphate will leave many (negative) cation vacancies unoccupied. Furthermore, each SO_4^{2-} ion transferred into the solid adds two negative charges instead of the one introduced by an HSO_4^- ion. As a consequence, a strong negative space charge develops which, in conjunction with the increasing barrier thickness, decreases the field strength and thus the rate of ion transfer. Aluminium ions and anion vacancies accumulate near the metal/oxide interface, giving rise to a positive space charge. Further increase in charge polarization results in discharge of oxygen ions at the electrolyte/oxide interface which will release electrons towards the positive region. The electrons are captured by anion vacancies and by interstitial Al^{3+} ions. The latter are reduced to metallic aluminium.'

Reynolds Metals Company process (U.S.A.)[63]

A process developed by Reynolds in the U.S.A. was in a slightly different category from other integral colour processes because of the inclusion of a colour donor component. It was similar in the respect that it used an organic electrolyte with a smaller proportion of sulphuric acid, economical in the fact that the former could be oxalic acid, and advantageous in the respect that whereas many processes depended on the use of special alloys to obtain adequate depth of colour, the colour here came principally from additions of heavy metals to the electrolyte (see Table 8-16).

It was claimed that a greater range of colours could be obtained than with other processes without the use of special alloys, and that the extremely hard coatings were not susceptible to thermal crazing at room temperature with consequent corrosion hazards. Treatment times were short, a 25 μm coating being formed in 15 minutes.

Some examples of the electrolyte compositions which could be employed were:

1. sulphuric acid	1.2 g/l	: oxalic acid	60 g/l	: ferric oxalate	80 g/l
2. sulphuric acid	10	: oxalic acid	90	: nickel oxalate	33
3. sulphuricacid	12	: malonic acid	2.7	: ferric oxalate	80
4. sulphuric acid	12	: succinic acid	60	: ferric oxalate	80
5. sulphuric acid	12	: hydroxyacetic	217	: ferric oxalate	80
6. sulphuric acid	10	: glycollic acid	60	: ferric glycollate	50

The current density specified in most examples was the unusually high one of 48 amp/sq ft (5.2 A/dm^2) and the terminal voltage was between 35 and 60 to give red-brown or amber-brown colours.

TABLE 8-16

Reynolds integral colour process[63]

Electrolyte type			*Preferred constituent*	
mineral acid	–	conductor	sulphuric acid	0.5-45 g/l
organic acid*	–	voltage component	oxalic acid	5 g/l-saturation
metal salt**	–	colour donor	ferric oxalate	5-80 g/l
current density		12-60 amp/sq ft (1.2-6 A/dm^2)		48 amp/sq ft (*5.2* A/dm^2)
temperature		10-27°C		20-22°C
voltage		20-250		20-35

* Saturated aliphatic alpha-hydroxy monocarboxylic acids.
Saturated and unsaturated aliphatic dicarboxylic acids, e.g., glycollic (hydroxy-acetic), lactic, malic. oxalic. malonic, succinic, maleic.

** Common metals of Groups IB. VIIa and VIII, i.e., copper, iron, nickel cobalt, manganese.

Double anodizing

One feature mentioned in the above process by Reynolds was that a pre-anodizing step in conventional sulphuric acid could be used and that this ensures a unique gloss on the final product. The sulphuric acid anodizing could be for as short a time as one minute but longer times could also be employed.[63]

A similar idea appeared subsequently in several places. It was embodied in a separate patent by V.A.W.[81] who claimed that the prior formation of a 2-10 μm sulphuric acid coating improved the uniformity of film thickness and colour, eliminated differences due to metal structure and avoided the occurrence of hair-line crazing during sealing.

Two stage anodizing also appeared in one of Kaiser's patents[59] and in Japanese patents by Showa Denko[148] and Showa Aluminium.[149]

White anodizing

An unusual process developed by Reynolds'" to provide a near white surface of 78-80% reflectivity was produced in an electrolyte containing titanium lactate plus lactic acid plus sulphuric acid plus glycerol. The coating was developed for use on space vehicles by N.A.S.A. where special properties are required in order to control the ambient temperature, and further severe restrictions operate because of the necessity to have a stable coating under high vacuum conditions, subject to intense ultraviolet light, and at the same time adding little to the total pay load. A white finish would, however, find wide application in architectural work. The

colour of the anodized coating is enhanced by impregnation with oxides of lead and barium by double decomposition.

The electrolyte patented by K.H. Dale contains sulphuric acid 15-30%; polyhydric alcohol, e.g. mannitol, sorbitol or glycerol 1-2%; an organic carboxylic acid, e.g. lactic, glycolic, oxalic or malic acid 1-5%; and an alkali salt of a titanium complex with hydroxyaliphatic acid, e.g. titanium-ammonium lactate 1-5%[151] (see also Ematal process, Chapter 7).

The possibilities of white anodizing have attracted much interest in Japan. Showa Aluminium[152] suggest a 0.01-0.1% chromic acid, 2-30% glycerol electrolyte used at a current density of 2.5 A/dm^2 and a temperature of 25°C to give a 5 micron thick film with an opaque enamel-like coating. Honey Chemicals[153] claim a method using a mixture of an amine and inorganic oxy acid at a pH greater than 7.5 using a.c. conditions. Nikkei Aluminium use mixtures of oxalic acid with triethanolamine[154] or alkali metal phosphates and citric or tartaric acid.[155] Sankyo Aluminium[156] suggest an electrolytic colouring process in which the aluminium is sulphuric acid anodized and then a.c. coloured in a neutral or alkaline solution containing barium or calcium salts. Pilot Pen[157] suggest dipping anodized aluminium into salts of calcium, magnesium, barium, strontium, zinc, lead, titanium or aluminium and depositing these salts within the film electrolytically or chemically. In a second step the work is dipped into a solution containing substances which react with the first deposit to produce white or greyish compounds. Among examples are a first treatment of the sulphuric acid anodized material in a 30 g/l calcium acetate solution at an a.c. voltage of 20 V for 10 minutes, followed by a.c. treatment under similar conditions in a 30 g/l phosphoric acid electrolyte. An opaque white film was obtained. Similar treatments first in zinc sulphate and then in oxalic acid, or treatment in barium chloride and then in ammonium oxalate are described.

In quite a different direction other Japanese workers[158] avoid the use of a pigmented anodic coating by whitening the film and then coating it with a protective lacquer. The anodized film is post-treated first in a solution containing a rice bran extract (could this be a residue of saki making!) at pH 4-10, and then it is whitened in a hydrochloric acid solution at pH 0.3-2. This is finally coated with a u.v. curable acrylate resin.

The whole field of white anodizing in Japan has been reviewed by Sato,[159] and he lists no fewer than 43 Japanese patents on this subject. Many different approaches are described including the use of special alloys, chemical etching methods, two-stage anodizing, electrolytic colouring, and the use of the current recovery process occurring when the anodizing voltage is suddenly lowered. This latter process, in conjunction with an oxalic acid anodizing electrolyte and a special copper containing alloy, is said to be in industrial use in Japan for producing opaque white finishes.

Work in India reported by John[160] uses anodizing in a 25 g/l sodium carbonate / 10 g/l sodium fluoride electrolyte containing 50 ml/l of glycerine. DC anodizing at 1.8-2.4 A/dm^2 and a temperature of 50-70°C produced milky white finishes. Full whiteness was developed in anodizing times of 10-20 minutes with a coating thickness of about 5 microns. Such coatings could also be dyed and were sealed conventionally.

3. ALLOYS FOR INTEGRAL COLOUR ANODIZING

The importance of carefully controlled metal quality in anodizing has been well stressed in Chapter 7. In the case of metal used for the integral colour anodizing procedures extra precautions were often necessary because the colour, in some of the processes, was related to the quantity and metallurgical state of the intermetallic constituents. It was very important therefore to see that these did not vary outside carefully fixed limits if a reproducible colour was to be achieved. It was also the practice to employ alloys of special composition to enhance colour effects, and in this case the production procedure had to be arranged to arrive at the same end-point for each batch of metal.

Kaiser Aluminum patented a metal composition for an improved 5005 alloy (0.8% Mg alloy) and a production procedure involving slow cooling of rolling blocks in which the iron-containing precipitate formed relatively large particles which were therefore fewer and exerted less effect on the reflectivity. This gave sheets of consistent and predictable colour which were an improvement on normal production.[161] A similar idea was proposed in Germany for the production of extrusions in AlMgSi alloy.[162]

The production of rich dark bronze colours, or if necessary black on integrally-anodized extrusions in 6063 alloy (HE9) has been brought about by additions of copper and manganese, the following composition being proposed:[163]

silicon	0.3-0.4%
iron	0.15-0.25%
copper	0.15-0.25%
manganese	0.1-0.2%
magnesium	0.45-0.60%

This was the basis of the Kaiser extrusion alloy known as KE 45. Heat treatment conditions for such an alloy have been described by Dorward.[164] Best hardness values were obtained most practicably by a two-step ageing treatment of 2 hours at 143°C followed by 4 hours at 180°C. A sheet material based on the addition of copper and manganese to a 0.8% Mg alloy has also been proposed.[165] The preferred composition was:

silicon	0.08-0.14%
iron	0.15-0.25%
copper	0.16-0.25%
manganese	0.16-0.25%
magnesium	0.70-0.90%
chromium	0.04-0.08%

Copper and chromium added together to 6063 alloy produce effects which are different from either element added singly, and it has been proposed to obtain

deep yellow, bronze or black colours on integral colour anodizing with the composition:[166]

Cu	0.35-1.0%
Mg	0.4-1.0%
Si	0.25-0.60%
Fe	0.4% max.
Cr	0.10-0.35%
Mn, Zn, Ti	0.1% max.
Mg_2Si	0.6-1.6%

Patents by the Sumitomo Chemical Co. included an alloy for forming a bronze colour[167] in an oxalic acid-sulphuric acid electrolyte which contains 0.3-3.5% magnesium and 1-10% zinc with additions of manganese, chromium, silver and vanadium; also a grey-black or brown anodic coating on an alloy containing copper 3.5-4.5%, magnesium 1.0-2.0%, nickel 1.0-3.0% heated at 500-520°C and annealed at 150-300°C.[168]

The use of an alloy of 5% silicon for obtaining grey shades when anodized in sulphuric acid is well known, the depth of reflectivity being determined by the production procedure which influences the size and distribution of the silicon particles which remain in the elementary form in the anodic film after anodizing. The formation of a grey colour with silicon at a much lower level was the subject of a Swiss patent using the following composition:[169]

silicon	0.5-2.0%	
iron	0.4-1.0%	
copper up to	0.2%	one or more of these
manganese up to	0.8%	
chromium up to	0.4%	
titanium up to	0.1%	
magnesium up to	1%	

An alloy containing 1.5-2.5% barium has also been proposed for forming a grey anodic coating.[170] More importantly both Kaiser[171] and Alcoa[172] developed alloys for producing: grey finishes in an integral colour anodizing process. The Kaiser alloy[171] (referred to as KE 50) contained the following:

silicon	0.30-0.60%
iron	0.10-0.40%
manganese	0.20-0.60%
magnesium	0.40-0.70%
chromium	not more than 0.10%
zinc	not more than 0.10%
copper	not more than 0.05%

The Alcoa alloy[172] was closer to the original Al-5% silicon alloys (AA 4043) and contained:

silicon	3.5-6.5%
iron	0.1-0.7%
manganese	0.3-0.65%
magnesium	up to 0.1%
copper	up to 0.3%
titanium	up to 0.1%

A later Alcoa sheet alloy[173] was similar to KE 50 but without the presence of magnesium. It essentially contained:

silicon	0.40-0.60%
iron	0.20-0.40%
manganese	0.30-0.60%

Good black finishes were difficult to produce by integral colour anodizing, and Alcoa[174] developed a sheet alloy with good forming properties that would produce an integral black finish in 30 minutes anodizing. The alloy contained:

silicon	0.08-0.18%
iron	not more than 0.3%
manganese	not more than 0.05%
magnesium	up to 0.1%
copper	0.4-0.6%
chromium	0.1-0.25%
zinc	not more than 0.05%
titanium	not more than 0.05%

Casting alloys have also been developed to give good integral colour coatings. Kaiser[175] described an alloy containing 3.2-3.8% Si, 0.25-0.6% Mg and 0.25-0.8% Cr which gave shades from light gold through bronze to black, whilst Sumitomo[176] covered an alloy containing 0.1-1.3% chromium and 0.2-3.4% manganese which gave gold shades when anodized in sulphuric acid.

Patents in Japan by the Nippon Light Metals Research Institute related to a black coating on an alloy containing 1.5-2.5% manganese which was worked, heated to 250-350°C for at least 1 hour and precipitation hardened at 400-500°C,[177] and also a method for producing an alloy containing 1.5-2.5% manganese and 0.2-4% magnesium which was quenched and worked at 400-550°C.[178]

But for sheer inventive genius in this direction the record must go to the Nippon Light Metals Company in an omnibus patent[179] which seems to have embraced almost every possible addition in the periodic table which could be made to aluminium and to have adjusted the method of production (admittedly on small scale experimental blocks) to give colours right through the spectrum. Tables 8-17 to 8-20 from the relevant patent show that a whole range of tones could be contrived with silicon contents of less than 1% upwards, yellow colours could be obtained with chromium at various levels, as is well known, while various other colour effects could be obtained with other metallic additions.

TABLE 8-17

Colours obtainable on different aluminium alloys[179]

Current density (A/dm²)	*Al-2.43% Cr*	*Al-5.43% Si*
0.5	light yellow	light black
0.8	bright yellow	jet black
1.0	bright yellow	jet black
1.2	bright yellow	jet black
1.5	bright yellow	jet black
2.0	bright yellow	jet black
3.0	bright yellow	jet black
5.0	bright yellow	jet black

TABLE 8-18

Colours obtainable on different aluminium alloys[179]

Si (%) *Hot rolling temp (°C)*	0.57	0.85	1.27	1.77	2.44	2.75	3.34	5.43	7.46	9.82
200	NC	VLB	LB	LB	LB	LB	LB	PJB	PJB	PJB
250	LB	LB	LB	PJB	PJB	PSB	PJB	PJB	PJB	PJB
300	LB	PJB	PJB	PSB	PSB	PJB	PJB	PJB	PJB	PJB
350	LB	PJB	PSB	PJB	PJB	PJB	PJB	PJB	PJB	PJB
400	LB	LB	LB	B	B	B	B	PJB	PJB	PJB
450	NC	NC	NC	NC	SG	G	GB	GB	GB	GB
500	NC	NC	NC	NC	NC	SG	SG	GB	GB	GB
550	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC

Note: The area of PSB indicates the most suitable condition for the invention.
NC not coloured. LB light black. B black. SG slightly grey.
VLB very light black. PJB pure jet black. GB greyish black. G grey

TABLE 8-19

Colours obtainable on different aluminium alloys[179]

Cr (%) *Hot rolling temp (°C)*	0.50	0.82	1.20	1.65	2.43	2.85	3.27	4.98
150	NC	LY	BY	BY	BY	BY	BY	BY
200	NC	LY	BY	BY	BY	BY	BY	BY
250	LY	BY	BY	BY	BY	BY	BY	**BY**
300	LY	BY	BY	BY	BY	BY	BY	BY
350	LY	BY	BY	BY	BY	BY	BY	BY
400	LY	LY	Y	BY	BY	BY	BY	BY
450	LGY	LGY	LGY	LGY	LGY	LGY	LGY	LGY
500	NC	NC	NC	LGY	LGY	LGY	LGY	LGY

Note 1: The area of BY indicates the most suitable condition for the invention.
NC not coloured. LGY light greyish yellow. LY light yellow. Y yellow.
BY bright yellow.

Note 2 electrolysis condition:
Electrolyte 15% sulphuric acid solution.
Current density 2.5 A/dm^2.
Temperature 20°C.
Time 40 minutes.

TABLE 8-20

Colours obtainable on different aluminium alloys[179]

Alloy	*Addition range of alloying* ***element,*** *% weight*	*Hot wrought temperature °C*	*Anodic current density A/dm^2*	*Colour oxidation film*
		(≤)		
AI-Ag	10-30	400	0.8-8	brown
AI-Au	0.3-5	400	0.8-8	pink
AI-B	0.8-5	400	0.8-8	white
AI-Ba	0.5-1.5	400	0.8-8	white
AI-Be	0.5-2.5	400	0.8-8	white
AI-Bi	0.5-4	270	0.8-8	purple grey
AI-Ca	0.8-3	400	0.8-8	white

TABLE 8-20 *(continued)*

Alloy	*Addition range of alloying element, % weight*	*Hot wrought temperature °C* (≤)	*Anodic current density A/dm²*	*Colour oxidation film*
AI-Cd	1-6	320	0.8-8	grey
Al-Ce	0.5-10	400	0.8-8	yellow
AI-Co	0.5-2	400	0.8-8	bluish grey
Al-Cu	0.5-10	400	0.8-8	yellowish brown
AI-Fe	0.5-3	400	0.8-8	yellowish grey
AI-Ge	0.3-5	400	0.8-8	black
AI-Li	2-8	400	0.8-8	brown
Al-Li_2Si	0.8-5	400	0.8-8	grey
Al-Mg	4-8	400	0.8-8	white
Al-MgAg	1-15	400	0.8-8	pale brown
Al-Mg_2Si	0.5-8	400	0.8-8	white
Al-Mg_2Sn	1-12	400	0.8-8	grey
Al-$MgZn_2$	8-20	400	0.8-8	grey
Al-Mn	0.5-3	400	0.8-8	pink
AI-MO	0.3-1	400	0.8-8	yellow
AI-Ni	0.5-3	400	0.8-8	bluish grey
Al-Sb	0 8-2	400	0.8-8	greyish white
AI-Se	0.2-2	400	0.8-8	**pink**
AI-Sn	0.5-5	200	0.8-8	grey
AI-Ti	0.2-1.5	400	0.8-8	grey
AI-V	0.2-1.5	400	0.8-8	grey
AI-W	0.3-1.5	400	0.8-8	grey
Al-Zn	10-25	250	0.8-8	grey
Al-Zr	0.2-1	400	0.8-8	grey

4. INORGANIC COLOURING BY ELECTROLYTIC METHODS

The use of inorganic pigments to impregnate the anodic oxide coating is a very old idea which attracted little attention because, as a colouring method, it could not compete with organic dyestuffs in cost, range of colours and ease of application. But scarcely any of the organic dyes have been able to furnish the permanent finish capable of withstanding weather and sunlight indefinitely which present-day architectural usage demands, and interest has accordingly revived in any method of pigmentation which can give a completely light-fast colour. The use of ferric ammonium oxalate to provide gold colours by a simple immersion technique satisfied this need to a certain extent.

One alternative method of achieving such pigmentation is to immerse the anodized work in an acid solution containing metallic salts and to apply an alternating voltage. Under the correct conditions metallic deposits in the form of metallic particles will form within the porous structure of the film, producing a colour characteristic of the metallic salt used.

Probably the earliest claim to colouring anodized aluminium in this manner belongs to Caboni[180] and is embodied in a 1936 Italian patent for impregnating coatings with finely divided metal from aqueous solutions of salts of copper, nickel, silver or metals electropositive to aluminium. The colour could be greatly enhanced if the work were made an electrode in the solution and alternating current passed through it by means of a counter-electrode. It was also possible to form an oxide coating and colour it simultaneously.

Elssner[181] in 1940 referred to the known methods for colouring oxidized aluminium with salts of copper, nickel or silver by an alternating current treatment as having unsatisfactory features because the colours were weak and patchy. He proposed an improvement which gave uniform colours of greater depth, uniformity and light fastness by using a counter-electrode of the same metal as in the metallic salts in the colouring bath. Thus, using copper counter-electrodes with copper salts the colour could be reddish, dark red or deep black according to the time of treatment, and with lead acetate solution a lead counter-electrode would be used. The current could be 50 cycle a.c. or lower, or periodically reversed d.c. The work could be transferred to the colouring bath without rinsing if the anionic constituent was compatible, and a further patented feature was a period without current in the colouring bath before switching on.

A later patent application[182] was filed in Germany in 1943, but understandably received little attention at the time; later it was also granted in Norway.[183] This covers alternating current treatment in solutions of salts of iron, cobalt, nickel, manganese and chromium, and also additions of up to 10 g/l of compounds containing arsenic, antimony, bismuth, tellurium, selenium or tin.

Examples of the electrolytes used were:

(1)	sulphuric acid	250-350 g/l
	arsenic	0.6-1 g/l
	ferrous sulphate	50 g/l
(2)	sulphuric acid	370 g/l
	antimony oxide	0.8 g/l
	nickel sulphate	40 g/l

Credit must go to Dr. T. Asada and the chemists of the Fuji Manufacturing Company for perfecting methods for electrolytic colouring which can be employed with confidence in large anodizing plants to colour large components uniformly and reproducibly for use in architectural installations. Buildings using this finish in Japan go back to the early 1960s, but outside Japan the process was not used industrially until 1967, when Alcan started to license the process under the name

of Anolok. Other companies quickly entered the field and electrolytic colouring processes became a significant factor in architectural colour anodizing. Today they have largely replaced integral colour anodizing processes, and very large tonnages of electrolytically coloured finishes are produced each year. Some of the trade names used for these processes and the colouring metal involved are shown in Table 8-21.

TABLE 8-21

Some industrial electrolytic colouring processes

*Process**	*Promoter*	*Main colouring metal employed*
Almecolor	Henkel (Germany)	Sn
Anolok	Alcan (Canada)	Ni, Co
Carmiol T.70	I.S.M.L. (Italy)	Ni, Co
Colinal 2000	Alusuisse (Switzerland)	Ni + Co or Sn
Colorox	Gartner (Germany)	Sn
Electrocolor	Langbein-Pfanhauser (Germany)	Ni or Sn-Ni
Endacolor	Endasa (Spain)	Sn-Ni
Eurocolor 800 and 1000	Péchiney (France)	Sn-Ni or Ni
Korundalor	Korundalwerk (Germany)	Sn
Metoxal	V.A.W. (Germany)	Sn
Metacolor	Metachemie (Germany)	Sn
Oxicolor	Riedel (Germany)	Sn-Ni or Sn
Rocolor	Rodriguez (Spain)	Sn or Ni
Sallox	Italtecno (Italy)	Sn
Summaldic	Sumitomo (Japan)	Ni (d.c.)
Trucolor	Reynolds (U.S.A.)	Sn
Unicol	N.K.K. (Japan)	Ni

* Some of these names, including Anolok, Endacolor and Eurocolor are Registered Marks.

Most processes are used to produce ranges of bronze or black finishes using electrolytes based on nickel, cobalt or tin. Various types of anodizing electrolyte can be used for producing the initial anodic coating but, in practice, sulphuric acid coatings are almost always used. The work is anodized under conventional conditions to produce anodic film thicknesses appropriate to the application, and it is then immersed in the metal salt solution and coloured, usually under a.c. conditions. The depth of shade produced depends essentially on the applied voltage or current and the colouring time. After colouring the work is sealed in the conventional manner.

The attraction of electrolytic colouring processes (or two-step colouring processes as they are often known in Germany) is that they do not require the use of special alloys, the colours are largely independent of anodic film thickness, the energy consumption is very much lower than that of integral colour processes, and the light fastness of the finishes is excellent, and it is these factors that have caused them to be so widely used. In technical terms the field is so large that a separate book could be required to detail all the developments that have been described, so the following pages can only provide a summary of the main developments. Other authors who have summarised the field include Herrmann,[184] John *et al.*[185] and Brace and Sheasby.[186]

Method of electrolytic colouring

In the first descriptions of the process[187,188,189] the deposits were made from dilute acid solutions using counter-electrodes of carbon or silicon carbide, although aluminium was also mentioned. **A** large number of examples were given of which those quoted in Table 8-22 are typical.

In addition to silver, cobalt, nickel, copper and tellurium salts as mentioned above other similar formulations used in a very similar manner were based on salts of selenium (red), manganese (yellow or gold), zinc (brown), cadmium (dark brown), lead (black) and chromium (green).

TABLE 8-22

Examples of colouring by the Fuji process[188,189]

Colouring bath		*Time*	*Voltage*	*Colour*
sulphuric acid	15 gll	5 min	20	brown
silver nitrate	1.5			
boric acid	25 gll	10 min	'15	black
cobalt sulphate	20			
ammonium sulphate	15			
boric acid	25 g/l	10 min	20	blue
nickel sulphate	20			
ammonium sulphate	15			
sulphuric acid	7 g/l	10 min	13	red
copper sulphate	20			
sulphuric acid	15 g/l	10 min	20	dark gold
sodium telluride	1.5			

Nickel-based electrolytes

In the early stages of electrolytic colouring, work concentrated on the industrial development of nickel based processes. Asada[190] claimed the benefit of using nickel counter-electrodes in a nickel electrolyte as an improvement over graphite, and this was said to give the dark colours with less tendency for spalling (see page 711) and better control of the pH of the electrolyte. A recommended electrolyte contained:

nickel sulphate	30 g/l
boric acid	30 g/l
ammonium sulphate	15 g/l
pH	3.5-5.5

Dark bronze colours were obtained with 5 minutes treatment in such an electrolyte. Boric acid is an almost universal addition in these electrolytes and acts as a buffering agent, whilst the ammonium sulphate is added to increase the conductivity of the electrolyte.

Ptchiney suggested the use of high levels of nickel sulphate (50-150 g/l) with higher levels of boric acid (45-60 g/l) used at a pH of 3.5-5.2,[191] again to make darker colours easier to produce without spalling. They also disclosed the use of a mixture of 5-100 g/l nickel sulphate and 50-250 g/l nickel chloride[192] at a similar pH. Boric acid and arnmonium sulphate were again preferred additions. Alcan, on the other hand, preferred additions of magnesium sulphate[193] to improve throwing power and levels of above 2 g/l are suggested. Aluminium sulphate[194] was an alternative possibility.

Low levels of aluminium building up in nickel based electrolytes have frequently been found to cause colouring difficulties, and Alcan[195] suggested operation of the baths at a higher pH (above 4.7) to reduce solubility of aluminium and hence precipitate it out. Deliberate additions of small quantities of aluminium sulphate were made to fresh electrolytes so that they were always saturated with aluminium. Other approaches have been to complex the aluminium using amino acids[196] or carboxylic acids.[197] Control of pH can also be a problem with nickel-based electrolytes and the use of small amounts of mono-, di- or tri-ethanolamine for this purpose has been disclosed by Alusuisse.[198] An alternative method is the use of heavy metal carbonates, oxides, hydroxides or hydroxycarbonates.[199]

Another problem with nickel-based electrolytes is the difficulty of producing very dark finishes, particularly black, and several solutions have been proposed. The most common is to add a small amount of a copper salt to the nickel baths, and Péchiney[200] and Alusuisse[201] have both used this method. Péchiney suggest addition of 1-7 g/l of copper ions,[200] and claim the production of a good black finish after 15 minutes colouring at a current density of 0.4 A/dm^2. Alusuisse use much lower levels of 0.02-0.75 g/l of copper,[201] and claim this to give improved uniformity of bronze colouring as well as producing a black finish. A different approach, again by Péchiney, has been the use of a nickel sulphamate based electrolyte.[202] This,

unusually, is used under d.c. rather than a.c. conditions, with interruptions of the d.c. current during which the work being coloured is discharged. A solution containing 0.2-1.6 mol/litre of nickel sulphamate and 25-50 g/l boric acid at a pH of 3.5-5.5 and a temperature of 1.5-35°C is suggested. Under these conditions the following colours are obtained:

0.1 A/dm^2 for 1 min	light bronze
0.15 A/dm^2 for 2 min	medium bronze
0.15 A/dm^2 for 5 min	deep bronze
0.2 A/dm^2 for 8 min	black

The interruption of the cycle improves colouring rate and prevents spalling problems, which is a common problem when attempting to use d.c. for colouring. A.C. colouring in nickel sulphamate solutions is claimed by Kaiser[203] and this is used at elevated temperatures (above 35°C), as is a simple nickel sulphate solution also claimed by Kaiser.[204]

Workers in Greece[205] have studied the use of heterocyclic organic compounds in a.c. colouring in nickel sulphate / boric acid solutions. They found that saturated compounds were beneficial to both throwing power and colouring rate, and that additions of about 0.7 g/l piperidene-4-carboxylic acid gave the best results. Indian workers[206] have looked at a range of anions in nickel-based electrolytes and have found that sulphate, sulphamate and chloride were effective, but nitrate and acetate were not suitable. Workers in Egypt[207] have studied the kinetics of nickel sulphate / boric acid electrocolouring processes.

Summarising the use of nickel electrolytes, in general terms they are nearly all based on solutions of nickel sulphate and boric acid and operate at a pH of about 3.5 to 5.5 and a temperature of 15-35°C. Colouring voltages of about 10-18 volts and current densities of 0.1-0.5 A/dm^2 are used to give shades of bronze from very light to very dark, and in some cases black. The electrolyte in comparison with many others, such as those based on cobalt or tin, is relatively cheap, but it is probably the most difficult to operate, as it is sensitive to contamination by ions such as aluminium and sodium,[208] is difficult to use to produce the very dark finishes and is liable to produce spalling. Nevertheless, in Japan, in particular, nickel-based electrolytes are still widely used, the problems having been solved by careful electrolyte formulation and operation, and by the use of modified electrical conditions which will be described later.

Cobalt-based electrolytes

Whilst the use of nickel-based electrolytes for electrolytic colouring has been widely described, information on cobalt-based electrolyte is more difficult to find. Basically such an electrolyte can be formulated in a similar manner to a nickel electrolyte, and Asada[187] describes use of a 15 g/l boric acid, 15 g/l cobalt sulphate solution at pH 5.8 to give a black colour. As with nickel electrolytes, additions of

ammonium sulphate or magnesium sulphate are frequently made to improve throwing power.

The main attraction of cobalt-based electrolytes in comparison to nickel is that they can be formulated to be less sensitive to sodium and aluminium contamination, they are less likely to give spalling, and darker colours are easier to produce, so, unlike nickel, the full range of bronzes and black can be obtained. Alcan have used cobalt-based electrolytes since the early 1970s and Sheasby and Kellermann[209] have described their use in general terms. They indicate that the baths also have high stability and some have been in continuous use for more than 10 years. The pH range for the electrolytes is 4-6 and they are normally based on cobalt sulphate.

Alsuisse have also made use of cobalt containing electrolytes, but in their case it has usually been a nickel-cobalt mixture. In one of their patents[y8] they describe an electrolyte containing:

$CoSO_4.7H_2O$	80 g/l
$NiSO_4.7H_2O$	40 g/l
H_3BO_3	40 g/l
$CuSO_4$	1 g/l

This was used at 20-25°C, and an a.c. voltage of 15 V applied for 2 minutes gave a bronze colour, and 16 V for 15 min gave a black. Piesslinger in Austria also used nickel-cobalt mixtures,[210] and covers solutions containing 10-100 g/l cobalt sulphate or cobalt acetate, 5-100 g/l nickel sulphate, 10-40 g/l boric acid and 10 g/l of the calcium salt of a polybasic aromatic sulphonic acid, such as lignin sulphonic acid or sulphosalicylic acid. Such electrolytes are used at pH 3-S, voltages of 5-20 V and colouring current densities of 0.2-0.5 A/dm^2.

In summary, cobalt-based electrolytes give the full range of bronzes and black, have good throwing power, are less sensitive to contamination than nickel-based electrolytes and do not readily produce spalling. Their main disadvantage, in comparison with nickel, is the relatively high cost of the cobalt salts. On the other hand the electrolyte has a long life and most of the salts used (about 80%) are said to be lost through drag-out rather than by metal deposition,[209] so recovery of these salts from the rinse waters can be an attractive proposition. For this reason reciprocal flow ion-exchange systems, mentioned in Chapter 7 for sulphuric acid recovery, have been used in several plants for cobalt recovery.[211]

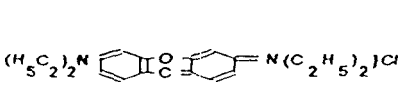
Tin-based electrolytes

In the early stages of electrolytic colouring electrolytes based on tin salts seem to have been overlooked, though in later years they have become more widely used than any other type. Outside Japan, the first serious attempt to formulate a tin-based electrolyte was by Gedde[212] and a typical electrolyte contained 20 g/l of stannous sulphate, 10 ml/l of conc. sulphuric acid and 10 ml/l of phenol sulphonic acid. Colouring voltages with such a bath were very low, with 5-8 volts being used

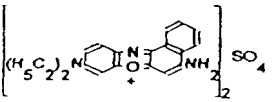
for times of 5-15 minutes to give bronze and black finishes. The preferred pH of the bath was about 1.5, much lower than that used for nickel or cobalt-based electrolytes. The other feature of this type of electrolyte was the use of aromatic carboxylic acids such as phenol sulphonic acid or sulphophthalic acid to stabilise the tin solution. This is a problem not encountered with the previously described electrolytes as they are essentially stable to oxidation, but stannous sulphate is readily oxidized to stannic sulphate, which precipitates out and takes no further part in the colouring process. As this happens when the bath is standing as well as when it is used, it is a factor of major concern in the operation of tin-based electrolytes, and it has been suggested that twice as much tin is lost through oxidation as is lost by drag-out and deposition in the film.[208] Many different stabilising agents have been suggested in addition to those described above. These include cresol sulphonic acid,[213,214,215] aliphatic organic thio-compounds such as thiomalic acid,[216] aliphatic sulphonic acids,"' or pyrogallol, resorcinol and similar compounds.[218]

More recently Sandoz[219] have claimed the benefits of diphenylamines, and work in Greece[220] covers d.c. colouring in tin-based electrolytes containing certain diphenyl methane derivatives. These are in the form of cationic dyestuffs of the type shown in Fig. 8-24. They are added in low concentration to stannous sulphate electrolytes where, under d.c. conditions, the cationic dyes move, under the influence of the electric field, to the cathode, enter the anodic film and migrate to the base of the pores. There they are reduced and are codeposited with the tin, and their effect is to increase the rate of colouring to reduce the tendency of the film to spall, especially in the case of Nile Blue. No mention is made of their colouring effect but they may be present in too low a concentration to give visible colours. In other work by Henkel[221] the benefits of substituted diphenols, phenyl ethers containing two oxygenators attached to a benzene nucleus, and napthols as stabilizers are claimed. A different approach by Mitsubishi in Japan[222] has been to use a ferrous salt as a stabiliser in amounts greater than 0.1 times the amount of stannous salt present. The idea is that oxidation occumng at the electrode will preferentially be of iron rather than tin. Clearly these additions are essential to the successful operation of a tin bath, but they reduce rather than eliminate the oxidation problem. In another direction Moshohoritou ***et al.***[223] have used heterocyclic organic compounds such as nicotinic acid and piperidene-4-carboxylic acid to improve the throwing power of tin-based electrolytes. Henkel[224] have reported work on a large number of stabilising agents in conjunction with additives to improve throwing power. They conclude that two separate additives are necessary to obtain best results, but as with most areas where proprietary additives are sold, they don't reveal what the best additives are.

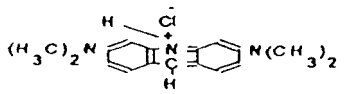
Unlike cobalt-based electrolytes there is quite a lot of information on the operation of tin-based electrolytes, and Gohausen, in particular, has published useful details.[225,226] He indicates that typical colouring electrolytes have a pH of about 1 and contain 8-10 g/l of stannous sulphate and 16-22 g/l of sulphuric acid. They contain proprietary organic stabilising agents, often phenolic compounds. The electrolytes are used at 20-24°C so no heating or cooling equipment is required.



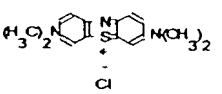
Pyronine B (C.I. 45010)



Nile Blue A sulfate (C.I. 51180)



Acridine Orange (C.I. 46005)



Methylene Blue (C.I. 52015)

Fig. 8-24. Structure of the cationic dyes[11]

Colouring is either carried out for a fixed time at a range of voltages or at a constant voltage for varying times, the latter being preferred. At the start of the colouring cycle the voltage is increased smoothly, within a minute, to a value between 10 and 18 volts according to conditions. Colouring times vary from 10 sec for a light bronze to 15 min for a black. At the beginning of the colouring cycle current densities up to 1 A/dm^2 occur, but within a minute these fall to a steady value of about 0.2-0.4 A/dm^2.

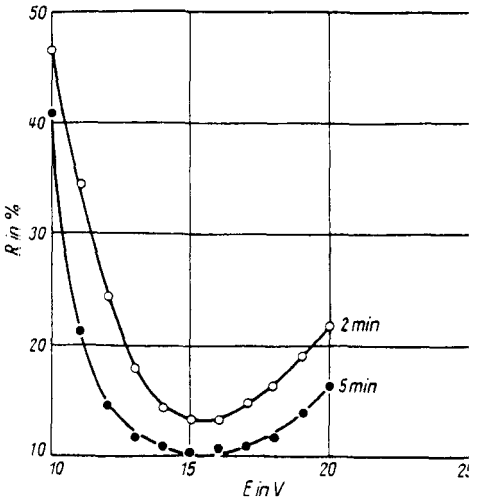


Fig. 8-25. Influence of colouring voltage E on the rate of colouring (determined as degree of reflection R in %); electrolyte: 10 g/l Sn^{2+}, 20 g/l H_2SO_4[225]

Colouring voltage has an important effect with tin-based electrolytes, and colouring rate only increases with voltage up to a level of about 15-16 V. Above this, colour lightens again as shown in Fig. 8-25, and this means that when producing the darker colours colouring times should be kept as short as possible. This same effect is shown in a different form in work by Sautter and Meier,[227] who show the critical relationship between colouring time and colouring voltage with tin electrolytes (Fig. 8-26). **A** possible colouring range of 8-20 volts is shown with short colouring times, but only about 10-16 volts for colouring times of 15 minutes. As can be seen from Fig. 8-26, 10 g/l is considered to be a suitable level of the cresol sulphonic acid stabilising agent, and a similar level is suggested by Bhattacharya[228] for phenol sulphonic acid.

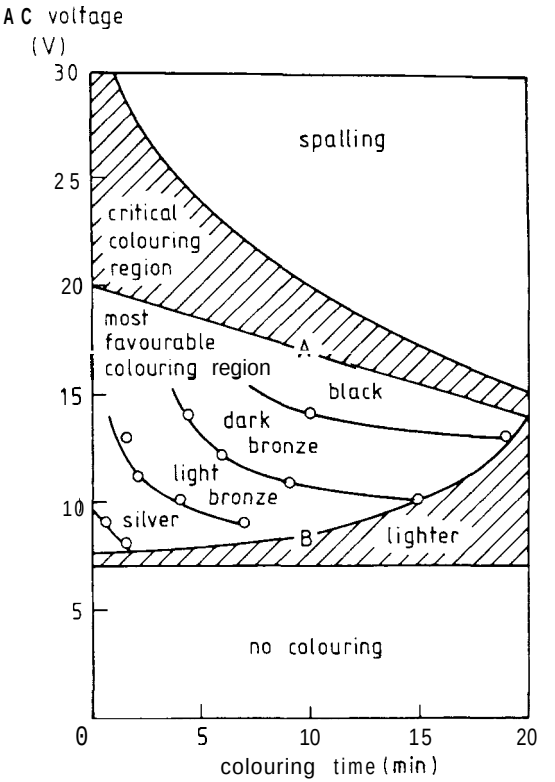


Fig. 8-26. The influence of voltage and time of treatment in the electrolytic colouring of anodized aluminium[227]
(electrolyte 10 g/l $SnSO_4$, 20 g/l H_2SO_4, 10 g/l cresol sulphonic acid)

Sensitivity to contamination has been mentioned in connection with nickel-based electrolytes, but little detailed information is available; however in the case of tin Göhausen has again provided details."' Sensitivity, in terms of the depth of colour obtained in a standard colouring time of 2 minutes, is shown in Fig. 8-27.

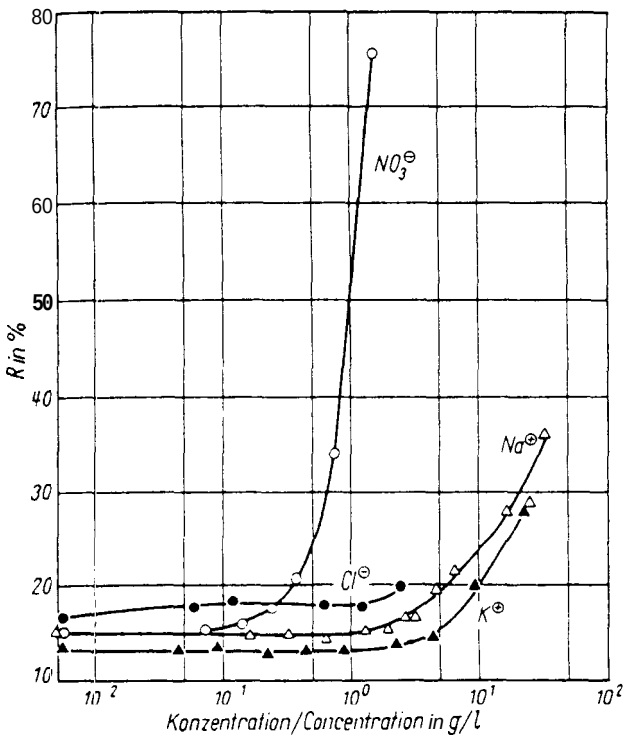


Fig. 8-27. Influence of bath contamination on the colouring efficiency (determined as degree of reflection R in %)[225]

Sodium, potassium, calcium, magnesium, ammonium, nitrate, chloride, borate and oxalate were investigated. Nitrate ions were shown to be most harmful, reducing colouring efficiency drastically at concentrations as low as 0.2-0.3 g/l. High chloride levels (above 2 g/l) produced spalling and high levels of sodium and potassium (more than 5 g/l) reduced colouring efficiency. Other ions only showed harmful effects at higher levels, and this indicates the general insensitivity of tin-based electrolytes to contamination. Dalla Barba[229] indicates the importance of

using high purity stannous sulphate, and gives limits of 100-150 ppm for nitrates and 500-600 ppm for chlorides. He also indicates the dangers of stannic sulphate in the solution and advises that the tetravalent tin content should be below 0.4-0.5%. In another paper[230] he gives many factors that affect the deposition of tin, including the beneficial effect of tin electrodes and the use of d.c. / a.c. power supplies. He gives the optimum conditions as 4-8 g/l stannous tin, 18-23 g/l sulphuric acid used at 20-25°C with tin electrodes and an a.c. voltage of 15-17 volts. Use of d.c. plus a.c. in these conditions improves throwing power and colouring rate.

In general terms, there is little doubt that tin-based electrolytes are the easiest colouring baths to both formulate and use, and this is a major reason for their current popularity. They are available from chemical supply houses as proprietary formulations, and generally give fast rates of colouring and produce a full range of bronze and black finishes. They give good throwing power and are not very sensitive to contamination. Their main operating problem is the oxidation of the stannous to stannic sulphate and consequent loss of tin, and the fast rate of colouring can make light colours difficult to control and can cause the deposited metal to spread through the film rather than being concentrated at the aluminium/aluminium oxide interface. In addition the low electrolyte pH means that some attack of the anodic film itself is possible, and anodizing conditions must be controlled to minimize this.

Copper-based electrolytes

Copper-based electrolytes were among the earliest to be used for electrolytic colouring, and buildings using these finishes have been in existence in Japan since the early 1960s. They are formulated very simply consisting essentially of copper sulphate and sulphuric acid and, as with tin baths, are used at a pH of about 1-1.5. A typical formulation[193] is:

cupric sulphate	25 g/l
sulphuric acid	5-6 g/l
pH	1.3

In the case of copper electrolytes, the finishes produced are ranges of pink, through maroon to black, and in that way they are unique as colouring electrolytes. However colour control with the maroon finishes can be quite difficult to achieve and they were at first mainly used for producing black finishes, though production of maroons is now more common. As with other colouring electrolytes they are used at ambient temperature, and they are relatively insensitive to contamination. Colouring voltages are in the range of 10-20V and current densities of the order of 0.3-0.8 A/dm^2.

Workers in Chile?'' have studied the effect of barrier layer and porous layer thickness with copper-based electrolytes, and have found that it is the barrier layer thickness that controls the rate of copper deposition. However much of their work

was done with very thin anodic coatings and they were obtaining optical interference effects of the type described later in this Chapter.

Mixed electrolytes

The addition of small amounts of copper to nickel or cobalt-based electrolytes and the use of cobalt-nickel mixtures has already been mentioned, but many other mixed electrolytes have been considered. Alusuisse[232] suggest the use of mixtures of salts which give different colours, for example tin and copper or copper and silver. Thus in a bath containing 5 g/l cobalt sulphate, 0.5 g/l silver nitrate and 10 g/l of conc. sulphuric acid, a voltage of about 8 volts deposits silver and gives yellow shades and a voltage of 14 volts favours copper deposition and production of maroon shades. Similarly a mixture of tin and copper gives bronze to black shades with short times (1-2 min) at 14-16 volts, and reddish brown finishes with longer times at lower voltages.

Nickel-tin mixtures have frequently been used as an alternative to tin-based electrolytes and for some years, particularly in Germany, were the most common type of electrolyte in use. Such electrolytes were based on about 10 g/l of stannous sulphate and 20-30 g/l of nickel sulphate with appropriate stabilisers added, and were used at a pH of about 1. However under these conditions almost all the metal deposited in the film is tin, and the nickel takes very little part in the process, so simple tin-based electrolytes are now more common. Iongraf[233] have used low levels of tin or copper salts (less than 2.5 g/l) to help deposition of the less noble nickel, cobalt or cadmium group of metals at relatively low pH (less than 1.87), though they also use an interrupted voltage cycle to achieve this. **A** typical example given is:

nickel sulphate	150 g/l
stannous sulphate	2 g/l
phenol sulphonic acid	1 g/l
sulphuric acid to give pH	1.5

Norsk Hydro[234] claim the benefits of adding an indium salt to tin, nickel or copper-based electrolytes in order to improve colour uniformity. Typically they use 5-17 g/l of the tin, nickel or copper salt and 0.1-0.5 g/l of the indium salt, which is usually indium sulphate.

Piesslinger used a mixture of tin and zinc salts to give a range of grey finishes.[235] The electrolyte contained 5-50 g/l of stannous sulphate, 20-100 g/l of zinc sulphate, 10-100 g/l of concentrated sulphuric acid and 2-5 g/l of a stabiliser such as sulphosalicylic acid or tartaric acid. Under these conditions the following colours were achieved:

12-14 volts	4 min	silver grey
13-17 volts	4 min	light grey
15-18 volts	8 min	medium grey
16-19 volts	10 min	dark grey
18-22 volts	15 min	black-grey

Pilot Pen[236] suggest the use of a mixture of a selenium salt and a copper salt to give colours varying from cream, through yellowish green to chocolate brown. Copper sulphate in the range of 2-20 g/l, selenium dioxide or sodium selenite at 1-10 g/l and sulphuric acid at 5-20 g/l are used.

A rather different approach was taken by Péchiney[237] who proposed successive use of colouring electrolytes with different colouring characteristics. Thus treatment of an anodized sample first in a bath containing 20 g/l of copper sulphate and 5 g/l of sulphuric acid at 9 V for 15 sec, and then in a bath containing 100 g/l of boric acid at 0.4 A/dm^2 for 2 min, gave a chocolate shade. Similar treatment first in a 1.5 g/l silver sulphate and 5 g/l sulphuric acid electrolyte for 30 sec at 8 V followed by immersion in 50 g/l nickel sulphate, 20 g/l ammonium sulphate, 20 g/l boric acid solution at 0.4 A/dm^2 for 1 min gave a violet shade, and treatment in a silver sulphate electrolyte followed by a copper-based bath gave a greenish brown tint. A similar development by Henkel[238] uses a first treatment in a copper electrolyte followed by treatment in a second electrolyte containing tin, silver or both. Reddish gold shades are said to be produced.

Other electrolytes

Whilst nickel, cobalt, copper and tin-based electrolytes may be the most widely used in electrolytic colouring processes, many other colouring systems have been suggested. In Asada's original work[187] chromium, cadmium, vanadium, gold, silver, iron and lead-based electrolytes are mentioned together with selenium, tellurium and manganese solutions. Of these silver, selenium and gold-based electrolytes are of particular interest.

Silver-based electrolytes give gold shades and they usually consist of silver nitrate and sulphuric acid. As with the copper and tin electrolytes, they are used at low pH (about 0.7), and a 1-2 g/l silver nitrate solution is adjusted to this pH with concentrated sulphuric acid. A colouring time of 3-5 min in such an electrolyte at about 10-12 V produces gold to golden brown finishes. Gold-based electrolytes give purplish shades, but the high electrolyte cost limits their industrial use. The use of aliphatic carboxylic acids as additions to silver nitrate based electrolytes has been studied recently by workers in Egypt.[239] Mixtures of citric acid and oxalic acid appeared to be the most promising.

Selenium and tellurium-based electrolytes are described in some of Alcan's work.[193] the former giving gold shades and the latter more greenish-gold tints. Of these selenium has been most used, particularly in Japan. The following electrolyte composition is suggested:

$Na_2SeO_3.5H_2O$	5 g/l
$Al_2(SO_4)_3.18H_2O$	20 g/l
H_2SO_4 to give a pH of	1.1

Ten minutes colouring at 15 volts in this electrolyte produced a gold shade. Selenium electrolytes are still attracting attention in Japan as indicated by the mixed selenium-copper electrolyte described earlier.[236]

Molybdate or tungstate solutions have been used by Gedde to produce a blue coloured film.[240] A 2% (wt) ammonium heptamolybdate solution containing 2% sulphuric acid was used at a current density of 0.4-0.5 A/dm^2 for 4 minutes, and a deep blue colour was obtained; this changed to yellow on sealing. On the other hand a stable blue colour was obtained using a 1.5% silicomolybdic acid solution containing 1.5% of boric acid and colouring for 2 minutes at the same current density.

Péchiney[241] produced blue colours by using a combination of a special alloy containing cobalt and nickel, anodizing it in a chromic acid electrolyte, and then a.c. colouring in a nickel or cobalt-based electrolyte. Ranges of colour from light blue to deep violet are described. Workers in Japan[242] produced clear blue colours by first a.c. treating in a bath containing an inorganic ferrous salt to deposit iron in the pores of the film. The material was then d.c. anodized in a bath containing a hexacyanoferrous salt. This colour and others described in a more general patent?'' may well originate through optical interference effects. Sandoz[244] describe a range of colours produced by first anodizing conventionally, then a.c. anodizing in a sulphuric acid, glycolic acid (1-10% vol), glycerol (1-10% vol) electrolyte. Finally the work is electrolytically coloured in a copper-based electrolyte. Alusuisse[245] have used a complex organic copper salt in combination with molybdenum or vanadium salts to produce a grey colour.

Many other electrolytes and colour effects have been disclosed, particularly in Japanese patent literature, but these are too numerous to cover in detail.

Equipment for electrolytic colouring

The equipment required for electrolytic colouring is relatively simple in comparison, for example, with that required for integral colour anodizing, and this is one reason why this type of process has been so widely adopted. Addition to an existing sulphuric acid anodizing plant normally means the addition of one or two extra tanks. one for the colouring process itself and a second often required as an additional rinse tank. The relatively short colouring times mean that one electrolytic colouring tank can cope with the output of two or even three anodizing tanks, and many plants only have a single colouring bath. Tank design is similar to that for sulphuric acid anodizing and polypropylene, p.v.c., resin-coated fibreglass or acid-resistant rubber lined tanks are normally used. Good air agitation is required in the colouring tank, but, as it is usually used at ambient temperatures, most plants do not require facilities for heating or cooling the electrolyte. Fume extraction equipment is also not normally needed. The special features of the electrolytic colouring process are the electrodes used and the nature of the power supply.

Electrodes

Many different counter-electrode materials have been used for electrolytic colouring. Early work described the use of aluminium, carbon or carborundum,[187] but the benefits of a metal equivalent to the colouring metal, such as copper in a copper-based electrolyte or nickel in a nickel-based electrolyte, were quickly recognised.[190] Since then many other materials such as tin (for tin-based electrolytes), lead and stainless steel have become commonly used. Gedde describes the use of molybdenum, tungsten or titanium in conjunction with molybdate or tungstate electrolytes.[240] The electrodes are used in the form of rods, tubes, sheets or strips arranged down the sides of the colouring bath, and in many cases a central electrode system is also used. This is shown diagrammatically in Fig. 8-28. The central electrode is necessary to ensure even colouring on both sides of the work, which is placed centrally between each set of electrodes.

Few electrode systems have been described in detail, but Alcan[246] claims a spaced electrode arrangement in which the total current emitting area of the counter electrodes is 3-50% of the linear area covered. In practice this means a large number of relatively small rod or strip electrodes with an area less than that of the work being anodized. For tin-based electrolytes Göhausen[225] describes the use of stainless steel electrodes with a total area about the same as the surface area of the work being coloured. He stresses the importance of the uniformity of distribution of the tubes or sheet used. Additional information for tin-based electrolytes is provided by Dito and Tegiacchi[247] who recommend austenitic steel of the 316 or 304 type. They show that the steel counter-electrode surface area must be larger than that of the anodized work in order to minimise corrosion of the steel. They also suggest that graphite electrodes, despite their brittleness, avoid electrolyte contamination and reduce consumption of stannous sulphate. Although stainless steel is the most usual electrode mentioned in the use of tin-based electrolytes, tin or graphite electrodes can also be used and combinations of tin and stainless steel electrodes in the same bath have been tried. Such supplementary electrodes of graphite, stainless steel, iron, copper, nickel or titanium have also been described by Tateyama Aluminium.[248,249] Stainless steel electrodes are also used with nickel electrolytes and Cakir[250] has shown that the presence of cobalt ions in a nickel electrolyte reduces corrosion of the steel.

Power supplies for electrolytic colouring

As has already been indicated most electrolytic colouring processes use alternating current, and this is provided by a single-phase autotransformer type power supply. These usually have a voltage capacity of 25-30 V and a current capacity of ½-⅔ of the capacity of the anodizing rectifiers, and they are equipped with suitable automatic voltage, current and time controls.

However, whilst simple power supplies can be used in many cases, there has been considerable effort, particularly in the last few years, to develop more sophisticated power sources. The simple type of power supply provides an essentially

sinusoidal current output, but the rectifying action of the anodic film leads to a non-uniform current wave-form measured at the colouring tank, as indicated in Fig. 8-29. **As** can be seen the anodic part of the colouring cycle is reduced in comparison with the cathodic part, and they are slightly out of phase.'"

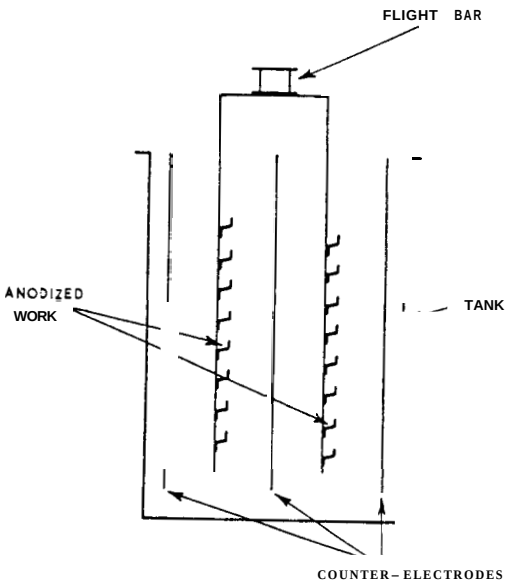


Fig. 8-28. Layout of counter-electrode system for electrolytic colouring[209]

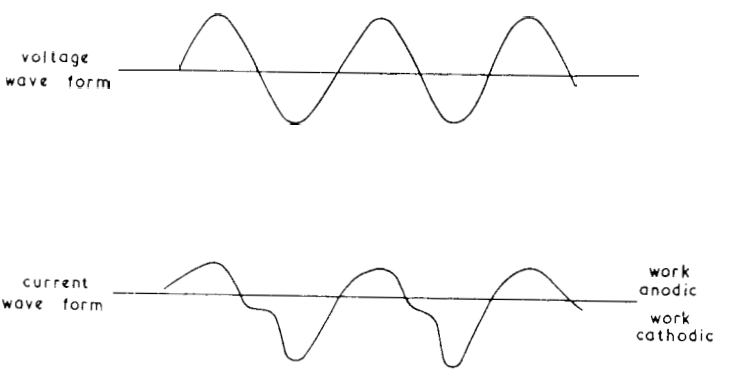


Fig. 8-29. Voltage and current wave forms during electrolytic colouring

As a result of this effect, some workers have proposed the use of asymmetrical wave-forms for colouring. Gedde[252] proposed that this should be done by means of diodes or thyristors such that the alternating voltage supplied was modulated as to its amplitude and/or frequency so as to make it asymmetrical. Typical arrangements are shown in Fig. 8-30, and they are said to give improved colour control and faster rates of colouring than conventional power supplies. Péchiney, on the other hand, produced an asymmetrical wave-form by superimposing d.c. onto the normal a.c.[253]

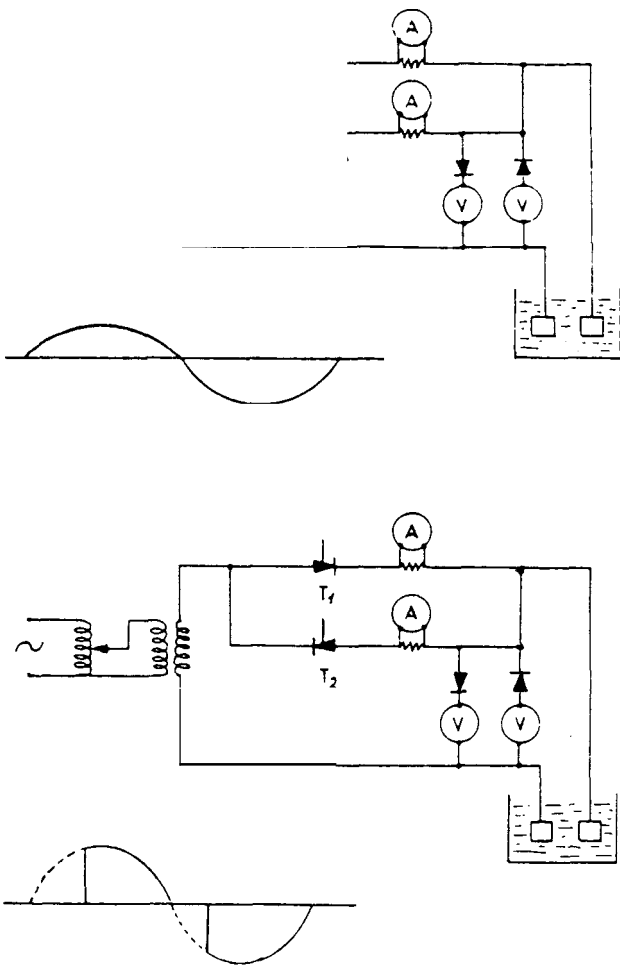


Fig. 8-30. Gedde systems for producing biased waveforms"?

Since then there has been considerable activity in the power supply field, particularly by companies in Spain, Japan and Germany. The use by Iongraf of an interrupted power supply[233] has already been mentioned and this is also described by Showa Aluminium*" and Endasa.[255] Such wave-forms are readily achieved using thyristors, and thyristor control is the basis of a further invention by Rodriguez.[256] The apparatus used comprises a power transformer the secondary winding of which has one phase connezted directly to the load and the other phase connected to the load through anti-parallel thyristors. One of the thyristors is triggered in accordance with a predetermined programme and the other is triggered according to the unbalance in the average values of the voltage applied in the negative and positive half cycles of the a.c., in such a manner as to tend to eliminate the unbalance. In practice the negative (colouring) half-wave is used as the reference point and the positive half-wave is balanced to this. This technique is claimed to give much improved throwing power and good metal distribution in the film. A later version of this system from Endasa[257] describes an even more complicated use of an operational amplifier, but again the objective is to balance the positive and negative parts of the voltage wave-form. The need for this arises from the capacitance effects occurring in the load. When a.c. is applied to an anodized load the oxide layer acts as a condenser which is charged to the peak value of the applied voltage. However, as the cycle reverses, the rate of discharge is slower than the reduction of applied voltage and it varies with the size of the load, the anodic film thickness and the anodizing conditions, so the effective values of the voltage which the load actually experiences are higher than expected. As this is a variable effect it is difficult to control by conventional colouring practices and it leads to difficulties in load to load colour uniformity.

Another approach has been to use pulsating voltages, and Endasa[258] claim a system in which a two-stage treatment in the colouring electrolyte is carried out. The first stage involves a positive pulsed voltage of the order of 20-30 V, and a negative pulse is then superirnposed on this for the main colouring period. Nippon Light Metal Co. in Japan[259] have taken a similar approach but using a series of discrete voltage pulses which are periodically reversed. Square wave pulses are preferred and the positive and negative pulse wave-forms can be symmetrical. In a further development of this technique[260] they describe the use of a direct current (cathodic) on which is superimposed a series of pulses with a positive voltage. The type of wave-forms used are shown in Fig. 8-31. They recommend that an initial short period, with the work made anodic in the colouring bath, is used in order to modify the barrier layer of the coating. Colouring then takes place in the usual way using a direct current with superimposed pulses of positive voltage as shown in Fig. 8-31, the ratio of the positive (ta) to negative (tc) part of the cycle being in the range of 0.005-0.30. A titanium counter-electrode is recommended for this system, and good colouring with high throwing power are claimed. The use of this 'Unicol' colouring process in Japan has been detailed.[261] Use of pulsed currents and periodic reversal of current have also been described by Riken.[262,263] Novomax[264] have disclosed a system which uses thyristor controls in the secondary of the power supply to generate a waveform in which the rate of voltage rise in the negative (colouring) part of the

waveform is lower than that in the positive half cycle. As usual the voltage waveform is biased towards the negative side. This is claimed to improve throwing power. The use of asymmetric current has also been claimed by Alusuisse.[265] Henkel[266] have covered a sophisticated power supply in which, by means of diodes and thyristors, the amplitude of the positive and negative half cycles, and the ratio of the amplitude level of the positive half cycle to the amplitude level of the negative half cycle of the applied a.c. colouring voltage, are variable and adjustable independently of one another. This method is said to give very short colouring times of 2 minutes for a dark bronze and 4 minutes for a black in a tin-based electrolyte. They also indicate that by varying the relative amplitude levels of the positive and negative half cycles, a range of shades can be produced in the same colouring time. This can be important with automatic and continuous plants. A similar principle is used by Elca.[267]

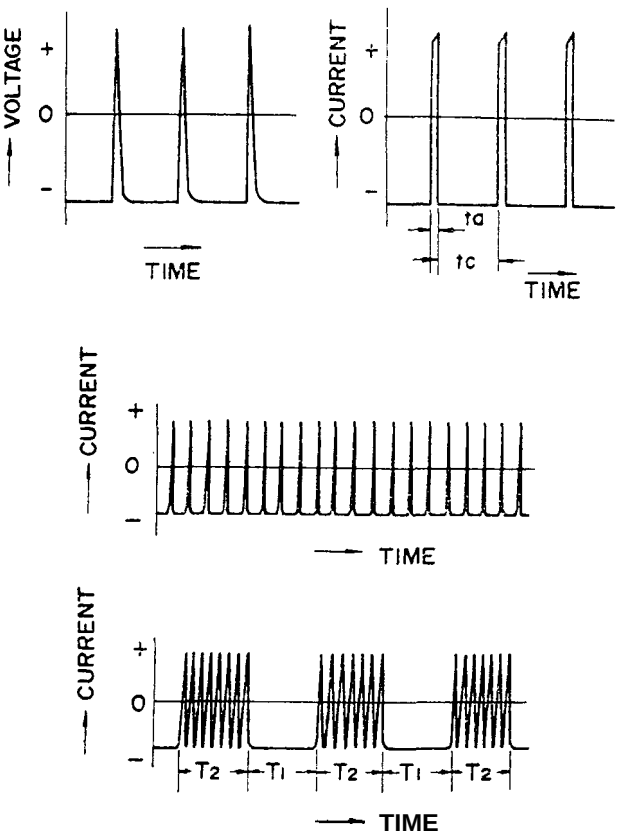


Fig. 8-31. Pulsed waveforms used for colouring by Nippon Light Metals Co. Ltd.[260]

A process that has become very important in electrolytic colouring is the use of an initial d.c. anodic stage before the actual a.c. colouring. This seems to have been first described by YKK.[268] In this they claim a process in which the work is made anodic in the electrolytic colouring solution and d.c. current is applied before a.c. colouring in the same solution. The colouring electrolyte must contain at least two metallic salts, with or without a strongly reducing compound. The examples show mixtures of nickel sulphate and magnesium sulphate as the metal salts, and ammonium thiosulphate as the reducing compound. The benefits of d.c./a.c. colouring are in improved colour uniformity, and this arises from modification of the barrier layer of the anodic film in the d.c. part of the cycle. In this regard Chemal[269] and Befeld[270] have shown the importance of carrying out this treatment in a solution capable of producing a barrier layer. In their studies the work was held in the colouring solution without current for 0.5-5 minutes between the d.c. and a.c. stages. As many colouring electrolytes contain salts such as boric acid the barrier layer forming requirement is easily satisfied. In this patent they also tackle another problem, that of passivation of the electrodes. To overcome this a d.c. voltage of 2-9 volts is passed between the counterelectrodes as anodes, and auxiliary electrodes as cathodes, before the d.c./a.c. colouring treatment starts. Fujisash[271] claim a process for colouring in which the work is first treated in the colouring electrolyte by applying a voltage of substantially positive waveform, and then colouring is carried out in the same electrolyte with an asymmetrical a.c. voltage such that the positive voltage is smaller than the negative voltage. Some details of this process have been published later[272] particularly in use with a nickel electrolyte. **As** usual improved colour uniformity and faster colouring are claimed, but also less sensitivity to impurities such as sodium in the colouring electrolyte.

Another approach has been disclosed by Ronain,[273] in which the work is first anodized conventionally and then treated in a bath of very dilute sulphuric acid (less than 4 g/l) under a.c. conditions with a peak voltage in the range of 55-85 V. The a.c. is supplied from the secondaries of a transformer with what is described as a polyphase network such that the charge distribution between the phases is balanced. The same power supply is then used to electrolytically colour the work in a metal salt solution, again at high peak voltages. A somewhat similar approach has been used by Aiden in Japan[274] who lowered the final voltage in the sulphuric acid anodizing bath[275] to very low values before conventional electrolytic colouring.

A number of workers, particularly in Japan, have tried to combine the anodizing and colouring processes in the same bath by using a.c. for the sulphuric acid anodizing, and adding appropriate metal salts to the bath. This, however, is likely to produce sulphide colours of the type described in Chapter 7, as well as giving conventional electrolytic colouring. Sulphide colouring is deliberately used in this way in other Japanese work.[276,277]

Clearly, from the intense activity in this field, there is much to be gained from the use of special power supplies for electrolytic colouring, but the complexity of some of the systems and the numerous alternatives that exist make any evaluation of such alternatives very difficult.

D.C. colouring processes

In the early stages of work on electrolytic colouring it was considered essential to use a.c. and, despite the similarities to electroplating processes, that it was not possible to colour under pure d.c. conditions. The closest to a d.c. system was that developed by Péchiney[202] and already referred to under nickel-based electrolytes. This process used d.c. for colouring, but required interruptions to the cycle to allow the work to discharge. A somewhat similar system was described by Aiden who used alternate periods of d.c. followed by low voltage a.c. for colouring.[278]

Sumitomo, on the other hand, demonstrated that pure d.c. could be used for colouring and they have carried out a considerable amount of work to develop the d.c. process. The first disclosure of this system[279] claimed very broad cover for deposition of most of the known metals, but the examples concentrated mainly on deposition from nickel and cobalt based electrolytes. They were fairly conventional and typically contained:

nickel sulphate	*50* g/l
ammonium chloride	*25* g/l
boric acid	*25* g/l

A graphite anode was used and colouring was carried out at relatively high current densities (up to 2.5 A/dm^2), so colouring rates could be very high. Voltages were low being typically in the range of 10-14 V. Benefits claimed were fast colouring times, low operating voltages, the ability to colour castings as well as sheet and extrusions, and good colour control.

However, later work[280,281] showed that one of the reasons that others had experienced difficulties with d.c. colouring was the great sensitivity of this system to sodium contamination. This is indicated in Fig. 8-32, these results being obtained with a 9 micron anodic film on 1100 sheet coloured in a 50 g/l nickel sulphate, 30 g/l boric acid solution used at 0.5 A/dm^2 d.c. for a time of 0.5 min. Sensitivity to very low levels of sodium, potassium and ammonium ions is indicated, and an upper limit of 6 ppm of sodium is stated.[281] At this level special precautions need to be taken to avoid sodium contamination, as a bath made up with normal chemicals will have a much higher level than this, and Sumitomo suggest cation exchange[282] to keep the sodium at this low level. Use of alternate cathodic and anodic cycles is also said to make the system less sensitive to sodium contamination,[283] as is the use of d.c. followed by periodic reverse a.c.[284]

Most of the work carried out by Sumitomo has been with nickel-based electrolytes and the pH of these baths is preferably between 3.0 and 4.5,[285] a level rather lower than that preferred for a.c. colouring. As with a.c. colouring the nickel baths give a range of light bronze to black finishes, but other colours produced in cobalt, iron, tin and copper-based electrolytes are shown in Table 8-23.

Alcoa have also investigated d.c. colouring treatment[286] and in addition to accepted colouring metals such as copper, silver, cadmium, tin, selenium and tellurium they also coloured with arsenic, antimony and bismuth salts. They

pointed to the necessity for having intermetallic particles such as Mg_2Si, $MgZn_2$, Cu-Cr, Cu or Mn bridging the barrier layer of the anodic coating so that these could act as preferential sites for metal deposition.

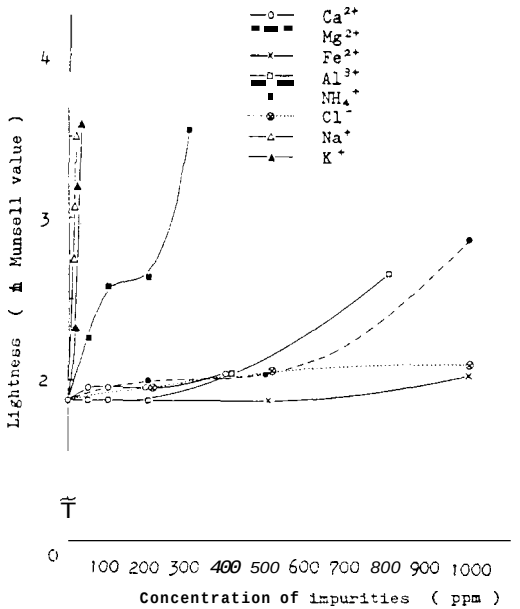


Fig. 8-32. Influence of impurities in colouring solution on the lightness of the coloured film[280]

Articles: 1100 sheet with 9 microns anodic oxide film
Composition of colouring solution: $NiSO_4$ 50 g/l, H_3BO_3 30 g/l, H_2O balance
Conditions in the 2nd step:
current density: 0.5 A/dm², d.c.
time of electrolysis: 0.5 min.
temperature: 22°C

D.c. has been used in another sense by Péchiney.[287] One of the general problems of electrolytic colouring is that, if the colour produced is darker than required, the deposited metal cannot readily be removed and the work has to be completely reprocessed. Péchiney suggested the use of d.c. after the normal a.c. colouring stage to lighten the colour to the required level. The d.c. treatment is carried out in the colouring bath with the work made anodic and better colour control is claimed by deliberately over-colouring and then lightening the colour to the desired shade in this way. An earlier patent[288] covers the use of a d.c. treatment in separate sodium thiosulphate solution after colouring. D.c. colouring in acid tin solutions in the presence of cationic dyestuffs has already been mentioned.??"

TABLE 8-23

D.C. colouring electrolytes[281]

Metal salts	Composition *of solution*		*Colours produced*
Nickel sulphate	$NiSO_4$	50 g/l	light brown
	NH_4Cl	30 g/l	
	H_3BO_3	30 g/l	
Nickel sulphate	$NiSO_4$	*50* g/l	deep brown
	H_3BO_3	*30* g/l	
Cobalt acetate	$Co(CH_3COO)_2.4H_20$	60 g/l	brown
	CH_3COONH_4	10 g/l	
	H_3BO_3	10 g/l	
Ferrous sulphate	$FeSO_4$	*75* g/l	yellow
	NH_4Cl	40 g/l	
	H_3BO_3	*25* g/l	
Stannous sulphate	$SnSO_4$	saturated	black
	H_2SO_4	10 g/l	
Stannous chloride	$SnCl_2$	saturated	blackish brown
	NH_4Cl	10 g/l	
	H_2SO_4	10 g/l	
Cupric sulphate	$CuSO_4$	10 g/l	reddish brown
	NH_4Cl	10 g/l	

Continuous electrolytic colouring

Just as electrolytic colouring has become an important process for batch anodizing so it has also in the field of continuous anodizing, and many hundreds of tonnes of colour anodized aluminium are produced this way each year. The continuous process presents some difficulties as both d.c. (for anodizing) and a.c. (for colouring) are applied to the moving strip. Alcan[289] have proposed a system using a.c. with a superimposed d.c. component in the colouring cell and with the a.c. circuit completed by means of an electrode immersed in the anodizing electrolyte at a position facing substantially unanodized aluminium so as to effect a liquid contact. This arrangement is shown in Fig. 8-33.

In this Figure aluminium is drawn from a supply reel (not shown) into an anodizing cell into which a stream of sulphuric acid electrolyte (for example 15% H_2SO_4) is supplied through inlets *(2)* and withdrawn through outlets (3) for recirculation. The cell (1) is shown as having five pairs of spaced electrodes (4). For performance of the

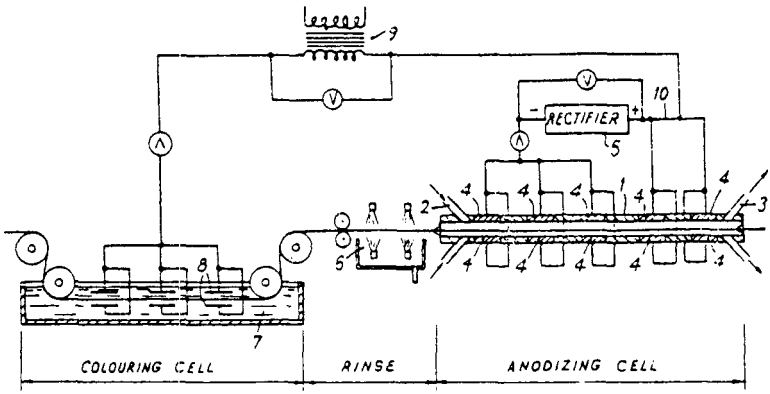


Fig. 8-33. Alcan system for continuous electrolytic colouring[289]

anodizing operation the first two pairs of electrodes (4) are connected to the positive of a rectifier assembly (5) and the remaining three pairs of electrodes (4) are connected to the negative.

After leaving the anodizing cell the now anodized strip is passed through a rinsing stage, shown diagrammatically at (6), which serves to remove the sulphuric acid electrolyte. The strip then enters the electrolytic colouring cell (7) in which it passes between an array of counter-electrodes (8). The counter-electrodes are connected to one terminal of **a** variable voltage a.c. supply (9), the other terminal of which is connected to the anode electrodes (4) in the cell, from which current flows to a substantially unanodized portion of the surface of the aluminium strip. Lead electrodes were used and the electrolyte composition (nickel bath) was essentially the same as that used for batch colouring. All the metals normally used for electrolytic colouring could be deposited continuously.

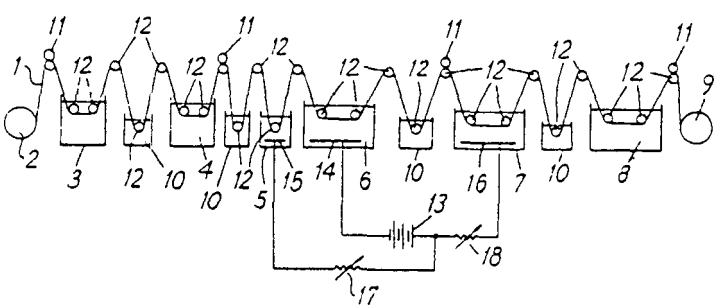


Fig. 8-34. Sumitomo system for continuous d.c. electrolytic colouring[292]

A similar arrangement has been described by Pilot Pen,[290] whilst Alusuisse[291] use an intermediate, acidic contact electrolyte between d.c. anodizing and a.c. colouring. Sumitomo, on the other hand, have translated their experience of batch d.c. colouring into a continuous process"' and this is shown in Fig. 8-34. In this system an aluminium strip or wire 1 is supplied continuously from a supply roll or a recoiler 2, passed successively through a degreasing bath 3, an etching bath 4, a current adjusting electrolyte bath 5, an anodic oxidation bath 6, an electrolytic colouring bath 7 and a sealing bath 8, and is recoiled on a recoiler 9. If desired several rinse baths 10 and drive rollers 11 may be in the line together with guide rolls 12. The negative terminal of a d.c. power source 13 is connected to a cathode 14 placed in the anodizing bath 6 and the positive terminal is connected through a rheostat 17 to an electrode 15 placed in the current supply bath 5, and through a rheostat 18 to an electrode placed in the colouring bath 7. The need for the current adjusting bath now becomes obvious as one power supply is feeding current to both the anodizing and colouring cells and they may be controlled independently by appropriate use of rheostats 17 and 18. Electrodes 14, 15 and 16 can be graphite or an insoluble lead alloy, but a metal of the same type as is being deposited (e.g. Ni in a nickel electrolyte) can be used in the colouring cell 7.

A later development by Sumitomo[293] describes the use of an anode box through which the colouring electrolyte is pumped onto the surface of the strip. Suitable arrangements of the anode box allow colouring on one or both sides of the strip.

General colouring practices

Whilst much information has already been provided on electrolytic colouring practices, some other general comments may be useful. The processes are normally applicable to a wide range of alloys and, unlike integral colour anodizing processes, are not very alloy dependent. However most satisfactory results will be obtained with the Al-Mg sheet alloys (5000 series) and the Al-Mg-Si extrusion alloys (6000 series). Alloys with a high silicon content (4000 series) or a high copper content (2000 series) may give serious colouring problems, as intermetallic particles in these alloys can bridge the barrier layer of the anodic coating. This gives very high current flow at these points and much hydrogen evolution which prevents effective colouring. Casting alloys often give colouring problems for the same reason.

The jigging operation is a very important aspect of most electrolytic colouring processes as many have a poorer throwing power than the normal sulphuric acid anodizing electrolyte. The use of a central electrode system to improve throwing power has already been mentioned and work has to be carefully arranged on the anodizing jigs to ensure good colour uniformity within the load. Unlike the anodizing operation, the more closely the work is placed the slower will be the rate of colouring, so this is a factor which must be taken into account in order to obtain good load to load uniformity. Jigging should be firm as contact must not be lost between anodizing and colouring so clamped or bolted contacts are preferred. In

this connection, titanium clamps or jigs cannot be used for electrolytic colouring as due to their very thin oxide film they thieve current during the colouring operation.

The electrolytic colouring process is not very sensitive to anodizing factors such as anodic film thickness variation, but in some cases, particularly with the very acid tin or copper-based electrolytes, the quality of the anodic film produced is important. Göhausen[225] recommends a maximum anodizing temperature of 18°C and a minimum anodizing current density of 1.5 A/dm^2 when colouring to dark shades in a tin-based electrolyte. Higher anodizing temperatures or lower current densities produce a film which can be attacked further in the colouring electrolyte and significant reduction in abrasion resistance has been seen with such films. Where harder than normal films are required, anodizing can take place at lower temperatures or sulphuric-oxalic acid electrolytes can be used, and Reynolds have used their multi-purpose electrolyte (see Chapter 7) for electrolytic colouring.[294] The ability of electrolytic colouring processes to produce a full range of shades on thin anodic films (5-10 microns) has made them interesting for automotive finishes and several processes have been used in this way.[295,296,297]

Rinsing between anodizing and colouring can be important, particularly for the electrolytes used at higher pH (4-6), and, with electrolytes that are sensitive to aluminium build-up, transfer of aluminium from the anodizing electrolyte must be minimised.

Agitation of the colouring electrolyte is probably more important for obtaining good mixing of the chemicals in the bath than being essential for colouring, but it can be important with the high pH colouring electrolytes. Continuous agitation is undesirable with tin-based electrolytes as it increases oxidation of the stannous sulphate. Temperature control in electrolytic colouring processes is much less critical than with anodizing and most baths operate at ambient temperature, whatever that may be. However, high ambient temperatures (above 30°C) may give increased colouring problems particularly with the darkest finishes. In contrast in a patent from Kaiser[298] a nickel sulphamate-based colouring electrolyte is deliberately kept at a temperature above 35°C.

Rinsing after colouring can also be important so as to avoid contamination of the sealing bath. With some electrolytes colour loss can occur in the stages between colouring and sealing, particularly when producing very light shades. Sealing operations after electrolytic colouring are not normally influenced by the colouring process, so conventional sealing practices are used, but sealing smut is always very visible on coloured surfaces and anti-smutting additives are commonly employed in the sealing solution.

The mechanism of electrolytic colouring

In the early stages of electrolytic colouring little information was available on the mechanism of the colouring process, and indeed it was not certain whether a metal or a metal compound was being deposited. Asada's early patents indicated

that a metal oxide or hydroxide was being deposited, but later work has generally indicated that the main deposition is of metallic particles. Laser[299] investigated electrolytes based on tin and copper and showed, in these cases, by X-ray goniometry that the deposits were metallic in character. Sandera[300] reported a thorough investigation of a range of colouring electrolytes including those based on cobalt, nickel, molybdenum, copper, tin, silver, iron and gold. He used a variety of examination techniques including X-ray and spectroscopic methods. Electron spectroscopy (E.S.C.A.) generally showed the presence of oxide, but most other methods indicated that the deposits were largely metallic. Lichtenberger[301] also concluded that the deposits were metal on the basis of the examination of copper-coloured films and Sautter *et al.*[302] showed by X-ray methods that, in the case of tin and copper, metal particles 60-250 μm in length were deposited in the film pores.

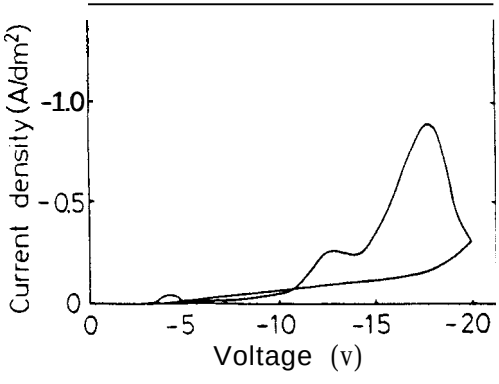


Fig. 8-35. Cathodic polarization of anodic oxide films in $NiSO_4$-H_3BO_3 mixed bath. (Thickness of porous layer 9 μm, barrier layer 150 Å)[305]

Later work concentrated more specifically on deposition of particular metals. The state of tin in tin-coloured anodic films has been studied by Cohen *et al.*,[303] who used Mossbauer spectroscopy to show that the tin was predominantly present as tin metal. Saji *et al.*,[204] studied copper-based electrolytes and showed that metallic copper could be deposited on the surface of the anodic film as well as within the pores. In the former case defects in the anodic film structure appeared to be the main cause of surface deposition.

Sato and Sakai[305] used polarization studies to investigate deposition from nickel-based electrolytes. They measured the cathodic polarization curve in a nickel sulphate-boric acid electrolyte and this is shown in Fig. 8-35. Three peaks were measured, the first at -4 V representing reduction of hydrogen ions, the second at −13 V being uncertain in origin and the third at −18 V representing reduction of

nickel ions. These polarization peaks were shown to be affected by both the anodic film thickness and the barrier layer thickness of the film and these results are shown in Figs. 8-36 and 8-37. When the porous layer was thinner than 2 tnicrons cathodic current due to hydrogen production was very high and the film was not coloured (Fig. 8-36). The first and second cathodic current peaks were observed with a 4 micron film but the colouring peak at –18 volts was still absent; all three peaks were seen with the 9 micron film. This effect of low anodic film thickness almost certainly varies with the colouring electrolyte and conditions used, but when the film is too thin colouring is difficult. The effects of barrier layer thickness (Fig. 8-37) are also significant with a thin barrier layer not only affecting the shape of the polarization curve but moving the position of the main colouring peak. Although the origin of the middle peak is uncertain it is important as these workers showed that it was strongly affected by sodium or ammonium ions, the fonner ion at least being a major cause of spalling problems in nickel-based electrolytes.

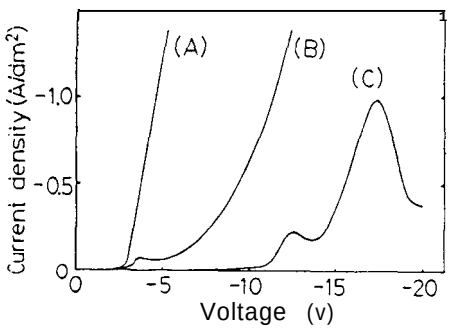


Fig. 8-36. Cathodic polarization of anodic oxide film in $NiSO_4$-H_3BO_3 mixed bath. Effect of porous layer thickness: barrier layer thickness -150Å, porous layer thickness – **(A)** 2 µm, (B) 4 µm, (C) 9 µm[305]

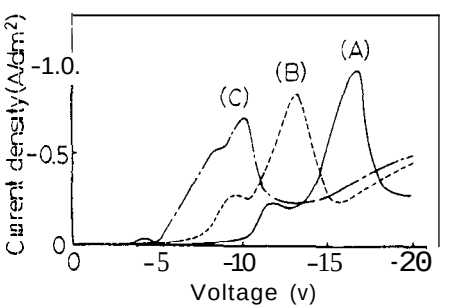


Fig. 8-37. Cathodic polarization of anodic oxide film in $NiSO_4$-H_3BO_3 mixed bath. Effect of barrier layer thickness: porous layer thickness - 9 µm, barrier layer thickness – **(A)** 1SO **A,** (B) 100 Å, (C) 50 Å.[305]

Later Sato[306] has proposed a gel layer model (Fig. 8-38) in which he suggests that a sol layer of aluminium hydroxide exists at the bottom of the pores of the film in the colouring bath (a). When cathodic current flows through the film, hydrogen ions and metal ions are cathodically reduced. The pH in the pores rises as a result of the reduction of hydrogen ions and the sol layer changes into a gel layer. At the same time reduced metal ions deposit in the pores and the cathodic current reduces due to the gel layer (b). Continued electrolysis produces thicker gel layers and more metal is deposited (c).

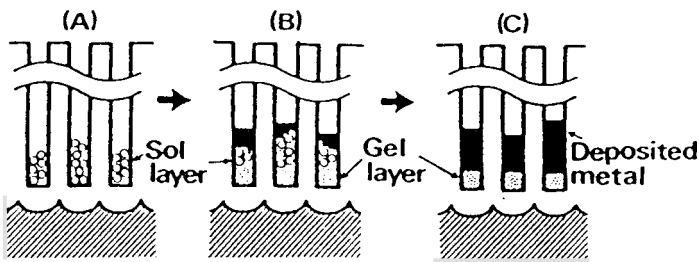


Fig. 8-38. Schematic diagram of the Gel layer model[306]

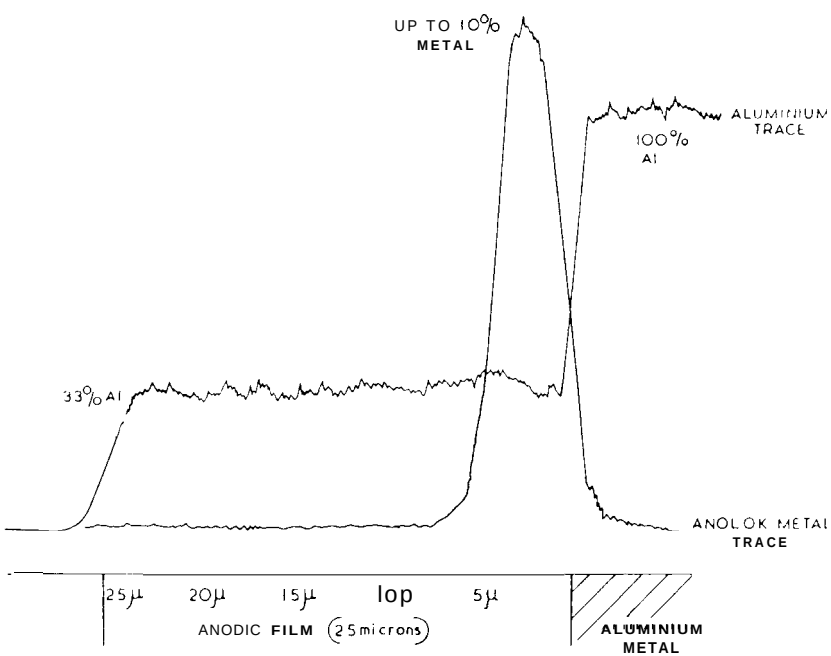


Fig. 8-39. Electrolytically pigmented anodic film (Anolok)[307]

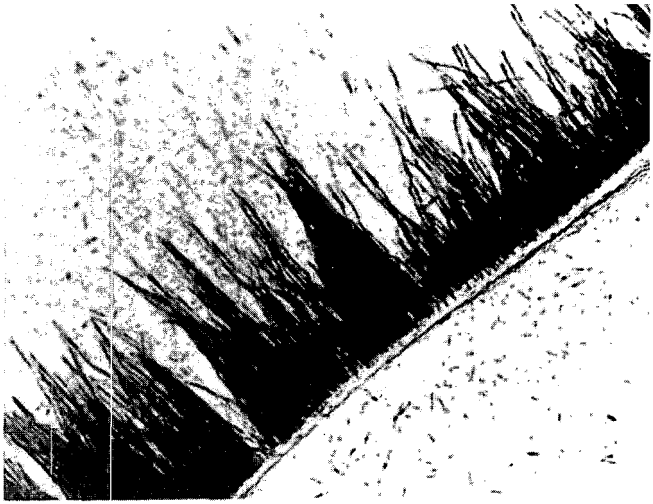


Fig. 8-40. Cross-section of anodic film coloured bronze by deposition from tin-nickel electrolyte (x 30,000)
[Photo courtesy of Nippon Light Metal Research Laboratory Ltd.]

Whilst there was, in the early stages, some controversy over the nature of the deposits, it was always clear that in contrast to dyestuffs, the majority of the deposit was close to the aluminium/aluminium oxide interface and that deposition started at the base of the pores. The height of the metal deposits increased with increasing depth of shade and typically occupied the lower 2-10 microns of the anodic film. A convenient way of demonstrating metal distribution is by means of an electron-probe microanalyser and a typical trace is indicated diagrammatically in Fig. 8-39.'''' In more recent times more direct observation of metal deposits within pores has been possible and a typical metal distribution produced from a tin-nickel electrolyte is shown in Fig. 8-40. This has been produced using an extraction replica technique and the long narrow columns of deposited metal can clearly be seen. The irregularity of the deposit lengths is also obvious, and it is clear that on an individual pore basis, deposition occurs at different rates in different pores, presumably depending on the flaw density in the barrier layer at individual pore bases. Metal distribution can also be demonstrated using a back-scattered electron imaging technique developed by Amor[308] for use with a scanning electron microscope. The results obtained with this technique are illustrated schematically in Fig. 8-41 and actual metal distributions for a nickel bronze, a cobalt black and a tin black finish are illustrated in Figs. 8-42 to 8-44. The irregular metal distribution can clearly be seen, as can the increase in metal spread occurring with increasing depth of colour. On the samples shown, the distribution of tin with the black finish shown in Fig. 8-44 is much wider than that with cobalt

in Fig. 8-43. This difference is commonly seen and strict control of colouring conditions in tin and copper-based electrolytes is essential in order to avoid spread of the deposited metal right through the film, as this can lead to reduced corrosion resistance and sealing problems.

The actual amount of metal deposited is not often quoted but it is small and has been given as within the range of 5-20 mg/dm^2 of anodized surface for tin coloured finishes.[227] Hirayama *et al.*[309] give figures for nickel and show the relationship between the amount deposited and the colouring time (Fig. 8-45). These results were produced using a 25 g/l nickel sulphate, 25 g/l boric acid, 15 g/l ammonium sulphate and 10g/l magnesium sulphate electrolyte at pH 5.0 and colouring at 10 V a.c. They show figures of 6-14 mg/dm^2 for nickel, though the darkest specimens were not black. Another interesting aspect of their work is the observation of what they call an 'anomalous point' in the colour developed using nickel-based electrolytes. This is shown up when measuring the L, a, b tristimulus values using a Hunterlab colour-difference meter. If aL or bL are plotted against the lightness value L the curves show a sharp dip at an L value of about 37% (Figs. 8-46 and 8-47). This is not related to the rate of nickel deposition, which is more or less linear over this period, but could be related to a changing form of the nickel deposits. The same effect has not been found with tin deposition. Whilst many metals produce bronze finishes they are all slightly different in tone and this can change with depth of colour or colouring conditions, and this may be an indication of slightly different deposit forms.

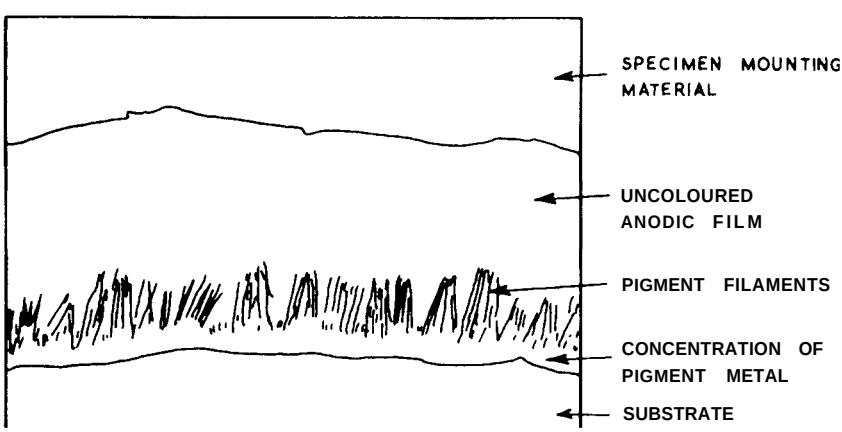


Fig. 8-41. Schematic diagram of metal distribution in cross-section of anodic film

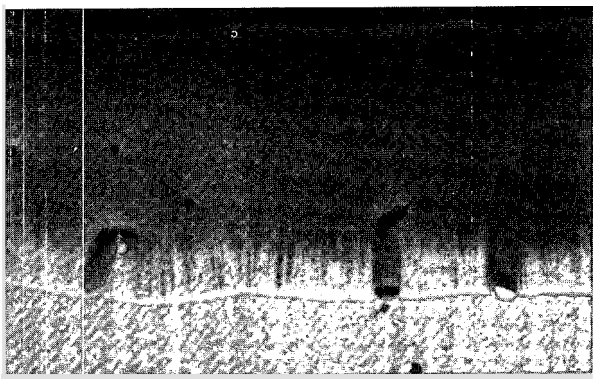


Fig. 8-42. Metal distribution in dark bronze finish produced in nickel-based electrolyte (25 micron film) (x 2500)

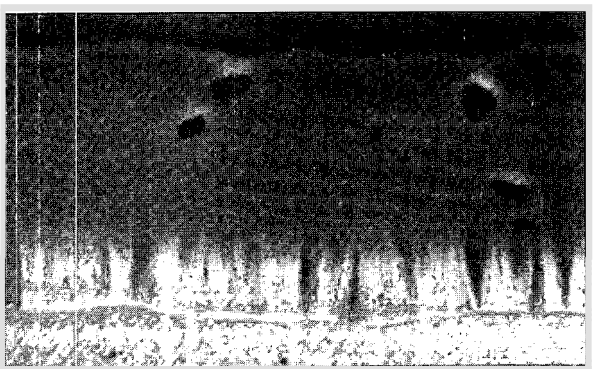


Fig. 8-43. Metal distribution in black finish produced in cobalt-bad electrolyte (25 micron film) (x 2500)

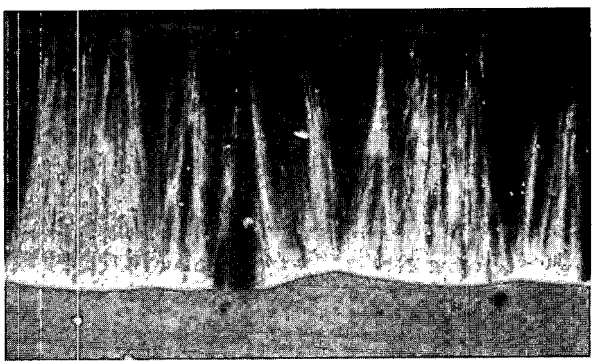


Fig. 8-44. Metal distribution in black finish produced in tin-based electrolyte (25 micron film) (x 2500)

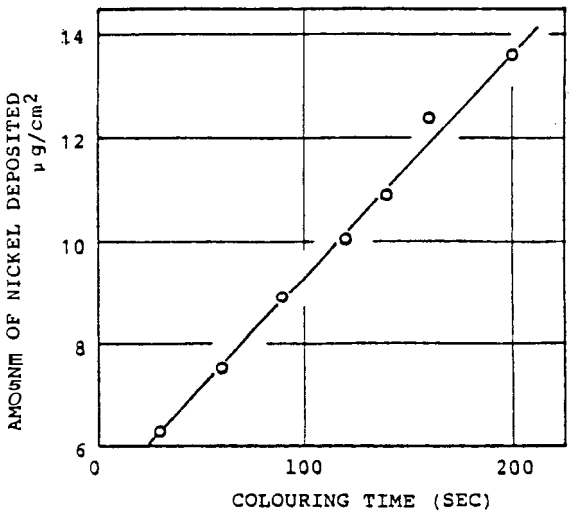


Fig. 8-45. Relation between the nickel deposition and colouring time[""]

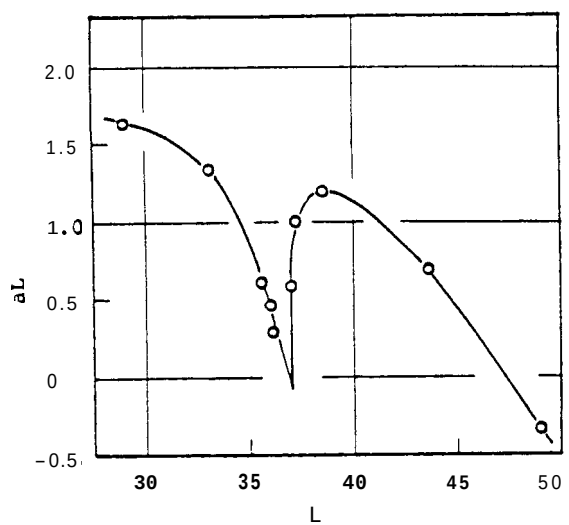


Fig. 8-46. Relation between L and aL at the anomalous point[309]

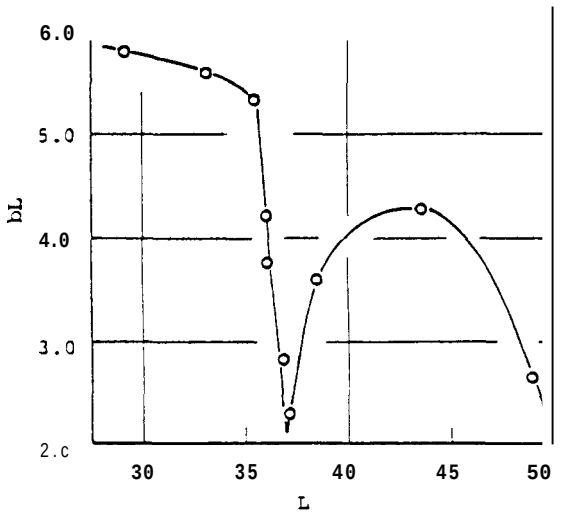


Fig. 8-47. Relation between L and bL at the anomalous point""

As has been noted earlier the condition of the barrier layer of the previously formed anodic coating can play an important part in the electrolytic colouring process, and the condition of the barrier layer during the very early stages of colouring has been studied by Doughty *et al.*[310] at U.M.I.S.T. They used an oxalic acid electrolyte to produce the initial film in order to grow larger pores which could be more readily examined, and they coloured using an acidic silver-based electrolyte (pH 1.0). They concluded that, in that electrolyte, the first stages of colouring involved a conditioning of the barrier layer of the film, during which, through thermally enhanced field-assisted dissolution, tiny incipient pores developed in and transformed the barrier layer. This 'recovery' process is essentially similar to that occurring when the voltage is reduced during anodizing (see Chapter 6) and may have been particularly noticeable in the U.M.I.S.T. work because of the high anodizing voltage required in oxalic acid. The metal (silver) then started to deposit at flaws in the base of the pores, but the nucleation and growth process occurred at different rates in different pores presumably because of different flaw densities. This is shown at an early stage of colouring in Fig. 8-48. Although a 9 minute colouring time has been used, most of this time represented barrier layer modification rather than metal deposition, and colouring only started after some 7-8 minutes of treatment. As deposition proceeded in the cathodic part of the cycle, reanodizing to form fresh film beneath the original barrier layer took place during the anodic half cycle. This latter process is clearly favoured by the very

acid conditions used with the silver electrolyte, and similar effects could occur with tin and copper-based baths, but it is less likely with the higher pH nickel and cobalt-based electrolytes.

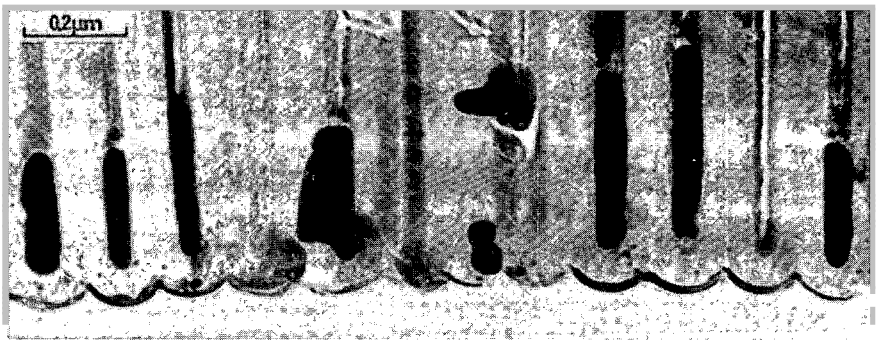


Fig. 8-48. Transmission electron micrograph of carbon replica of fracture section through anodic film formed on aluminium for 22 niin. at 65 V in 0.75M oxalic acid at 20°C and subsequently electrolytically coloured for 9 min. at 15 V in 0.15M sulphuric acid containing 0.01 M silver nitrate (pH 1.0) at 20°C[310]

Thus metal is being deposited in the cathodic part of the cycle at the base of the pores; it does not appear to penetrate the barrier layer and is not in direct contact with the aluminium, and the reactions occurring are similar to that with normal electroplating. What then is the importance of the anodic part of the cycle and why is colouring so difficult with d.c. alone? Well it seems, according to Thompson and Wood,[311] that the use of a.c. activates a larger population of flaws in the eventual barrier layer than does d.c., and this allows a much higher proportion of the pores to fill with metal. This is likely to be aided by some form of disruption or puncturing of the barrier layer and may be thermally enhanced as more heat is generated under a.c. conditions. Increasing the voltage and frequency of the a.c. waveform increases the speed of colouring but excessive values cause the film to spall. The pH conditions in the barrier layer region of the film may also be important. Mizuki ***et al.***[312] point out, in their study of colouring in copper-based electrolytes, that, because of the rectifying action of the anodic film in the cathodic part of the cycle, it is only H^+ ions which can migrate through the barrier layer, causing H_2 to be generated by trapped electrons in the barrier layer or discharge at the aluminium surface. This causes the pH at the pore base to rise allowing Cu^{2+} reduction. In the

following anodic period Cu^{2+} ions are supplied again from the bulk solution by diffusion down the pores. Once copper starts to plate out in this way, the rectifying action of the film is inhibited and hydrogen evolution reduced. However differences exist in the flaw densities at pore bases and prolonged colouring exaggerates these differences, with hydrogen generated preferentially in the low-resistancc pores. Current concentrates at these points leading to barrier layer breakdown and film spalling.

Spalling has been mentioned several times but has not been described and it is appropriate to do so here. Spalling is a defect that is almost unique to electrolytic colouring, though it has sometimes been seen during a.c. anodizing, and it represents local disruption of the original anodic film leading to local film detachment. The effect is shown in Fig. 8-49. In very severe cases the film can become detached over large areas of the sample but more usually small round pieces of film about 1 mm in diameter break away. The effect is caused by high colouring voltages or current densities and very long colouring times and can be severely aggravated by contaminating ions such as sodium. It is probably most prevalent in nickel-based electrolytes but can occur with most processes. It is almost certainly caused by hydrogen generation within or beneath the barrier Nayer of the film, and the pressure produced can locally separate the film from the aluminium. Rauscher[313] has shown that spalling is accompanied by acoustic signal emissions which can be monitored. Interestingly they could be detected in both the anodic half cycle (hydrogen evolution) and in the cathodic half cycle.

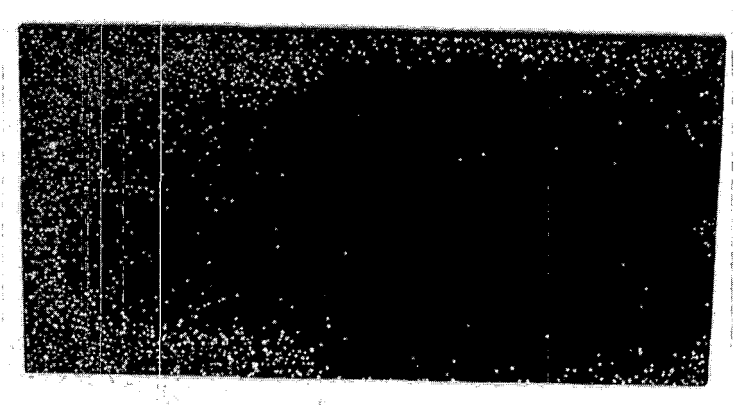


Fig. 8-49. Electrolytically pigmented bronze finish showing spalling

Returning to the significance of a.c. it may be that some barrier layer attack or disruption can occur during the cathodic part of the colouring cycle, and that some type of barrier layer repair is required during the anodic part of the cycle for colouring to proceed normally. Small ions such as sodium or ammonium may help barrier layer penetration, initially making colouring more difficult and later leading to catastrophic film breakdown and spalling. Evidence for barrier layer growth during colouring has been provided by Tachihara *et al.*,[314] and constituents which bridge the barrier layer, such as silicon, certainly prevent colouring completely.[315] The localised effect of a bridging constituent and the lack of metal deposition resulting can also be seen in Fig. 8-42. Under special conditions d.c. can of course be used for colouring, as already indicated, but the general need for absence of sodium in these situations is significant. Under d.c. conditions the process is more like electroplating, but the presence of an anodic film and its rectifying action make the situation much more complex with a.c. On the other hand Péchiney[316] have shown that an anodic film is not necessary in order to get colour, and have obtained colours from red through yellow to green and blue by a.c. treating bare aluminium in metal salt solutions. In this case the colours are almost certainly obtained by thin film optical interference. They are highly decorative but need to be protected by a clear coating such as a lacquer.

Having discussed many aspects of colouring the physical reason for colours being produced has still not been discussed, and again there are some differences of opinion. Many observers believe that the metal particles in the pores act as light scattering centres, rather than giving colour by light absorption as do dyestuffs. This is because the diameter of the metal deposits is small in comparison with the wavelengths of light and hence is of the Rayleigh type, which is strongly wavelength dependent. Thus the blue end of the spectrum is scattered more than the red end (and hence absorbed to a greater extent in the film) and the light emerging is therefore brown or bronze. The higher the deposit columns the more light that is lost by multiple scattering between the columns and hence the darker the colour. It is thus the arrangement of scattering centres that is responsible for the colour seen, and this explains why many metals give similar ranges of colour. It is only the strongly coloured metals, such as copper, that produce different ranges of colour. Goad and Moskovits[317] showed that colours could be explained on the basis of colloidal metal particles within the pores of the film, but no direct confirmation of the presence of fine individual particles within the pores has been obtained. However, the fact that similar colours are obtained by integral colour anodizing, and these are ascribed to the presence of free aluminium in the film, lends this theory some support.

More recently, films with much brighter colours (red, yellow, blue, etc.) have been produced by electrolytic colouring, and in these cases colour has been shown to have been produced by optical interference rather than by normal light scattering,[318] but these will be discussed in detail in a later section of this Chapter.

Properties of electrolytically coloured coatings

The properties of electrolytically coloured finishes have been described by many authors, and some of the papers already referred to[208,225,227,296,307] give details. In general terms electrolytically coloured finishes have many of the properties of normal sulphuric acid films, as factors such as abrasion resistance, corrosion resistance and sealing quality are not norinally affected. However specific electrolytes can affect film properties and this needs to be recognised.

In terms of light-fastness, finishes produced in nickel, cobalt or tin-based electrolytes are very lightfast, and it is this property that has led to their widespread use in architectural applications. The lighter pinks and maroons produced in copper-based electrolytes, and the gold shades produced in silver and selenium-based electrolytes, are more likely to show colour loss or change, and must be used with care in external applications, but Knutsson and Dahlberg[319] have reported good colour retention, after 5 years exposure, with dark maroon finishes. Sheasby and Cooke[307] indicate the very high lightfastness of the finishes in intense UV light, and report that the nickel and cobalt bronze finishes will withstand 200 hours exposure in the Uviarc apparatus (ISO 6581: 1981) without showing significant colour change. This is an exceptionally severe test and some of the dyed finishes used in external architectural applications show changes after 24 hours exposure. Other work with the test has indicated that, in terms of lightfastness, 24 hours exposure is equivalent to about 8 years outdoor exposure in the U.K.[320] Short *et al.*[296] report the good lightfastness of bronze and black finishes produced in nickel, cobalt and copper-based electrolytes with 5 micron anodic finishes, and their results are shown in Table 8-24.

TABLE 8-24

U.V. lightfastness of 5 micron electrolytically coloured finishes[296]

Colouring electrolyte based on	*Grey scale grade after:* 24 hours		113 hours	
	bronze	*black*	*bronze*	*black*
cobalt	5	5	5D	5D
nickel	5	–	5D	–
copper	–	5D	–	5D

Grey Scale Grades (BS '2662: 1961) U.V. Light test to ISO 6581 (1981)
5 = no change
4 = very slight fading
3 = slight fading
D = dulling of surface

The abrasion resistance of the finishes is also generally similar to that of normal sulphuric acid anodized coatings, and this is always true in the case of

finishes produced in high pH electrolytes (e.g., Ni and Co). On the other hand abrasion resistance can be reduced in the very low pH electrolytes (e.g., Cu and Sn) and this is dependent on the conditions used in anodizing as well as in colouring. Göhausen[225] shows the effect of anodizing current density when producing dark bronze and black finishes in tin and cobalt-based electrolytes (Table 8-25). Abrasion resistance has been measured using an abrasive wheel test (ISO 8251: 1987) in which the loss of anodic film thickness is measured after 400 double-movements of the wheel. It can be seen from Table 8-25 that, particularly when producing black finishes (i.e. the longest colouring time) in tin-based electrolytes, care must be taken to keep the anodizing current density to at least 1.5 A/dm^2. In the same way tin black finishes have a lower abrasion resistance than uncoloured finishes when produced at an anodizing temperature of 21"C (Fig. 8-50). For this reason Göhausen[225] recommends a maximum anodizing temperature of 18°C when producing dark finishes in a tin-based electrolyte.

Because of the influence of the more abrasion resistant integral colour anodized finishes on the architectural anodizing market, architects sometimes require electrolytically coloured finishes with a higher than normal abrasion resistance. This can be achieved by using a lower sulphuric acid anodizing temperature[321] or by using sulphuric-oxalic acid mixtures for anodising and, as already mentioned, Reynolds[294] have used an electrolyte containing sulphuric acid, a polyhydric alcohol such as glycerol, and an organic carboxylic acid such as glycolic acid, for anodizing. This at high anodizing current densities (2.5-3.5 A/dm^2) is said to give very abrasion resistant coloured finishes using a tin-based electrolyte, but no figures for abrasion resistance are quoted.

TABLE 8-25

Comparison between cobalt and tin colouring as regards the influence of current density[225]

Colour	*Anodizing current density in A/dm^2*	*Weight loss in the chromic-phosphoric acid test, in mg/dm^2*	*Film thickness reduction in the abrasive wheel test (400 double-movements, 1.96N) in µm*
uncoloured	1.2	15	3.4
	1.5	13.1	1.7
Sn, dark bronze	1.2	15	3.7
	1.5	13	2.6
Sn, black	1.0	16.4	10.7
	1.5	12.8	2.7
Co, black	1.2	18.4	3.0
	1.5	14.3	1.8

Material: A199.5; anodizing electrolyte: 160 g/l H_2SO_4, 7 g/l Al, 19°C; film thickness 25 µm; acid content of tin electrolyte: 20 g/l H_2SO_4

The corrosion resistance of electrolytically coloured finishes is another important property that has claimed considerable attention. With all electrolytically coloured finishes there is some reduction in corrosion resistance, in comparison with equivalent clear anodized finishes, when going to the very dark colours. This has been reported by Patrie and Colombier[322] with films coloured using nickel, cobalt and tin-based electrolytes and exposed in France for 8 years. They stressed the importance of long sealing times (greater than 2 min/micron) to minimise this effect. In earlier work Patrie[323] reported results of exposure of nickel and copper-coloured finishes and noted the much better performance of dark nickel finishes in comparison with copper. Again the importance of good sealing was recognised and Patrie found that the CASS test (ISO 9227: 1990) was a good accelerated test for predicting outdoor performance of such finishes. The problem of corrosion resistance of black copper finishes was also recognised by Qualanod[12] who exclude these finishes from their quality labelling scheme.

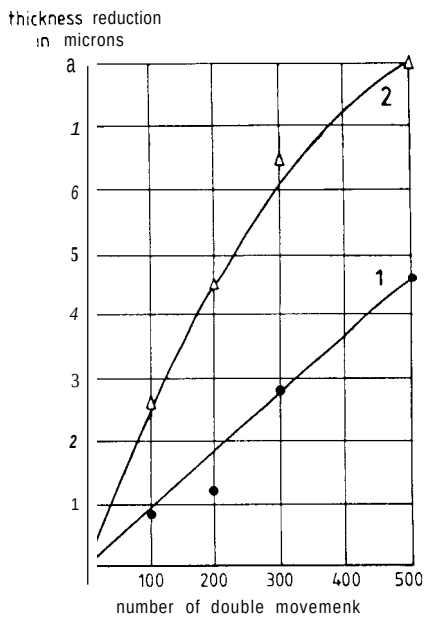


Fig. *8-50.* Influence of electrolytic colouring on the wear resistance of anodic films;[225] basis alloy AlMg 1, anodizing 200 g/l H_2SO_4, 1.5 A/dm², 21°C, film thickness 20-22 µm, sealed in deionised water + 1 g/l ammonium acetate.

1 = uncoloured 2 = electrolytic tin black

Sheasby[208] has described experience with cobalt, nickel and tin-based finishes exposed in the U.K. and reports up to 12 years' exposure of nickel and cobalt finishes without signs of pitting. He indicates that, with bronze finishes, nickel,

cobalt and tin all give similar, good corrosion resistance, but that with the very dark finishes, particularly black, tin black finishes show more pitting corrosion. This is demonstrated using acidified salt spray as an accelerated test (ISO 9227: 1990) and is confirmed in exposure performance at Sheffield. He ascribes this poorer corrosion resistance to the spread of metal through the anodic coating, but points out that if a good metal distribution is achieved then corrosion resistance of all the black finishes is similar. The effect of poor metal distribution for both copper and tin black finishes is also shown on samples exposed in Europe by the Qualanod organisation.[324] In this work both 15 and 25 micron black coloured coatings were exposed at several aggressive sites, and, particularly with the 15 micron finishes at the Duisberg site in Germany, significant deterioration of the tin and copper black finishes could be seen after only 5 years exposure. Equivalent nickel and cobalt coloured finishes showed little change. On the other hand, Göhausen[225] shows that, in his accelerated salt spray tests, there was little difference in corrosion resistance of bronze or black tin-based finishes and Faller[325] reports good performance of tin-based electrolytic finishes after 5 years' exposure in Germany. Brace[326] also reports good performance of tin-based electrolytic finishes on actual buildings in Germany.

For the tin anodic coatings used in automotive applications, Short *et al.*[296] examined the acidified salt spray performance of 5 and 9 micron bronze finishes produced in nickel and cobalt-based electrolytes, and similar black finishes produced in cobalt and copper-based electrolytes. The results are shown in Table 8-26. Again the poorer performance of copper-based finishes and the general trend towards slightly lower corrosion resistance with the darker finishes can be seen. Of course, with such thin films, the spread of the deposited metal through the film is of critical importance, as when producing black finishes the metal can fill the pores and even plate out on the anodic film surface. Colouring conditions must therefore be closely controlled to avoid excessive metal spread so that corrosion resistance and seal quality are not adversely affected.

It has been indicated earlier that sealing practices are not normally different for electrolytically coloured and clear anodic finishes, but excessive metal spread through the film will inhibit sealing even when using 20 to 25 micron coatings. In addition certain sealing tests, notably measurement of admittance values (ISO 2931: 1983), are strongly affected by the metal that is deposited during electrolytic colouring particularly copper and tin. This effect has been widely reported and Brace and Sheasby[186] give values for nickel, cobalt and copper based electrolytes as shown in Table 8-27. It can be seen that, although weight losses in the acid dissolution test (ISO 2932: 1981) are unaffected by the metal deposited, admittance values are strongly affected, particularly in the case of copper. Similar effects are noted in the case of tin-based electrolytes by Göhausen[225] and are shown in Table 8-28. This effect is due to the conductivity of the metallic deposits and the changes in the resistance and capacitance values of the anodic film that this produces, but the high admittance values obtained with dark tin and copper-based finishes may also be an indication of metal spread through the film. As a result admittance measurement is not a reliable method of assessing the sealing quality of dark electrolytically

coloured finishes and as the dye-spot test (ISO 2 143: 1981) also cannot be used, acid dissolution tests (ISO 2932: 1981 and 3210: 1983) are the only tests available.

Finally mention should be made of the heat resistance of electrolytically coloured finishes. Cooke and Sheasby[307] report that bronze finishes produced in nickel and cobalt-based electrolytes can be taken up to a temperature of 550°C for 1 hour without serious loss of colour. Copper and tin-based finishes will show colour changes at lower temperatures but all are stable at temperatures up to about 250-300°C. This is significant, for example, in reflector applications where surface temperatures may become quite high and dyestuffs are often not sufficiently stable.

TABLE 8-26

Acidified salt spray performance of electrolytically coloured finishes (ISO 3769 (1976))[296]

Finish	*Electrolyte based on*	*Film thickness (microns)*	*Time in test (hours)* 25	50	74	100	125	153	176	457
bronze	cobalt	5	1f	1m	1m	1m 2f	1m 2f	3m 16f	5m 30f	–
		9	NP	NP	1f	1f	1f	1f	1f	1c 4f
	nickel	5	NP	NP	21'	2t	2f	2f	1m 4f	–
		9	NP	NP	NP	NP	NP	NP	NP	6c 9m **14f**
black	cobalt	5	3f	1m 2f	1m 5f	1m 5f	1m 10f	2m 18f	5m 28f	–
		9	2f	1m 1f	1m 2f	2m 1f	2m 1f	2m 1f	2m 1f	2c 4m
	copper	5	1m	1c 2m 3f	1c 2m 10f	3c 5m 12f	6c 12m 18f	6c 12m 18f	11c 10m 24f	–
		9	NP	1m	2m	2c 3m 3f	5c 10m 17F	25c 11m	33c 10m 3F	>100c 20m
natural control		5	1m	1c 1m 1f	1c 2m 7f	1c 8m 10f	2c 10m 28f	3c 9m 45f	5c 34m 50f	–
		9	5f	4m 14f	6m 13f	8m 18f	9m 24f	4c 5m 30f	7c 5m 27f	10c 36m 35f

f = fine pits
m = medium pits
c = coarse pits
NP = no significant pitting

Number in each square equals number of pits counted

TABLE 8-27

Effect of seal tests on electrolytically coloured finishes (20 µ films sealed 2 min/micron)[186]

	Nickel electrolyte		*Cobalt electrolyte*		*Copper electrolyte*	
Colour	*Admittance value x tlzickness*	*Acidified sulphite wt. loss in mg/cm²*	*Admittance value x thickness*	*Acidified sulphite wt. loss in mg/cm²*	*Admittance value x tlzickness*	*Acidified sulphite wt. loss in mg/cm²*
None	253	0.03	253	0.03	246	0.04
Light	240	0.04	261	0.03	304	0.04
Medium	240	0.04	266	0.04	323	0.04
Dark	244	0.03	314	0.03	513	0.04
Very dark	300	0.04	329	0.02	3115	0.04

TABLE 8-28

Admittance values of dark films coloured with tin[225]

Colour	*Colouring conditions*		*Admittance*
	Voltage in V	*Time in min*	y_{20} *in µS*
dark bronze	16	4	23
black	16	8	77
black	16	9	100
black	16	10	130
black	16	15	200

Material: A199.5
Anodizing: 200 g/l H_2SO_4, 8 g/l Al, 1.5 A/dm², 18°C, 19 µm
Colouring electrolyte: 10 g/l Sn, 20 g/l H_2SO_3, 20 g/l P3-almecolor S
Sealing: 3 min/µm in deionised water

Interference colouring

In the late 1970s electrolytic colouring took yet another turn with the development by Alcan and Asada of a brighter, wider range of colours, which were shown to depend on optical interference effects for colouring.[327] This work was later described in detail by Sheasby *et al.*[318] The effect was found when anodizing in sulphuric acid was followed by a pore enlargement treatment, which could be carried out in many ways, but was most conveniently done by anodizing for a short period in a phosphoric acid-based electrolyte. Conventional electrolytic colouring in, for example, a nickel-based electrolyte for increasing time then gave a progression of colours going through blue-grey, grey-green and yellow-brown to, in some cases, even purple shades.

The effects occurring are shown diagrammatically in Fig. 8-51. Part (a) shows the structure of a conventional sulphuric acid film with long, parallel-sided pores, the diameter and separation of which are controlled by the anodizing voltage. Part (b) shows the same film after phosphoric acid anodizing for about 5 min at 25 V. The pores have become slightly enlarged throughout their length as a result of chemical dissolution, but the bottom 1 micron or so of the pores has become further enlarged, partly as a result of field assisted dissolution and partly from film growth under the new conditions. Electrolytic colouring in a conventional metal salt solution then produces shallow metal deposits capable of giving visible interference effects (Fig. 8-51 (c)). For such interference effects to occur the incident light beam must be scattered from two parallel surfaces separated by a difference of the order of the wavelength of light (a few hundred nm). The way the portions of light reflected from the upper and lower surface recombine, and the optical path difference between them, controls whether constructive or destructive interference occurs and hence the colour seen. In the case of the electrolytic finishes, the upper surface of the metal deposit formed one of the scattering surfaces and the aluminium/aluminium oxide interface the other. As more metal is deposited the separation of these two surfaces is increased and the colour changes from bluish to greenish to yellow and reddish colours.

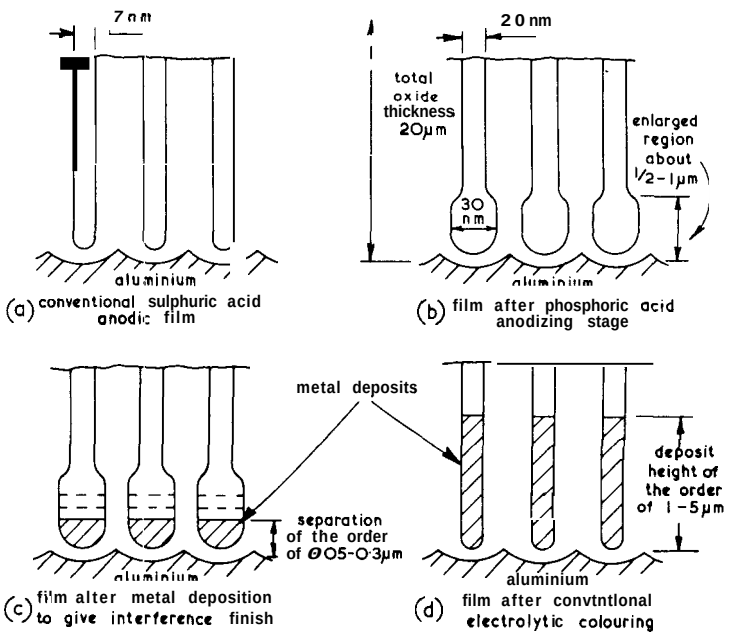


Fig. 8-51. Pore structure and metal distribution in conventional and interference finishes"'

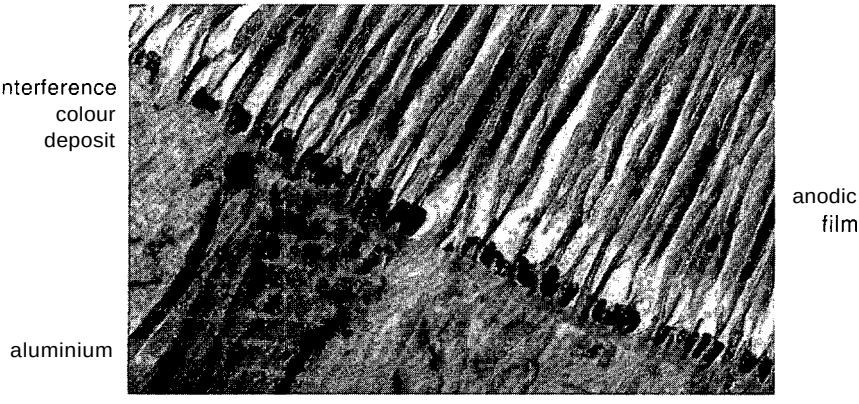


Fig. 8-52. Cross-section of typical interference finish produced in a nickel electrolyte[318] (x 100,000)

For comparison with the interference finishes the metal deposition in a conventional bronze electrolytic finish is illustrated in Fig. 8-51 (d). The much greater height of the deposit (too great for interference effects to be visible), the narrowness of the deposits and their irregularity (see Fig. 8-40) are the reasons that quite different colouring mechanisms take place. As a contrast to Fig. 8-40, an ultra microtomed cross-section of a typical interference finish is shown in Fig. 8-52. The pore enlargement at the base of the anodic film, the larger diameter deposits, their small height and their regularity can all be seen. The metal deposited in this case was cobalt.

These workers found that the colouring electrolyte, the metal deposited and the colouring conditions used to produce interference finishes were not very critical, the colour range being controlled by the pore structure developed in the intermediate anodizing stage. Both the enlargement in pore diameter and the vertical extent over which this took place were important. If the increase in pore diameter was too little only weak interference effects were visible, and if the increase was too great the pores tended to merge and the whole anodic film structure broke down, so that the production of satisfactory finishes was a compromise between an acceptable degree of pore enlargement and the achievement of the desired colours.

Phosphoric acid based electrolytes used for the pore enlargement stage could be used over a wide range of conditions, but typically 100-150 g/l phosphoric acid at 15-35°C for times of 2-10 min at 10-40 V was used (see Table 8-29). Desirable results could be achieved using both d.c. (work anodic) or a.c. conditions, or appropriate combinations of these. Any of the normally deposited metals could be used for colouring and deposition of nickel, cobalt or tin produced interference

TABLE 8-29

Example of conditions used to produce interference finishes on 6063 extrusions[318]

	H_2SO_4 anodizing conditions	2nd stage anodizing conditions	Electrolytic colouring conditions	Effect of colouring time on colour produced [in minutes] 1	2	3	4	6	8	12	16	20	24	28
Example 1	165 g/l H_2SO_4 20°C 30 min 1.5 A/dm² 17 V	120 g/l H_3PO_4 + 30 g/l oxalic acid 32°C 8 min 25 V (dc)	Sn-Ni electrolyte 20°C pH 7.0 15 V (ac)	–	No significant colour	Very light bronze	Light bronze	Mauve-grey	Grey	Grey-yellow	Purple-brown	–	–	–
Example 2	As above	100 g/l H_3PO_4 20°C 4 min 10 V (ac)	Ni electrolyte 24°C pH 5.6 11.5 V (ac)	–	Light bronze	Blue-purple	Blue-grey	Green-grey	Grey-brown	–	–	–		–
Example 3	As above	120 g/l H_3PO_4 25°C 10 min 20 V (dc)	Co electrolyte 20°C pH 6.0 9 V (ac)	–	–	–	Bronze-grey	Blue-grey	Grey-green	Yellow-green	Orange-brown	Red-brown	Purple	Dark bronze

finishes with a slight bronze overtone which increased with colouring time. Use of copper-based electrolytes gave interference effects with a pinkish overtone, and of silver gave a yellowish overtone. Deposition conditions in the colouring stage were not very important and controlled the rate of colouring rather than the colours seen.

Of the colours produced by this technique the blue-grey finish is particularly attractive for architectural applications and, after extensive production trials,[328] this finish,[329] under the name of Anolok II, was commercially introduced in the U.K. by LHT Anodisers Ltd. in 1984. An extension to their anodizing line was built to accommodate the new phosphoric acid anodizing stage, the extra rinses and the new colouring bath, and the arrangement is shown in Fig. 8-53. In practice a parallel line for interference colouring had to be built, with the work transferred to this new line after anodizing and back into the original line for sealing. More than 50 buildings have now been produced using this finish[329], one of the largest being the refurbishment of the Commercial Union building in London.

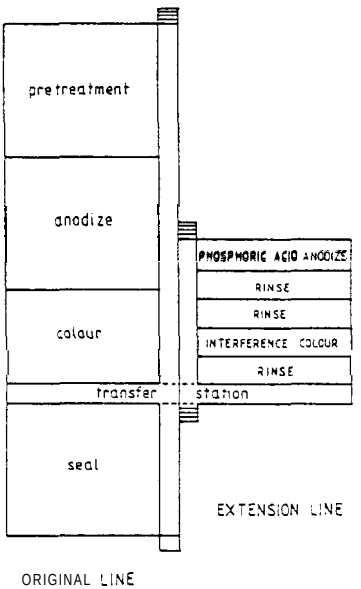


Fig. 8-53. Interference colour line in the plant of L.H.T. Ltd., Uxbridge[328] (not to scale)

Since the first work on interference colouring many other workers have studied this type of process, particularly in Japan.[330,331,332] Many of these workers did not recognise that they were dealing with interference effects and Sato[333]

attributes the blue and green finishes that he produced to a branched pore structure. In his case he produced large pores initially, by anodizing at 70 V in a chromic acid electrolyte, and then deposited nickel from a nickel sulphate-boric acid mixture.

Nippon Light Metal Co.[334] used their pulsed current power supply to produce interference finishes with either a phosphoric acid or chromic acid anodizing intermediate stage, and they have also described work using an alkaline bath for the intermediate pore modification stage.[335,336] Grace[337] have produced yellow or orange colours in a selenium-based colouring electrolyte after an a.c. phosphoric acid anodizing intermediate treatment.

Endasa have done much work on interference colouring using strongly acid colouring electrolytes in which both pore modification and metal deposition can take place. In one such disclosure[338] a sample anodized to a thickness of 15 microns in sulphuric acid was immersed in a bath containing 150 g/l of sulphuric acid, 5 g/l of stannous sulphate and 10 g/l of tartaric acid. A stainless steel counter-electrode was used and the a.c. voltage applied was raised from 0 to 25 V in 2 minutes, being then kept constant at that value. The colours obtained are shown in Table 8-30. With this system the ratio between the acid concentration and the metal salt concentration was shown to be critical, and was preferably between 40:1 and 20:1. Too high a ratio led only to anodizing and no colouring and too low a ratio produced only bronze finishes. A similar effect was also achieved by using pulsed voltages for colouring and first biasing it positively to give pore modification and then negatively to give colouring.[339] The reactions taking place with such a process have been described by Gazapo *et al.*[340]

TABLE 8-30

Colours obtained with increasing treatment time[338]

Treatment time (min)	*Colour*
2	light bronze
3	in-between bronze
4	intense blue
5	light blue
6	intense green
7	yellowish green
8	yellow
9	violet
11	blue
14	green

These highly acid systems are similar to further developments of interference colouring made by Alcan.[318,341] In this work it was found possible to produce a wider range of brighter clearer colours by using a colouring electrolyte in which anodizing could take place as well as colouring. Under appropriate conditions the oxide growth was found to take place beneath the metal already deposited, and the increase in separation of the two scattering surfaces (the top of the metal deposit and the aluminium/aluminium oxide interface) could be achieved without producing the bronze overtones seen in the initial work. This effect is shown diagrammatically in Fig. 8-54. Under these conditions very bright clear interference colours could be produced and it was possible to pass through the whole spectrum more than once to obtain 2nd and 3rd order effects.

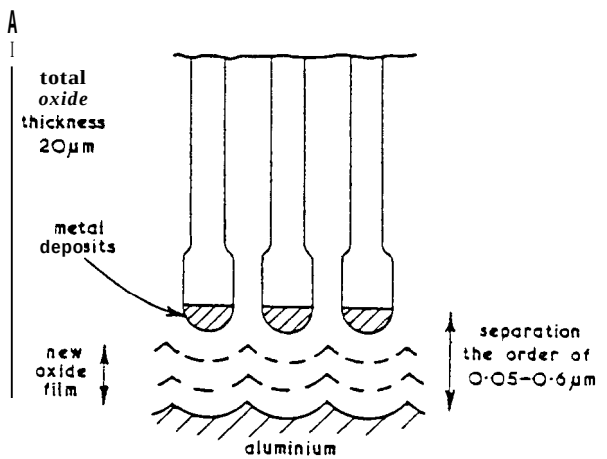


Fig. 8-54. Interference effects produced by anodizing beneath metal deposits''*

The effects could be obtained over a wide range of colouring conditions and the anodizing could even be carried out after colouring in a separate anodizing electrolyte. If both metal deposition and then anodizing were to take place in the colouring electrolyte then it needed to be sufficiently acidic (usually below pH 2.5) for anodizing to be possible. Metal deposition was the first reaction to take place and then anodizing followed, and the equilibrium between these reactions required fairly critical conditions. Typical conditions used and the colours produced are shown in Table 8-3I.

The fact that anodizing could take place below already deposited metal was surprising but could be clearly demonstrated, as similar colouring effects could be obtained by only making the initial metal deposition in a colouring electrolyte and then transferring the work to a suitable anodizing electrolyte, such as dilute

TABLE 8-31

Examples of conditions used to produce bright clear interference effects on 6063 extrusions[318]

	H_2SO_4 anodizing conditions	*2nd stage anodizing conditions*	*Electrolytic colouring conditions*	*Effect of colouring time on colour produced (in minutes)* ⅓	2	3	4	5	6	8	10
Example 1	165 g/l H_2SO_4 20°C 30 min 17.5 V (d.c.)	100 g/l H_3PO_4 22°C 4 min 10 V (a.c.)	Ni-Sn electrolyte 22°C pH 1.5 20 V (a.c.)								
Example 2	As above	100 g/l H_3PO_4 20°C 4 min 10 V (a.c.)	Sn electrolyte 22°C pH 0.5 10 V (a.c.)			ong yellc	ong oran				

solutions of sulphuric acid, sulphosalicylic acid or oxalic acid. The effect produced is shown in Fig. 8-55, where the original anodic film structure, the enlarged pores with the metal deposited, and the new anodic film beneath the deposits can be seen (cf. Fig. 8-52).

Whilst the production of interference finishes is inevitably a complicated operation, and many of the processes described have only been carried out under laboratory conditions, the wide range of coloured finishes that they produce makes them of potential interest for both decorative and architectural applications, and in the 1990's these processes have attracted a lot of attention with a number of processes reaching commercial application.[342]

One of these was developed by Garriga[343] in Mexico and had the potential of reducing the number of processing baths required. In this process the work is first sulphuric acid anodized; then the barrier layer is modified by using d.c., a.c. and then again d.c., either in the anodizing electrolyte, in a separate modification bath or in the colouring electrolyte. Finally metal is deposited in the modified pores in a conventional way to produce a spectrum of interference colours. A typical example shows anodizing in a conventional sulphuric acid electrolyte to produce an 18 micron film, then transfer to a modification bath of 50 g/l sulphuric acid where a d.c. current is applied at 16 V for 3 minutes. This is followed by a.c. treatment of 4 V for 3 minutes and then another d.c. treatment at 3 V for 4 minutes.

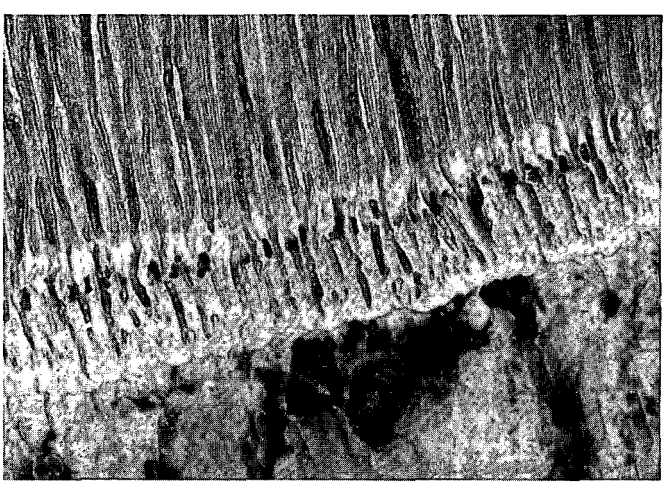


Fig. 8-55. Cross-section of interference finish showing growth of anodic film beneath the metal deposits (Ni-Cu colouring electrolyte)[318] (x 66,000)

The work is then transferred to a tin-based electrolyte and coloured for 4 minutes at 18 V to give a bright green colour. Changing the time of the barrier layer modification stage from 2-8 minutes gave colours of grey, blue, green, yellow, red and purple. Later patents from Garriga[344] describe a multi-layer process with different anodic film structures in each layer and metal deposited in these layers. The basic process involves conventional anodizing, then treatment to reduce the barrier layer thickness under d.c. conditions in a bath which may or may not be the colouring bath, then a.c. treating to produce an anodic film beneath the original layer but with finer pores, and d.c. anodizing, preferably in the same electrolyte, to produce a structure with fine pores but thicker pore walls. Finally metal is deposited in the film under normal a.c. conditions. This is clearly a very similar process to the first, but with more explanation of the structural changes that are taking place, and again a spectrum of colours is produced. Although these processes do not necessarily involve extra process tanks, they do require sophisticated power supplies and careful control of all the processes occurring.

Commercial processes developed in Europe include the Italtechno Greylox and Multicolor processes,[345,346] and the Novomax/Henkel Spectrocolor 2000.[347] Very little information has been published on the Greylox process, which is said to give a range of grey shades. It again involves an intermediate stage after anodizing in an acid solution capable of modifying the barrier layer but not damaging the existing coating, and it also uses a special power supply.

The Multicolor process produces the usual spectrum of interference colours. Once again it involves a pore modification step after normal anodizing, and this takes place **in a** weakly acidic solution containing an additive that protects the existing film from attack. It uses a special, computer-controlled power supply producing low voltage a.c. at a particular frequency and includes a d.c. stage. Metal deposition from a tin-based electrolyte then completes the process. Close control of the whole process is essential and anodizing temperature must be kept within $\pm 0.5\,^{\circ}C$ of the chosen value and the electrolyte within ± 5 g/l of the chosen sulphuric acid concentration. Throwing power and colour consistency are said to be good if the operating parameters are closely controlled, but central electrodes are recommended in all the baths.

Rather more information is available on the Spectrocolor 2000 process, which is described in patents.[348] It uses a low concentration (below 12 g/l) sulphuric acid containing electrolyte at low voltage (below 5V) with a complex alternating current to achieve pore modification. This bath can be the same as the colouring bath, so it may also contain stannous sulphate and appropriate stabilisers. Colouring then follows again using a complex a.c. treatment. This process is claimed to modify the crystalline lattice of the barrier layer and to give rise to colour by a different physical mechanism to optical interference. This phenomenon has been described by Rodriguez.[349] He sees the process as a light transmission process through a crystalline film which produces colour in a similar way to minerals such as rubies and emeralds. The barrier layer modification stage uses an a.c. current in which the positive part of the waveform is greater than the negative part (biased

towards anodizing). The peak voltage in the positive half-cycle must be below 7V and the current density below 200 mA/dm^2. This produces what Rodriguez calls barrier crystals which are said to develop between the base of the pores and the metal. They are claimed to have different physical characteristics to the rest of the film, including refractive index. Under these barrier layer modification conditions, the anodic film loses its transparency after a few minutes and becomes opaque in appearance. Formation of this opaque film is not dependent on the original film thickness but it is claimed to improve the corrosion resistance of the final finish. The final colouring stage deposits a very small amount of metal at the base of the pores and this needs very close control of both the electrical and the chemical parameters. In practice the baths tend to be more dilute (4 g/l $SnSO_4$) and less acidic (10 g/l H_2SO_4) than, for example, a conventional tin bath. An indication of the tight control of all conditions that is required with this type of process has been given in a paper by Korner.[350] He discloses that the temperature in the tin colouring bath needs to be kept within ± 0.2°C of the chosen value, and the sulphuric acid concentration in the bath within ± 0.25 g/l. Similarly in the anodizing bath the temperature must be kept within ± 0.5°C and the sulphuric acid concentration within ± 10 g/l. This sort of control is not easy to achieve, but the process, which has now been taken over by Henkel, has been installed in commercial plants, and the finishes are being used on buildings in North America and Europe.[348,349,350,351,352,353]

Alures[354] have claimed a process which seems identical to the processes described by Alcan, but with an acid conditioning stage between the phosphoric acid anodizing and colouring stages. Sumitomo[355] have summarised developments in the interference finishing of aluminium in Japan, and Munk[356] has described the importance of special a.c./d.c. power supplies in this type of colouring. In other Japanese work YKK[242] have produced blue colours from a.c. treatment in a bath containing a ferrous salt followed by d.c. anodic treatment in an electrolyte containing a hexacyano-ferrous salt. A conventional pore widening treatment is carried out before colouring. Kawai Engineering[357] disclose a process of anodizing in sulphuric acid first under d.c., then a.c. conditions, and then depositing tin-nickel particles in the modified pores to produce blue, green and gold finishes. They show, by means of back-scattered electron images, that the metal is deposited in the fine pores developed in the pore modification stage, and this is probably true of many of the processes that use low second stage voltages.

Alcan have proposed the use of interference finishes for other non-architectural applications, and these include colour change devices for tamper-evident packaging,[358,359] optical interference devices and magnetic media,[360] and sensors and security devices.[361] In another application they disclose multi-coloured devices.[362]

Taking two examples, the production of tamper-evident packaging involves the deliberate production of a weakened layer in the anodic coating such that the film is detached by bending and the colour changed or destroyed.[360] This can be done by controlled reduction of the anodizing voltage, in the same way

as for membrane production (see Chapter 7), or by incorporating adhesion reducing agents (usually 40-350 ppm of fluoride) in the final anodizing stage.

Because the metals deposited to produce colour can be redissolved in strongly acid solutions, it has been found advantageous to deposit a small amount of a noble metal, such as Pd, Au or Pt and this has been used selectively to provide multi-colour patterned articles.[""]

Combination colouring

Another interesting approach to widening the range of colours available for architectural anodizing has been the combination of electrolytic colouring and conventional immersion dyeing. This was first described by Nipp in Germany,[""] but has been extensively developed by Sandoz.[364] The principal is to anodize and electrolytically colour conventionally to *a* light to medium bronze shade, and then to colour this film by immersion in *a* normal dye solution and then to seal the film. Dyestuffs recommended for use in architectural applications are employed and by varying the shade of bronze used, a range of muted red, blue, yellow and gold finishes can be obtained. In all cases the dyeing is taken to saturation point and strict control of both electrolytic colouring and dyeing conditions is necessary to ensure good colour uniformity. Recommended dyestuffs are Sanodal Gold 4N, Sanodal Red B3LW, Sanodal Yellow 3GL, Sanodal Turquoise PLW and Sanodal Blue G. Bronze colouring can be carried out in nickel, cobalt or tin-based electrolytes.

Sandoz have shown that such finishes have excellent light-fastness and corrosion resistance,[365] and the process, known as Sandalor, has been adopted by several plants in Europe. An initial limitation of the technique was that production of the full range of colours required installation of 4 or 5 dye baths, and few plants had the space available to do this. However Sandoz then developed a spray dyeing system[365,366] which allows use of relatively small volumes of dyestuffs which can be stored off-line. A special spray dyeing and rinsing chamber is then required. The spray dye unit is illustrated schematically in Fig. 8-56.[365] It consists essentially of a spray chamber and one or several tanks for dye solutions, which are connected by a pump system to the spray chamber. In this chamber are a multitude of spray nozzles which direct a fine, strong jet of dye-liquor onto the anodized aluminium parts. After spraying, the excess dye liquor collects at the bottom of the chamber and is pumped back to the supply tanks. The dyeing time, temperature and concentration are the same as that used for conventional dyeing. The way in which such *a* unit could be incorporated in an existing anodizing line is illustrated schematically in Fig. 8-57.

Industrial experience with the spray dyeing technique[367] has shown that iron and copper must not be used for pipes, pumps and valves, and filters are required in the inlet system. A spraying angle of 60-90" is favourable and the distance between the spray nozzles is 20-50 cm. Two pumps are required, one

for the return of the dye liquor and one for spraying, the latter generating a spray nozzle pressure of at least 1.5 bar and a spray rate of 1-4 l/min per nozzle.

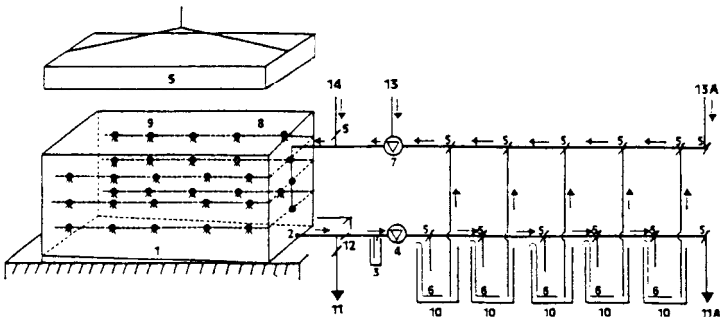


Fig. 8-56. Schematic diagram of a spray dye unit.[365]
Key:
1 Spray chamber with inclined floor.
2 Lowest point of chamber (outlet).
3 Filter.
4 Pump for backflow.
5 Valves.
6 Electrical immersion heater (thermostat controlled).
7 Pump for spray nozzles.
8 Pipes for nozzles.
9 Spray nozzles.
10 Outlet (to drains before colour change).
12 Pneumatic valves for control of outlet/backflow.
13 Rinsing water inlet.
13 A Rinsing water inlet before colour change.
14 Compressed air for evacuation of pipes.
15 Removable cover

Cleaning the system, before rinsing or colour changes, is achieved by blowing compressed air through the pipes and then rinsing them with water. Work is placed in the spray chamber at a slight angle so that dye solution runs off it readily; this is particularly important with hollow articles. In this way very uniform dyeing has been achieved.

Finally a rather different approach to combinations of electrolytic colouring and organic colouring has been disclosed by Erbsloh.[368] They describe the production of grey finishes using a metal salt solution at pH 4-5, and containing a salt such as cobalt sulphate and an azo dyestuff giving a violet-blue colour. The combination of bronze from the electrolytically deposited metal and violet-blue from the dyestuff gives a range of grey finishes. In other work Henkel[369] disclose electrolytic colouring using a solution containing cationic organic dyes. This process uses a.c. or a.c. superimposed on d.c. to deposit the cationic dyestuffs at

the base of the pores of the anodic film, thus giving better protection against corrosion and abrasion.

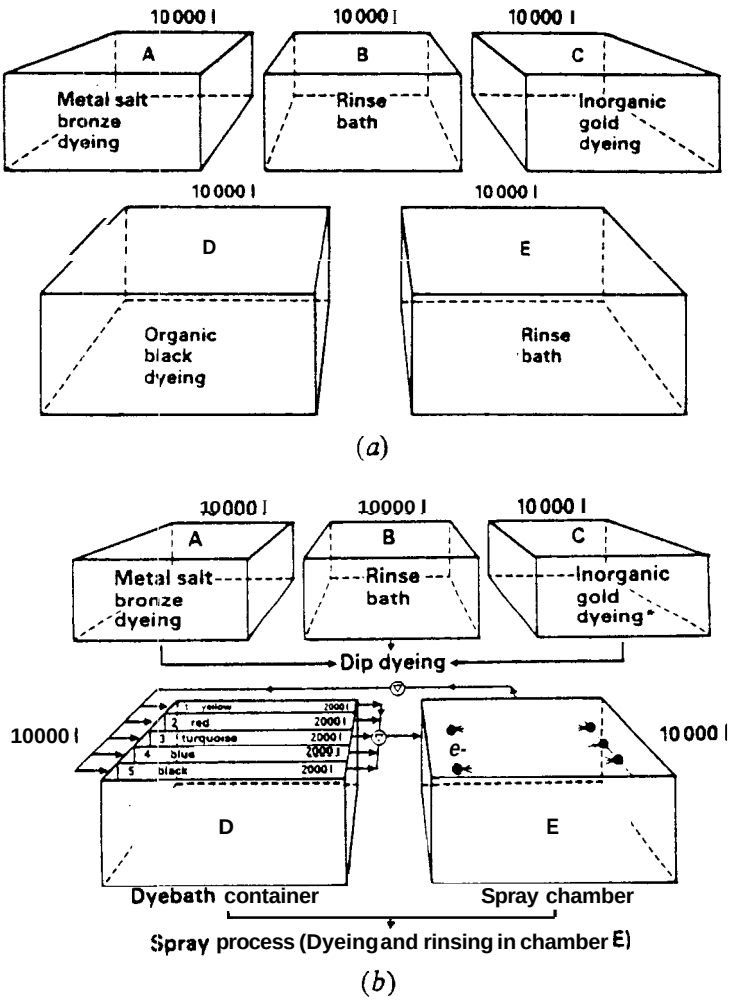


Fig. 8-57. Schematic illustration of how a conventional dip dyeing system can be integrated with a spray dyeing system, within the same anodizing and dyeing line without major modifications.[365]

(a) Conventional dip dyeing installation producing three basic shades of 30,000 litres dye volume.

(b) Spray process (dyeing and rinsing in chamber E) within same area as (a)

5. INORGANIC COLOURING BY CHEMICAL METHODS

Ferriammonium oxalate

A number of inorganic salts have the property of imparting some degree of colour to the anodic coating by absorption into it. Chromates for instance give a pale yellow colour which is commonly encountered because of the frequency with which chromates appear in formulations for sealing, but in the field of architecture the only medium which has achieved much importance is the chemical ferriammonium oxalate which has been extensively used. It was originally covered by two patents[370,371] and yielded gold, yellow or reddish-brown colours according to the methods of application. The colour is light fast and is practically indestructible since it remains at above the melting point of aluminium. It is due to the precipitation of ferric hydroxide within the pores of the anodic film brought about by the slightly alkaline alumina (see also Chapter 10).

A 10 g/l ferric ammonium oxalate solution is generally recommended for light shades and a 25 g/l solution for dark shades. Both are used at a temperature of 50 ± 1°C and a pH of 5.0 ± 0.5. An immersion time of 2-5 minutes is normally required. If too high a temperature or concentration are used the uptake of colour will be very rapid and may be difficult to control. In general the more dilute solution, although less stable, gives more lightfast dyeings than the concentrated solution. The pH level is controlled by additions of oxalic acid or ammonia as required. If the pH goes too high ferric hydroxide will be precipitated in the bath, and this can be redissolved by addition of 5 g/l oxalic acid and a little hydrogen peroxide to the warm solution.

The ferric compounds are probably not in a simple oxyhydroxide form on the alumina surface but have entered into some form of chemical combination. It has been shown for instance that the yellow and brown colours produced in ferric chloride have different Mossbauer spectra at the temperature of liquid nitrogen, and that by heating to 400°C there is no consistent pattern in the effective field value for magnetic splitting of resonance lines.[372]

Cobalt acetate-potassium permanganate

Colouring by double or sequential dipping is a logical extension of inorganic dyeing in which a soluble salt is first absorbed into the film from an aqueous solution and, instead of relying on spontaneous transformation within the film, a second colour is used to develop or deposit a precipitate.

There are. in fact, quite a number of combinations of compounds which can be employed for producing colours in this manner, and a number of these are referred to in the appropriate section of Chapter 10 on dyeing and colouring. However one method was particularly used in the 1960's for producing rich bronze colours for architectural applications.[373]

The two colouring solutions contain the inorganic salts in concentrations that may be varied widely, but typically they might contain about 10 g/l of cobalt acetate and 5 g/l of potassium permanganate. Both of these may be used at room temperature or higher. The method is to rinse the anodized work well, give a short immersion period in cobalt acetate, rinse and transfer to potassium permanganate. The colour will at first be a very light bronze but may be made darker by repeating the cycle several times. It is also relatively easy to bleach the colour in acid and to repeat the procedure if the colour has become too dark or is not uniform.

Alcan[374] recommended the use of a 35 g/l cobalt acetate solution (50 g/l for dark bronzes) used at 35-50°C, followed by treatment in a 35 g/l potassium permanganate solution at 35°C. After anodizing and rinsing the work was dipped alternately in these two solutions starting with a 20 second dip in cobalt acetate. After thoroiigh rinsing the work was dipped for 10 seconds in potassium permanganate and this cycle was repeated, with 10 second dips in each solution, until the desired shade of bronze was achieved. The final dip was always in the potassium permanganate solution.

In principle the method was very easy and relatively cheap. In practice a fair degree of experience was required to obtain uniform and reproducible colours with good penetration into the anodic film, and this relates to temperatures, Concentrations, times of immersion and manner of rinsing. The lightfastness of the finishes produced was critically dependent on the conditions used and in Alcan's experience longer immersion times and more dilute solutions, though easier to control, gave poorer lightfastness.

Clearly this type of process required a high degree of operator skill, and it was better suited to a manually operated plant than to one with crane transfer. **In** practice it has now been completely superseded by the electrolytically produced bronze finishes.

Richter[375] described a very similar technique using cobalt oxalate in place of acetate, the solutions both containing 1-2 g/l at 35-40°C. He stressed the care with which anodizing must be carried out, since most defects related to a failure in obtaining a film of uniform properties. The oxalate bath was periodically regenerated with small additions but the permanganate bath hardly ever needed regeneration or replacement. Cobalt oxalate was sometimes altered by fermentation.

The bronze colours obtainable by the double decomposition process covered light and medium bronze shades but did not extend to as deep tones as one might wish to achieve. The colour range could be extended by applying the colouring procedure to special alloys which when anodized gave a grey or dark grey finish, such as the 5% silicon alloys. An example of this was described in Zurich where a new building was required to be integrated into a street of strongly traditional buildings.[376]

The method was used very little in the United States, but a patent in America proposed the coloration of anodized aluminium by using an aqueous solution unstable at elevated temperatures containing a precipitant ion donor and an ion of a metal capable of forming a coloured precipitate with the precipitant ion.[377]

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CHAPTER 9

Hard Anodizing

1. GENERAL

Hard anodizing is a term used to describe the production of anodic coatings with film hardness or abrasion resistance as their primary characteristic. They are usually thick by normal anodizing standards (greater than 25 microns) and they are produced using special anodizing conditions (very low temperature, high current density, special electrolytes). They find application in **the** engineering industry for comporients which require a very wear resistant surface such as pistons, cylinders and hydraulic gear. They are often left unsealed, but may be impregnated with materials such as waxes or silicone fluids to give particular surface properties.

2. PR0CESSES AND EQUIPMENT

The first work in the production of thick and hard anodic coatings for engineering applications was carried out with oxalic acid' in Germany and with sulphuric acid in Russia[2] and in the U.K.[3]. Tomashov showed that by cooling the sulphuric acid electrolyte and thus slowing down the rate of dissolution of the oxide, coatings of **up** to 250 μm (10 mil) could be obtained with a loss of metal of only about 0.3 g/dm^2 (3 gm per sq ft), and that these coatings could give excellent wear resistance and heat insulation and would absorb and retain oil when used on cylinders and pistons, etc.

As has been described in Chapter 7, the limiting film thickness is reached when the rate of chemical dissolution of the film in the electrolyte is equal to the rate of film growth. Factors most affecting film dissolution are the anodizing electrolyte

temperature and concentration, and that affecting film growth is the anodizing current density. The production of very thick films is therefore best achieved using electrolytes with a low oxide dissolving power at low temperatures, and anodizing at high current densities. This inevitably involves the use of much higher voltages than normal which can lead to very high local temperatures in the vicinity of the work. Electrolyte agitation is therefore a very important factor in hard anodizing and local breakdown of the anodic film can be a serious problem.

Tomashov worked with a 20% sulphuric acid solution at 1-3°C and 2-5 A/dm^2 (20-50 amp/sq ft), and during the course of four hours built up oxide coatings on aluminium of 200 μm (8 mil) thickness using a gradual rise in voltage from 23 to 120 volts as the thickness increased. In the case of aluminium alloys lower voltages were generally required.

The porosity, too, was found to vary with the alloy composition. Thus, on commercial aluminium, films of 20% porosity were obtained, compared with 35% porosity in coatings on an aluminium aircraft piston alloy containing 2.2% copper, 1.6% magnesium, 1.35% iron, 0.85% silicon, 1.25% nickel, 0.91% titanium. The coatings were found to be heat resistant up to 1500°C.

In later work on this process, Tomashov[4] found that these coatings, as distinct from thinner coatings, were only partially hydrated, and both hydration and porosity were more pronounced at the surface, as shown by a decrease in micro hardness in the top layers. Film growth in 10-30% sulphuric acid at 0.5°C and 2-4 A/dm^2 was limited by sparking, and the thickness at which this occurred increased with the acid concentration.

The production of thick, hard anodic films is now practised to an increasing extent, and, in many of these applications, hard anodizing is an alternative to hard chromium plating (see Chapter 13). Compared with the latter, the hard anodic coating is generally cheaper to apply, presents fewer adhesion problems and will give better oil-retention properties than many types of chromium deposit. On the other hand, hard anodizing cannot be used indiscriminately on all aluminium alloys.

Production of thick coatings

As seen from the discussion of the relationship of operating conditions on the properties of the anodic film, the coating thickness is influenced by the solution composition, the bath temperature, the current density and the composition of the alloy. The maximum film thickness obtainable for a given electrolyte increases with decrease in temperature, increase in current density and voltage, and increase in solution concentration. The difference in growth of coatings under 'hard' anodizing conditions, i.e., low temperatures and high current densities, as compared with normal anodizing is seen in Fig. 9-1.[5] These conditions all reduce attack within the pore wall structure, and, in combination with the higher anodizing voltages and hence the larger pore and cell diameters produced, leads to increased hardness and decreased porosity in the coating.

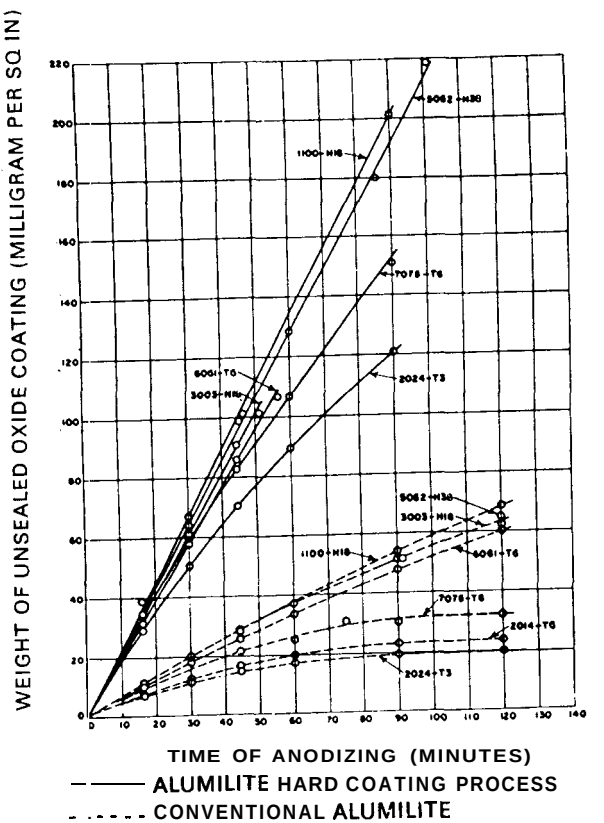


Fig. 9-1. Weight of anodic oxide coating against time on several aluminium alloys in conventional sulphuric acid anodizing and in the Alumilite Hard Coating Process.[5] 1 mg/sq in = 0.155 mg/cm^2

By itself, however, the production of thick films does not necessarily ensure that they will be hard. As seen in Figs. 7-26 and 7-27[6] (Chapter 7), at the higher current densities a soft superficial layer tends to be formed which has a low wear resistance and may in extreme cases be powdery.

In practice, most hard anodizing is carried out in sulphuric acid using concentrations of 5-15% (vol) at current densities of around 3 A/dm^2 and temperatures below +5°C, with vigorous air or mechanical agitation. However, a number of other electrolytes, many of them containing mixtures of acids, are being used today and often enable the use of higher operating temperatures and increased current densities. Many of these were primarily developed as integral colour anodizing electrolytes and have been described in detail in Chapter 8.

Sulphuric acid processes

A number of commercial hard-anodizing processes have been developed using direct current or superimposed a.c. on d.c.

One of the best known of the d.c. processes is the M.H.C. process developed by the Glenn L. Martin Co.[7] and acquired by the Aluminum Co. of America. This process uses a 15% sulphuric acid electrolyte operated at 20-25 amp/sq ft (2-2.5 A/dm^2) and 0°C. To maintain this current density, the initial voltage of 25-30 volts is increased to 40-60 volts, and the rate of film growth under these conditions is shown in Fig. 9-2. In the M.H.C. process, the 15% sulphuric acid solution may also be used saturated with carbon dioxide.

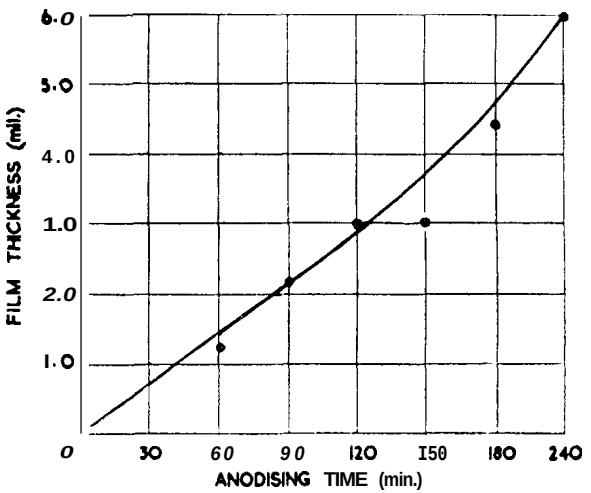


Fig. 9-2. Growth of M.H.C. hard anodic coating with time on pure aluminium. 1 mil = 25.4 μm

This process is particularly suitable for the production of thick coatings. Where thinner films are required it has been found possible to work at slightly higher temperatures, and this has been made use of in a range of alternative processes of the Aluminum Co. of America, designated Alumilite 225 and 226 for wrought alloys and Alumilite 725 and 726 for cast alloys. These processes work at approximately 8-10°C and are used for building up coatings of 25-50 μm (1-2 mil) in thickness. A limitation associated with the d.c. processes is a tendency to 'burning' unless the anode is provided with efficient agitation and electrical

contacts are good, and, according to Jenny,[8] alloys containing over 3% copper or 7.5% silicon are difficult or impossible to treat by these processes.

The Sanford process is claimed to be useful for hard anodizing difficult aluminium alloys in a solution containing:[9]

sulphuric acid	7%
peat extract	3%
nonyl alcohol	0.02%
polyethylene glycol	0.02%
methyl alcohol	7%

This solution is used at -10°C and a 50 μm (2 mil) coating is stated to be obtained in 53 minutes at 10-20 amp/sq ft, the voltage being raised in stages from 15 to 60 V.

Black anodic coatings 25-50 μm (1-2 mil) thick of good abrasion resistance and with hardness values of 1400 VPN are reported to be obtained from a solution containing:[9]

oxalic acid	50 g/l
calcium fluoride	0.1 g/l
sulphuric acid	0.5 g/l
chromic sulphate	1 g/l

Defence Specification DEF 151[10] allowed hard anodizing to be carried out in any suitable electrolyte and gave as an example a 10% solution by volume of sulphuric acid in water. In such an electrolyte the chloride level had to be kept below the equivalent of 0.20 g NaCl per litre. This broad tolerance of the electrolyte type is reflected even more strongly in more recent versions of DEF 151, which is now DEF STAN 03-26/2.[11] This states that: 'Unless otherwise specified by the Design Authority any suitable electrolyte may be used'. The chloride limit is maintained but the conditions of anodizing shall be chosen by the processor to suit the material being treated and the thickness of coating required. In effect a typical anodized sample is approved by the Design Authority and the method of treatment, i.e. electrolyte, temperature, agitation, current, voltage, time, method of jigging arid sealing treatment, are recorded in detail and incorporated in a process control schedule.

The nominal temperature of the electrolyte must be controlled within ±2°C and the electrolyte is normally operated between +5 and -5°C. Typical current densities are in the range of 250-4000 A/m^2. Previously DEF 151 had given guidance on such things as cathodes, power supply and electrolyte agitation.

The same sort of general recommendations are provided in the equivalent U.S. specification, MIL-A-8625 F.[12] Hard anodic coatings are described as Type III coatings and 'shall be prepared by any process operation to produce a heavy dense coating of specified thickness on aluminium alloys'. Unless specified in the contract the nominal thickness of the coating shall be 2 mil (50 microns). Unless

otherwise specified the thickness of the coating shall not vary by more than ±20% for coatings up to 2 mil. Coatings over 2 mil shall not vary by more than 0.4 mil (10 microns) in thickness. However another limitation is provided in that 'Unless otherwise specified in the contract, order or applicable drawing, Type III coatings produced from the anodizing baths shall not be applied to aluminium alloys with nominal copper content in excess of 5.0% or a nominal silicon content in excess of 8.0%. Alloys with a higher nominal silicon content than 8.0% may be anodized subject to the approval of the procuring activity'. No such limitation on either thickness or alloy type exists in DEF STAN 03-26/1, though it indicates that the maximum thickness is normally of the order of 100 microns and the total coating thickness must be limited to not more than 10% of the overall cross-section.

A similar thickness range is provided in the U.S. Aerospace Specification AMS 2468E[13] which designates a standard thickness of 2 mil ± 0.5 mil (50 μm ± 13 μm), with other thicknesses used if necessary. A minimum coating weight of 30 mg/in^2 per 1 mil of thickness (4.6 mg/cm^2 per 25 μm of thickness) is also specified.

The European Aerospace Standard, BS EN 2.536:1995, which has replaced the DEF Standard, allows an aqueous sulphuric acid electrolyte with or without additional elements. Concentration of acid should not vary by more than ±10% from the values specified by the processor, chloride content should be less than 200 mg/l (expressed as NaCl) and the aluminium content less than 2.5 g/l. Electrolyte temperature may vary from -20°C to +15°C with a tolerance of ±2°C on the chosen temperature. Current can be d.c., d.c. with superimposed a.c., a.c. or pulsed. Two thickness ranges are indicated based on alloy, 30 to 120 microns for alloys containing less than 1% copper, and 30 to 60 microns for alloys containing between 1% and 5% copper.

The British Standard on Hard Anodizing (BS 5599:1993) gives no restriction at all on processing conditions, but for the first time it specifies minimum acceptance values of abrasion resistance in the abrasive wheel test (Table 9-1), the abrasive jet test (Table 9-2) and the Taber test (Table 9-3). Abrasion values are based on the alloy being tested, divided into the classes below:

Class 1	:	all wrought alloys except those in Class 2
Class 2a	:	2000 series alloys
Class 2b	:	5000 series alloys containing 2% or more magnesium, and 7000 series alloys
Class 3a	:	casting alloys with less than 2% copper and/or 8% silicon
Class 3b	:	other casting alloys

The standard also sets minimum surface density (coating mass per unit area) values for coatings with a nominal thickness of 50±5 microns as follows:

Class 1	:	1,100 mg/dm^2
Class 2	:	550 mg/dm^2
Class 3a	:	550 mg/dm^2

Minimum Vickers microhardness values (50g load) are also specified:

Class 1 : 350
Class 2a : 250
Class 2b : 300
Class 3a : 250

It is noted that coatings of thickness greater than 60 microns may have lower microhardness values.

Thus this is the first standard to set clear abrasion values for a whole range of coatings, and it was based on a great deal of international work and cooperation within ISO TC 79/SC2. This work is also reflected in the ISO Hard Anodizing Standard ISO 10074:1992.

TABLE 9-1

Acceptance values for the abrasive wheel test (BS 5599:1993)

Alloy	*Number of double strokes*	*Relative mean specific abrasion resistance acceptance value (comparative to standard specimen, see annex B)* %
Class 1	800 – 100	≥ 80
Class 2a)	400 – 100	≥ 30
Class 2b)	800 – 100	≥ 55
Class 3a)	400 – 100	≥ 30) or by agreement)

$$(\text{RMSAR}) = \frac{\text{mean wear rate of test specimen} \times 100}{\text{mean wear rate of standard specimen}}$$

where the wear rate is the loss in thickness (or mass) **per** unit double stroke.

NOTE 2. Castings are not always suitable for wear/abrasion testing because of the surface conditions and/or structure of the anodic oxidation coating. In the unusual event of class 3 alloys requiring to be tested, then the wear/abrasion resistance acceptance values should be agreed between anodizer and purchaser and may require special reference panels.

TABLE 9-2
Acceptance values for the abrasive jet test
(BS5599:1993)

Alloy	*Relative mean specific abrasion resistance acceptance value* *(comparative to standard specimen, see annex B)* *%*
Class 1 Class **2a)** Class 2b) Class 3a) Class 3b)	≥ **80** ≥ **30** *2 55* ≥ *55*) or by agreement, ≥ 20) see note 2

NOTE 1. Relative mean specific abrasion resistance

$$(\text{RMSAR}) = \frac{\text{mean wear rate of test specimen} \times 100}{\text{mean wear rate of standard specimen}}$$

where the wear rate is the time (in s) or mass of abrasive (in g) to remove 1 μm coating thickness.

NOTE 2. Castings are not always suitable for wear/abrasion testing because of the surface conditions and/or structure of the anodic oxidation coating. In the unusual event of class 3 alloys requiring to be tested, then the wear/abrasion resistance acceptance values should be agreed between anodizer and purchaser and may require special reference panels.

TABLE 9-3
Acceptance values for the Taber abrasion resistance test
(BS 5599 : 1993)

Alloy	*Maximum loss in mass* *mg*
Class 1 Class 2a) Class 2b) Class 3	15 35 25 See note

NOTE. Castings are not always suitable for wear/abrasion testing because of the surface conditions and/or structure of the anodic oxidation coating. In the unusual event of class 3 alloys requiring to be tested, then the wear/abrasion resistance acceptance values should be agreed between anodizer and purchaser and may require special reference panels.

The increasingly permissive nature of these specifications with regard to processing conditions reflects a growing complexity in what was once a simple subject. Thus in 1962, Johnson[14] was able to compare the Alumilite and Martin processes in the U.S.A. and outline the essential features of the Sanford process (U.S.A.) and the British proprietary processes Hardas and Hiduran. Now a large number of jobbers offer hard anodizing, and while many of them employ sulphuric acid with d.c. at low temperature under fairly standard conditions, others have introduced their own variations using mixed acids or different electrolytes some of which operate at higher temperatures, and frequently the conditions will be adjusted to suit the particular alloy being processed. Occasionally a compromise is adopted with a semi-hard coating which is adequate for the service intended. Although many hard anodizing standards still do not have rigid performance requirements, a great deal of experience has however been accumulated in designing optimum treatments for specific operations.

Hard anodizing in Switzerland by the sulphuric acid based process is called the Oxal-3 process. The properties of the coatings produced on a wide range of alloys has been discussed in some considerable detail by Oechslin who refers also to Oxal-4 which is a 'semi-hard' anodizing process."

Thompson[16] has reviewed the use of 10% and 20% (vol) sulphuric acid electrolytes for hard anodizing. He indicates that, if hard anodizing is attempted in I-5% (vol) sulphuric acid at 0°C with a simple d.c. power source using an alloy with a low copper content, the anodic film formed will be composed of isolated spherical nodules of great thickness and extreme hardness, the remainder of the surface being covered in a barrier layer only. If a high copper containing alloy is used, only a barrier layer coating will be formed, as the solubility of the oxide in the electrolyte is too low. As the electrolyte strength is increased, the number of nodules increases also until they link up to form an orange-peel effect which at higher concentrations transforms into a smooth, continuous film. At around 7.5% (vol) sulphuric acid such a normal film is produced on all wrought alloys low in copper level, though alloys high in copper content will only form a barrier layer when processed with d.c. only. In the range of 7.5% to 21% (vol) sulphuric acid, satisfactory hard anodic films are produced on most aluminium alloys, but at concentrations above 21% solubility of the film increases, reducing hardness and wear resistance of the outer layers, and decreasing the maximum film thickness obtainable. This latter effect is more noticeable on alloys high in copper. A general comparison of electrolyte characteristics with 10% and 20% (vol) sulphuric acid electrolytes, with the former used under d.c., and a.c. superimposed on d.c. conditions, is shown in Table 9-4.[16] Another factor which is pointed out by Thompson is that with baths operated at 20% (vol) acid concentration, aluminium sulphate crystallizes out at about 13 g/l of aluminium, so frequent electrolyte renewal is required. Baths operated at 10% (vol) do not build up the aluminium content so fast, so last rather longer.

Superimposed alternating current on direct current

One of the main developments in hard anodizing has been the use of more complex power supplies with biased, pulsed or interrupted current used to reduce burning problems and make highly alloyed materials easier to process. Much of the work has used a.c. superimposed on d.c.

The development of hard anodizing processes using superimposed a.c. on d.c. was doubtless influenced by Jenny's work with the oxalic acid electrolyte, which showed (see Fig. 9-3) that the use of a.c. will increase the film thickness.[8]

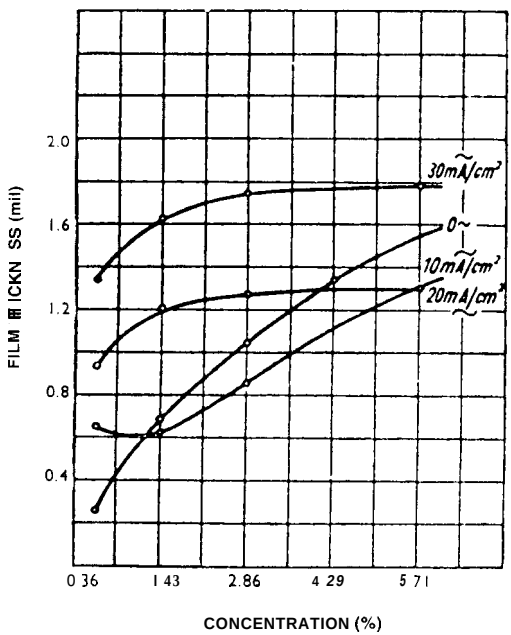


Fig. 9-3. Growth of anodic oxide coating in relation to oxalic acid concentration at 60 volts d.c. with varying a.c. component. 1 mil = 25.4 μm

Russian workers" found that the use of superimposed a.c. on d.c. improved the properties of thick coatings formed in sulphuric acid on aluminium alloys with high copper contents.

A British commercial process using this technique is known as the Hardas process and was developed by Campbell.[18] The value of the a.c. component in this process is primarily to raise the permissible current density. While not essential for hard anodizing pure aluminium and magnesium-containing alloys, the use of superimposed a.c. often renders control of the process easier and is essential for treating alloys containing a large proportion of heavy metals.

TABLE 9-4

Comparison of three processes[16]

Process	*Chemical control*	*Jigging technique*	*Electrolyte agitation*	*Hardness and wear resistance*	*Surface finish*	*Groups of alloy compatible with process*	*Film thickness range*	*Power supply*
10% Sulphuric acid	Simple	Conventional	Staticjigs Air agitation	Very high 400-500 VPN	Very little deterioration	All alloys with the exception of wrought alloys high in copper and pressure die castings suitable	Up to 100 μm on many alloys	d.c
20% Sulphuric acid	Simple	Conventional	Staticjigs Air agitation	High on alloys low in copper. Lower on alloys high in copper	Little deterioration on alloys low in copper. More so on alloys high in copper	All alloys may be processed	Up to 75 μm though alloys high in copper powdery in excess of 50 μm	d.c
10% Sulphuric acid	Simple	Components rigidly clamped or bolted to stem	Combination of rotation or rocking and high velocity pump	Extreme hardness and wear resistance on all alloys	Considerable deterioration, 50-60 μ on wrought alloys low in copper. 70-90 μ on alloys high in copper. Castings in excess of 100 microns	All alloys may be processed	Maximum films range from 75-150 μm	a.c./d.c.

In practice, the hard anodizing process is controlled by the treatment time and current density, the solution concentration and temperature being kept constant. The current density is adjusted to the particular alloy composition and should be maintained at a constant level by raising the voltage as the film thickness grows. Finally, the current is reduced gradually, as switching it off suddenly may adversely affect the adhesion of the coating. The magnitude of the a.c. component requirement varies with the alloy composition.

Sequences for the Hardas process carried out to different requirements of precision are given in Table 9-5. Although oxalic acid was used initially, the sulphuric acid electrolyte is now standard for the Hardas process.

In high current density anodizing processes operated with alternating current or with a.c. superimposed on d.c., a smell of hydrogen sulphide may frequently be observed[19] due, perhaps, to the cathodic reduction of sulphuric acid at the high local temperatures which are developed.

Sanford[20] have suggested the use of a d.c. voltage, modulated by a sinusoidal a.c. voltage of normal frequency, and later the use of a low voltage with a d.c. component and a superimposed a.c. component.[21] These processes allow the use of lower anodizing voltages than are usual for hard anodizing, by employing relatively low acid concentrations at higher than normal anodizing temperatures. They have been described by Lerner[22] who indicates that no more than 18-20 V d.c. is required at electrolyte temperatures from -4 to +10°C. The voltage waveform produced by the superimposed a.c. is shown in Fig. 9-4, and is best produced by a special power supply." This low voltage requirement means that a much lower refrigeration capacity is needed and burning during hard anodizing is much less likely.

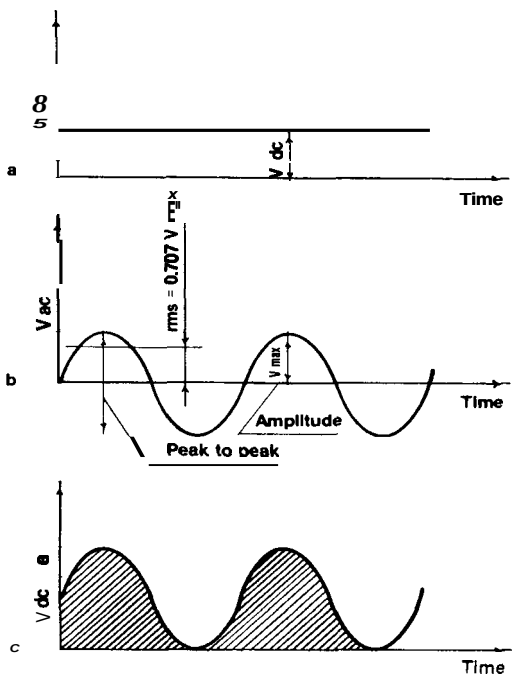


Fig. 9-4. (a) Voltage waveform in LV hardcoating (d.c. component); (b) voltage waveform in LV hardcoating (a.c. component); (c) voltage waveform in LV hardcoating (a.c. + d.c. voltage)"

TABLE 9-5

Hardas procedures for hard anodizing of aluminium alloys to various requirements

A	B	C	D	E	F	G
High dimensional accuracy and best surfacefinish with both ordinaty and hard anodizing	*Less critical sires and surfacefinish with both ordinary and hard anodizing*	*Dimensions andfinish not critical with both ordinaty and hard anodizing*	*High dimensional accuracy and best surface finish with hard anodizing only*	*Nan-critical sizes and surfacefinish with hard anodizing only*	*Thin coating, medium precision andfinish with hard or ordinary anodizing*	*Salvage of over-machinedparts and finish with thick non-critical coatings*
Machine to size except that surface to be Hardas treated is left 0.025 mm (1 mil) oversize	Machine to finish size all over	Machine and remove 0.025 mm (1 mil) extra from Hardas surface	Machine and remove 0.125 mm (5 mil) extra from Hardas surface	Machine and remove 0.037 mm (1½ mil) extra from Hardas surface	Machine to finish size all over	Finish to clean metal surface
Ordinary anodize	Ordinary anodize	Ordinary anodize			Ordinary anodize	Thick anodize*
Apply dye marking if required	Apply dye marking if required	Apply dye marking if required			Apply dye marking if required	
Hone or grind 0.025-0.037 mm (I-]%mil) from Hardas surface	Chemically strip ordinary anodizing from Hardas surface	Chemically strip ordinary anodizing from Hardas surface			Chemically strip ordinary anodizing from Hardas surface	
Hard anodize 0.056-0.075 mm (2%-3mil) thick	Hard anodize 0.062-0.075 mm (2%-3mil) thick	Hard anodize 0.062-0.075 mm (2%-3 mil) thick	Hard anodize 0.062-0.075 mm (2%-3 mil) thick	Hard anodize 0.062-0.075 mm (2%-3 mil) thick	Hard anodize 0.025-0.037 mm (1-1½ mil) thick	
Hone or grind	Hone or grind	Hand-hone or emery	Hone or grind	Hand-hone or emery	Hand-hone or polish	

* Recommended up to 0.1 mm (4 mil) thickness but 0.18 mm (7 mil) is possible on some alloys. Thick coatings are softer, rougher, crumble on edges and are less adhesive to the metal.

NOTES TO TABLE 9-5:

1. Chromate seal or silicone oil recommended on Hardas surface for increased corrosion resistance.
2. Radius of 0.25 mm (10 mil) recommended on external corners and maximum thickness of 0.062 mm (2½ mil) or less if critical.
3. Thickness on pressure die-casting in high silicon alloy limited to 0.037 mm (1½ mil).
4. Wrought and cast alloys with high proportion of copper or silicon (up to 15%) may be hard anodized, but the coating is softer as the proportion increases.
5. Alloy for hard anodizing should preferably be ordered as such and, if dimensions of finished articles are critical, suppliers' batches should be segregated.
6. Surface roughness is produced which may be lapped, honed or ground to precision limits or, for less critical work, polished with fine emery and oil or grease bobbed or glossed with chrome cake on a mop or felt bob.
7. Old ordinary anodizing or impregnated ordinary anodizing cannot be reliably chemically stripped on local areas, and should be machined off. Preferably for chemical stripping, ordinary anodizing should be carried out by the hard anodizer.

Permaloy[24] have used a pulsed direct current for hard anodizing in a sulphuric acid-sodium lignosulphonate electrolyte and Poll[25] has recommended the use of a 3-phase pulsed current rectifier. A whole range of different wave forms, including full wave and half wave rectified d.c., interrupted current, superimposed current and pulsed current, were examined by Ikuta *et al.* in Japan.[26] They found that pulsed currents produced harder coatings than d.c., particularly when using a ratio of 4:1 between the higher current level (4 A/dm^2, 30 sec) and the low current level (2 A/dm^2, 7.5 sec).

In the 1990's the use of pulsed current rectifiers for hard anodizing has increased considerably, and Brace" describes the use in the U.S.A. of several hundred rectifiers of this type with current capacities of **up** to 15,000A. Pulsed currents allow the use of much higher current densities than normal without creating 'burning' problems, and are particularly useful on what are considered to be difficult alloys for hard anodizing. The peak current is only applied for a short time (e.g. 10 milleseconds), and is followed by a short period (5 ms) at a much lower current density, with periods of zero current also sometimes included. This has the benefit of removing the heat, generated by the high current pulse, during the low current cycle. Brace[27] indicates that the total kVA used with a pulse current rectifier is lower than with a conventional rectifier, but the use of the high current density increases the film thickness variation over a component surface, particularly on high spots or edges near to the cathodes.

He also points out that good busbar connections from the rectifier to the anodizing tank are particularly critical with pulsed currents, because of the high instantaneous currents that are needed. Current densities 2-5 times higher than normal have been used in the U.S.A., but this means that more heat is evolved, and better agitation and increased cooling capacity are required in the bath.

Colombini[28,29] has been active in the development of pulsed current rectifiers and has described the rectifiers available, their control and their benefits. Workers in Taiwan[30] have studied the hard anodizing of 2024 alloy using both pulsed d.c. and a.c. power. Under the conditions used, pulsed a.c. failed to give satisfactory hard anodized coatings, but pulsed d.c. gave better results. However they observed crack:; and voids in the pulsed current films and a higher overall surface roughness.

Dilute sulphuric acid

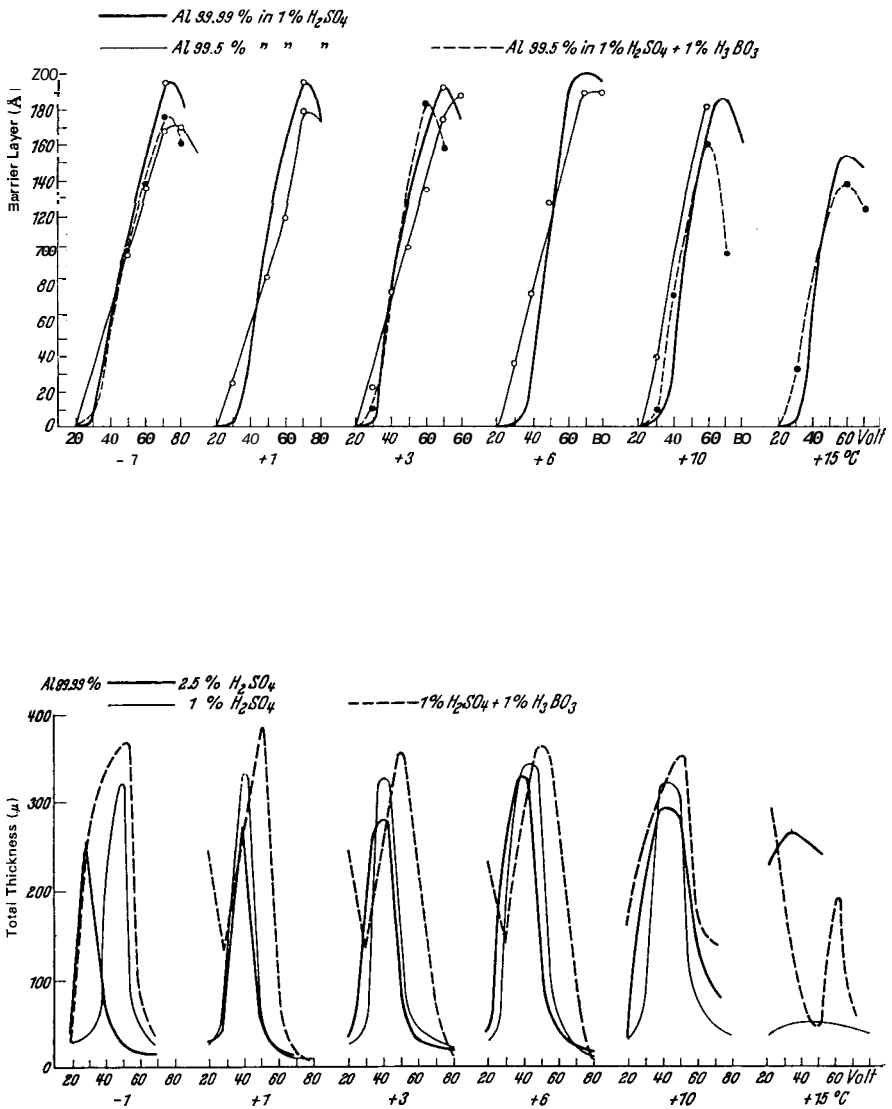
An interesting variant of the sulphuric acid hard anodizing process is the use in Hungary of very dilute solutions containing 0.5-2% sulphuric acid.[31,32,33,34,35,36] Under these conditions 150-200 μm (6-8 mil) coatings can be built up at 20-80 volts and at temperatures of +5 to −5°C in an hour, with higher hardness values, e.g. 450-520 kg/sq mm,[33,34] and lower porosities, e.g. 2-4%, than in concentrated acid (porosity normally 14-20%).

There is evidence that, in these dilute solutions, not only the structure of the main coating but also the formation of the barrier layer is different than in more concentrated acid.[37] These coatings have barrier films the thickness of which goes through a maximum of approximately 380 Å (380×10^{-4} μm) at a voltage of 40-50 volts. Barrier and total film thicknesses obtained in these dilute solutions are seen in Figs. 9-5 and 9-6. Analyses of these coatings show that they contain approximately 25% anhydrous aluminium sulphate as well as some boehmite.

Csokán arid Holló[38] produced hard coatings from 100-250 μm (4-10 mil) thick in 0.1M sulphuric acid at a temperature of −1 to +1°C and at 45-60 volts the hardness of which was as high as 600-620 VPN. They found that below 30 volts true hard film does not form, and that above 70-75 volts local over-heating occurs, so an intermediate working range must be observed when anodizing in dilute sulphuric acid. Plant practice in Hungary[39] is to work from −1 to +1°C at 50-65 volts and a current density varying from 4 to 20 A/dm^2.

A disadvantage of the very dilute sulphuric acid bath is that the electrolyte may freeze on the cooling coils at low temperatures, and this must be prevented by adequate circulation.

The coatings produced by this process have good corrosion resistance'' in the unsealed condition, particularly in warm and humid atmospheres. However, they tend to be somewhat rougher than films produced in more concentrated acid baths, although they have good polishing properties and are satisfactory for purposes in which grinding or polishing is carried out as the final operation. The same effect is pointed out by Thompson[16] in relation to films produced by a.c. superimposed on d.c. (see Table 9-4).



Figs. 9-5 and 9-6. Influence of voltage and temperature on (Fig. 9-5 above) barrier and (Fig. 9-6 below) total thickness of coatings produced by hard anodizing in the dilute sulphuric acid bath

Film formation

The formation of hard anodized coatings is accompanied by some unusual features not encountered in normal sulphuric acid anodizing, although these features are also known in integral colour anodizing procedures, which can be, of course, and sometimes are, used as hard anodizing processes. By working with dilute sulphuric acid Csokán[36,41] has described and illustrated with good clear photographs that at voltages up to 35 the normal anodizing pattern of barrier layer formation followed by the uniform growth of clear porous films is obtained, but when the voltage exceeds 35 the surface begins to develop small brown hemispherical spots of thick oxide, which constitute primary oxidation nuclei for a second phase of growth. Rosette-shaped secondary oxide zones proceed to form around these and they spread rapidly until they merge to form a uniform coating which is usually darker in colour than the first coating.

Scott[42] also observed similar behaviour in stronger sulphuric acid solutions at concentrations up to 10% by volume. The first-formed film was somewhat lighter in colour, but after a time secondary growth of a darker film set in at a few isolated centres, spreading out radially. More and more centres became evident as anodizing proceeded, until the spreading secondary growth covered the whole area of the work. In spite of the wide difference of appearance between the two types of film, the abrasion resistance of the primary film was only a little less than that of the darker secondary growth, a ratio of 3:4. Under some conditions of anodizing the appearance remained! at the mottled stage. Fig. 9-7 shows a range of samples prepared by Scott under the conditions indicated, where it can be seen that the mottled appearance is more characteristic of the low current density of 20 amp/ft^2 (1.9 A/dm^2) than any other parameter, and tends to disappear after about 30 minutes anodizing in 5 and 10% acid, but not altogether in 2.5% acid.

This mode of film formation is probably also present in normal hard anodizing, but the transition is niade too quickly to be observed. It is also known in integral colour anodizing but is less well documented in this commercially sensitive area, although the patents refer to the formation of 'islands of dark oxide' as a defect which must be avoided.[43]

Arrowsmith and Cunningham[44] have also studied the early stages of the hard anodizing process and, like other workers, they showed heterogeneous nucleation of the anodic oxide under certain conditions of hard anodizing. Their scanning electron microscope (examinationshowed that the lens-shaped islands of oxide or rosettes, seen in the early stages of anodizing by other workers, were cracked as a result of internal stress in the growing oxide. The cracks were roughly concentric and related to the direction of growth of the oxide and were clearly different to the type of cracking occurring during crazing of an oxide film. The nature of the original air-formed oxide film was shown to be important in this growth mechanism, as because of the very low dissolving power of the electrolytes used under hard anodizing conditions, initial current flow concentrated at flaws in the air-formed oxide film. Thus locally there was initially a very high current density in the flaw

and rapid local growth of anodic oxide. The rapid expansion of oxide in the flaw region fractured the oxide surrounding the flaw, allowing anodic oxidation to occur progressively in the surrounding region, and this gave the characteristic lens-shaped cross-section rosette with its rings of spalled oxide on the surface. As anodizing spread to surrounding regions there was a fall in the local current density until the entire surface was covered by anodic oxide.

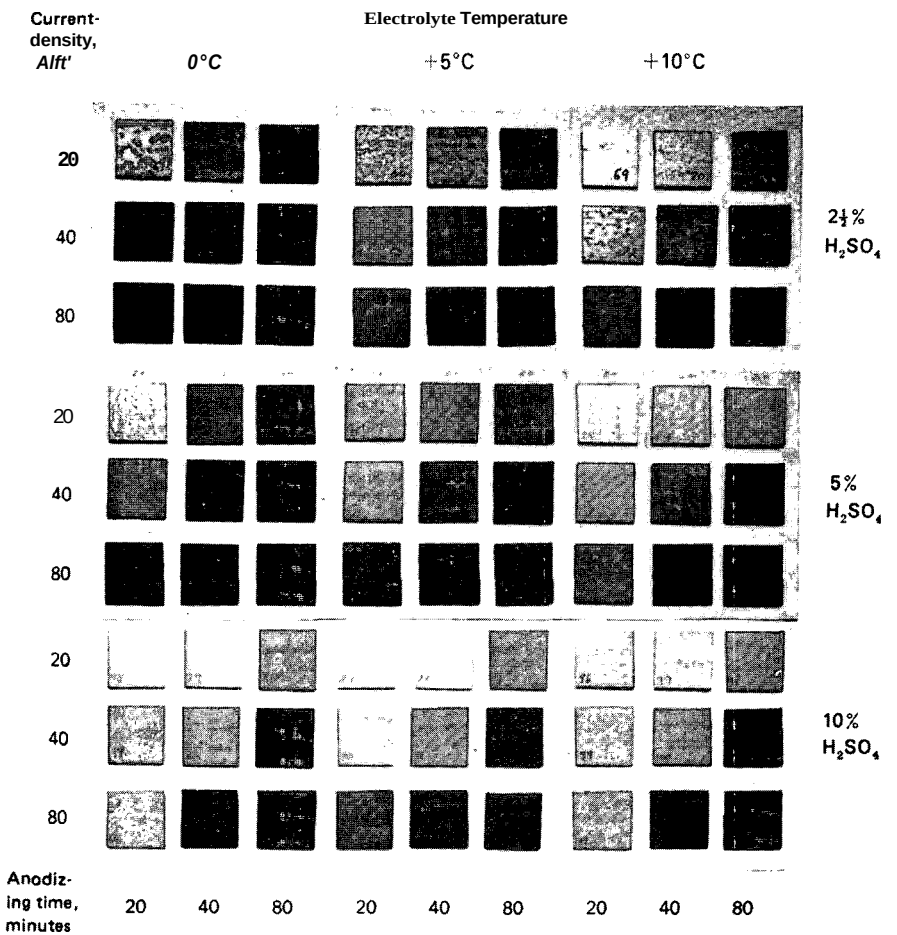


Fig. 9-7. Non-uniform film formation during hard anodizing of 99% aluminium[42]

Effect of anodizing conditions

Surprisingly little work has been done to relate temperature, current density and other anodizing variables to hardness and abrasion resistance. As noted previously most operators tend to work at a very low temperature and a high current density, and most studies which have been published on properties employ a fixed anodizing schedule and proceed to examine either the behaviour of various alloys, or the behaviour of the work under conditions of usage. The reason for this is that abrasion or wear tests are very time consuming, the apparatus for conducting them has not been readily available, and the results can be very variable because of factors which have taken a long time to identify.

Using the silicon-carbide abrasive jet method of B.S. 1615: 1972 to measure the specific abrasion resistance of anodized coatings in terms of grammes of abrasive per micrometre of coating for penetration, Scott and Harris[42] summarised the results of a large number of tests in Table 9-6, and were surprised to find that temperatures from –5 to +15°C gave almost identical results at 4 A/dm^2 for three strengths of acid, although the colour of these samples varied from light brown to deep black. The abrasion resistance increased a little with current density between 2 and 8 A/dm^2; it increased appreciably with film thickness and decreased by about 30% on normal sealing. It would appear from this that a temperature of 15°C is perfectly feasible for hard anodizing of pure aluminium, but in point of fact most hard anodizing has been judged irrationally by its colour, and to obtain the dark colours normally regarded as a necessary concomitant of a hard coating, the very low temperatures have been adhered to.

Laszewska[45] found that there was little difference between samples anodized in the –8 to 0°C range, but that harder films were obtained at 2.5 A/dm^2 than at 5 A/dm^2 at these temperatures. He also noted a reasonably good correlation between hardness and abrasion resistance.

Koizumi, Ninagawa and Ueda[46] in Japan have investigated wear resistance obtained at temperatures from –5 to +20°C and from 1-8 A/dm^2. They find that the best films are obtained at the lowest temperatures and at high current densities, but that the current density did not in fact have much effect. Their results were obtained by means of the Taber Abrasion Tester using a resilient-type rubber-bonded alumina wheel (CS-17) under an applied load of 1,000g. The weight loss for each specimen was determined after 15,000 revolutions of the wheel. The electrolyte which they used contained 100 g/l sulphuric acid and 15 g/l oxalic acid, and specimens were anodized for 45 minutes, so presumably different film thicknesses were tested at the various current densities. Fig. 9-8 shows on a three dimensional graph their results relating temperature and current density to the thickness of coating removed from various specimens. It can be seen that it is only at 20°C that the effect of current density is pronounced and that it has little effect below 5°C: similarly the wear resistance varies appreciably with anodizing temperature from 5-20°C when normal current densities up to 2 A/dm^2 are used, but for higher current densities temperature has much less effect.

TABLE 9-6

Effect of anodizing conditions on abrasion resistance of anodic oxide films[42]

Acid concentration	% vol	2%			5		10
	g/μm	26.1			24.9		25.2
	0-10°C, 40 A/ft^2						
Temperature	°C	−5	0	+5		+10	+15
	°F	23	32	41		50	**59**
	g/μm	*26.1*	*25.8*	**24.2**		*26.2*	26.0
	2½-10% acid, 5°C, 40 A/ft^2						
Current density	A/ft^2	20			40		**80**
	g/μm	22.3			**23.6**		*25.5*
	2%-10% acid, 5°C, 60 μ						
Film thickness	microns	30			60		120
	g/μm	18.1			23.6		27.1
	2½-10% acid, 5°C, 40 A/ft^2						

Sealing	microns	60	120
	unsealed, g/μm	23.6	18.3
	sealed, g/μm	15.7	21.1
	2%-10% acid, **5°C**		

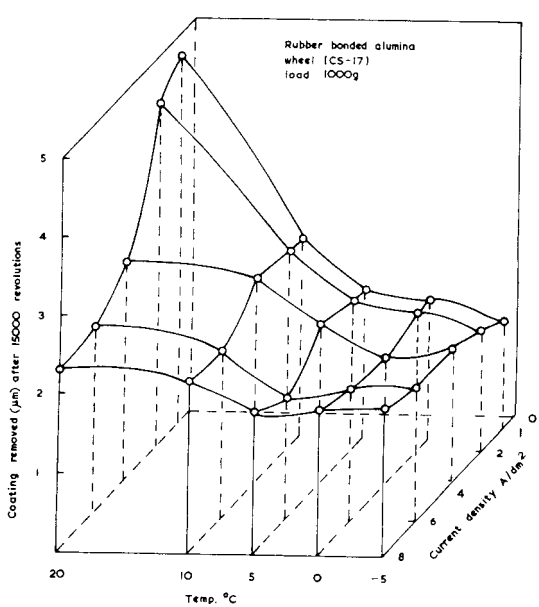


Fig. 9-8. Effect of current density and anodizing temperature on abrasion resistance of anodic oxide coatings[46]

A 12% (wt) sulphuric acid-1% oxalic acid solution has been used at a temperature as high as 9-11°C for hard anodizing aircraft fuel metering components.[47] In this case, a voltage of 10-75 volts was required to produce a 25 μm (1 mil) coating in 20 minutes at a current density of 4 A/dm^2 (36 amp/sq ft) using both mechanical and air agitation. An interesting method of 'stopping-off' was used which consisted of applying a thin anodic oxide coating to surfaces which were not to be hard anodized, and sealing it.

Alcoa workers[48] showed that when processing high copper containing alloys such as 2024, there was benefit in using high sulphuric acid concentrations (greater than 250 g/l), in that burning of the alloy was much less likely. Abrasion values, as measured with the Taber Abraser on 6061 material, using these electrolytes in comparison with the conventional Martin or Alumilite 225 processes are shown in Table 9-7.

TABLE 9-7

Taber test results comparing the experimental hard coating with Alumilite and Martin hard coatings on 6061-T6 alloy[48]

Anodizing process	*Weight loss – mg*				
	Revolutions				
	5000	*10,000*	*15,000*	*20,000*	*25,000*
Alurnilite 225[1]	4	8	11	15	18.5
Martin'[2]	7	12	16	19	23.0
Experimental No. 1[3]	4	7	11	14	**18.0**
Experimental No. 2[4]	4	***8***	**11**	**15**	**18.0**

1. 20 min at 3.9 A/dm^2 (36 A/ft^2), 10°C in 125 g/l H_2SO_4 + 10 g/l $C_2H_2O_4$
2. 30 min at 2.6 A/dm^2 (24 A/ft^2), -4°C in 165 g/l H_2SO_4
3. 20 min at 3.9 A/dm^2 (36 A/ft^2), 10°C in 250 g/l H_2SO_4
4. 20 min at 3.9 A/dm^2 (36 A/ft^2), 10°C **in** 250 g/l H_2SO_4 + 10 g/l $C_2H_2O_4$

Two CS-17 wheels with 1000 g loads were used for Taber testing. Wheels were refaced every 5000 revolutions

More recently Hitchcock[49] has reported extensive work on the abrasion resistance, microhardness and surface density of coatings produced on a wide variety of alloys. He used the BS 5599:1993 Class designations and reported results for alloys in each class (Tables 9-8 to 9-11). He used the abrasive jet test (BS 6161:Part 10) for measuring abrasion resistance, the microhardness test (BS 5411:Part 6) for measuring hardness and BS 5411:Part 1 for measuring surface density. In this paper he also reported the work carried out within ISO, between the UK and Japan, to establish minimum abrasion values for the British and ISO hard anodizing standards. This work showed that the abrasion testing apparatus needs to be carefully controlled (especially air pressure), and that use of a reference panel, produced under the strict anodizing conditions prescribed in BS 5599 Annex B, was essential.

TABLE 9-8

Class 1 alloys (Wrought except 2000 & 7000 series) properties[49]

Alloy	*Thickness (μm)*	*Surface Density (mg/dm² at 150 μm)*	*Hardness VPN50*	*Jet Factor (BS6161 Part 10)*	*Jet Air Pressure (mm Hg)*	*Rel. Mean Specific Abrasion Resistance*
(1 Sealed 2 Overheated 3 Very high current densities)						
				0.91	58	132%
1050	45	–	397	1.55	68	110%
				2.56	76	100%
				9.05	130	113%
1050	117	–	375	5.43	22	92%
				0.88	58	136%
1050	31	–	544	6.6	124	79%
1050'	32	–	551	8.4	124	62%
1200	65	1253	424	3.35	76	76%
1200	70	1267	387	3.1	76	83%
1200[3]	68	1267	413	6.4	76	40%
12003	81	1190	409	6.2	76	41%
1200[3]	71	1240	440	4.1	76	62%
1200[3]	45	1064	397	3.9	76	66%
1200[3]	69	1285	397	3.2	76	80%
5083	35	–	400	18.1	130	56%
5083[1]	34	–	430	30	130	34%
6061	49	–	–	1.41	58	85%
				0.21	24	95%
6061	27	–	–	0.18	24	111%
6061	52	–	–	0.18	24	111%
6061	28	–	–	0.19	24	105%
6061	*56*	–	–	0.17	24	118%
6061	25	–	–	0.17	24	118%
6061	27	1207	490	–	–	–
6061	57	1247	496	–	–	–
6061	30	1240	492	–	–	–
6061	52	1291	457	–	–	–
6061	28	1384	419	–	–	–
6061	47	1157	452	–	–	–
6063	44	1137	367	14.2	130	72%
6063	116	–	434	16.9	130	60%
6063	40	–	–	13.5	130	76%
6082	39	1181	360	11.3	130	90%
6082'	39	–	443	15.9	130	64%
6082'	70	–	362	21.1	130	48%
6082	40	–	–	12.8	130	80%
6082	34	–	433	11.9	130	86%
6082	31	–	–	5.07	124	103%
6082	36	–	–	4.84	124	107%
6082	32	–	–	4.67	124	111%
6082	31	–	–	4.57	124	114%
6082	27	–	–	4.27	124	122%

TABLE 9-9

Class 2(a) alloys (2000 series) properties[49]

Alloy	*Thickness (μm)*	*Surface Density (mg/dm² at 50 μm)*	*Hardness (VPN50)*	*Jet Factor (BS 6161: Part 10)*	*Jet Air pressure mm Hg*	*Rel. Mean Specific Abrasion Resistance*
2014	35	1040	287	16.5	130	62%
2014	32	1074	293	15.2	130	67%
2014	33	–	271	23.2	130	44%
2014	28	–	–	16.8	130	61%
2014	38	–	–	15.8	130	65%
				2.8	58	58%
2024	32	–	–	0.30	14	67%
2024	26	–	–	0.40	24	56%
2024	22	–	–	0.33	24	61%
2024	43	–	–	0.3	24	65%
2024	28	–	–	0.4	24	49%
2024	54	–	–	0.45	24	44%
2024	29	1091	338	–	–	–
2024	51	1069	242	–	–	–
2024	22	1177	343	–	–	–
2024	49	1032	274	–	–	–
2024	31	932	339	–	–	–
2024	38	1154	291	–	–	–
2024	24	–	248	20.4	130	56%
2618	50	–	355	5.6	76	46%
2618	10	–	–	8.2	76	31%
2618	75	–	156	12.2	76	21%
2618	74	–	194	9.5	76	27%
2618	53	–	271	9.9	16	26%

TABLE 9-10

Class 2(b) alloys (7000 series) properties[49]

Alloy * *Sealed*	*Thickness (μm)*	*Surface Density (mg/dm² at 50 μm)*	*Hardness (VPN50)*	*Jet Facior (BS 6161: Part 10)*	*Jet Air Pressure (mm Hg)*	*Rel. Mean Specific Abrasion Resistance*
7010	64	1115	390	3.1	58	39%
				6.3	72	30%
7010*	57	1407	350	4.4	58	27%
				5.0	72	38%
7010*	59	1365	352	3.0	72	63%
7010*	71	1249	377	3.2	58	40%
				6.1	72	31%
7150	54		388	16.3	130	63%

TABLE 9-10 *(continued)*

Alloy * Sealed	Thickness (μm)	Surface Density (mg/dm^2 at50 pm)	Hardness (VPN50)	Jet Factor (BS 6161: Part 10)	Jet Air Pressure (mm Hg)	Rel. Mean Specific Abrasion Resistance
7075	26	–	–	1.46	58	82%
				0.22	24	91%
7075	52	–	–	1.13	58	106%
				0.19	24	105%
7075	38	–	–	1.17	58	103%
				0.17	24	118%
7075	**43**	–	–	1.16	**58**	**103%**
				0.19	24	105%
7075	27	–	–	0.24	24	83%
7075	21	–	–	0.23	24	87%
7075	33	1153	420	–	–	–
7075	50	1382	367	–	–	–
7075	22	1189	402	–	–	–
7075	46	1230	396	–	–	–
7075	31	1166	428	–	–	–
7075	48	1177	417	–	–	–

TABLE 9-11

Class 3 alloys (cast) properties[49]

Alloy	Thickness (μm)	Surface Density (mg/dm^2 at 50 pm)	Hardness (VPN50)	Jet Factor (BS 616: Part 10)	Jet Air Pressure (mm Hg)	Rei. Mean Specific Abrasion Resistance
[1] Thin film VPN 25 used [2] Sealed						
LM4 (cast surface)	10	–	–	33	130	31%
LM4 (cast surface)	6	–	–	36	130	28%
LM4 (cast surface)	9	–	–	38	130	21%
LM4 (cast surface)	12	–	–	34	130	30%
LM6 (cast surface)	13	–	–	42	130	24%
LM6 (machined)	9	–	–	31	130	28%
LM24 (cast surface)	17	–	268'	29	130	35%
LM24 (machined)	25	–	346'	17	130	60%
LM25 (machined)	51	–	417	13	130	18%
LM25[2] (machined)	55	–	379	28	130	36%

Mixed acid electrolytes

Bisulphate and organic electrolytes

Lelong, Segond and Herenguel[50] have shown that higher temperatures can also be used for hard anodizing when the sulphuric acid is partially neutralized, e.g. by adding 66.5 g/l or 6.65% w/v sodium hydroxide to an 18% w/v sulphuric acid anodizing bath. Moreover, higher current densities in this sodium bisulphate bath may be obtained by adding organic acids such as citric, oxalic, tartaric or formic acid.

The last also improves the maximum current density in oxalic acid electrolytes. Wire and strip may be anodized continuously in oxalic acid-formic acid solution at current densities of up to 2500 amp/sq ft (over 250 A/dm^2), when the rate of film growth is of the order of 60 μm (2.4 mil) per minute.

Two electrolytes (described by Lelong, Segond and Herenguel for the production of thick coatings contain respectively:")

A.	oxalic acid	80 g/l
	formic acid	55 g/l
B.	sodium bisulphate ($NaHSO_4.H_2O$)	240 g/l
	citric acid	100 g/l

At current densities of 60 amp/sq ft, the voltages rise from 2.5-60 volts in electrolyte A and from 50-100 volts in electrolyte B when anodizing at 15°C for 100 minutes. Very much higher current densities are, however, possible.

According to these authors both solutions **A** and B are suitable for anodizing the wrought AI-Mg alloys containing 5% magnesium to thicknesses up to 200 μm (8 mil). Temperatures of up to 27°C can be used, and while A gives a grey or black coating, B produces yellow-brown to black films. B gives somewhat smoother coatings.

The wrought Al-Zn-Mg alloys are a little more difficult to coat and cooling is more important, particularly in electrolyte A. In this solution, the best results are obtained by anodizing first at constant current density and later at constant voltage.

In solution B, anodizing is started at 30°C and the solution is cooled gradually at the rate of 10-15°C per hour. By this means a coating more than 200 μm (8 mil) thick can be obtained at 60 amp/sq ft (6 A/dm^2) in 100 minutes.

The French casting alloys A-G3T (Al-3% Mg-0.15% Ti), A-S2G (Al-2% Si-0.3% Mg), A-G4Z (Al-4% Mg-0.2% Zn) and AI-Si alloys containing more than 10% silicon can be anodized in solutions A and B though it is necessary to hone the coating if a smooth finish is required.

Creep-resistant composites made by extrusion from 99.5% aluminium flake which is heated in air and sintered can be anodized at 100-300 volts in electrolyte B at 3 A/dm^2 (30 amp/sq ft) at 25°C, or in electrolyte A at 80-90 volts. Coatings 50-200 μm (2-8 mil) thick have been produced in this way.

John *et al.*[51] have described a hard anodizing electrolyte consisting of 10% (vol) sulphuric acid containing 30 g/l of sodium sulphate. This is used at 0°C and 3.6-5.4 A/dm^2, but unusually is recommended with applied a.c. Voltages of 30-60 V were used with different alloys and the process was considered particularly suitable for processing copper and silicon containing alloys. In later work the same authors[52] reported results based on a 200-250 g/l aluminium sulphate, 110-140 g/l tartaric acid, 60-90 g/l oxalic acid, 40-60 ml/l triethanolamine electrolyte. The special characteristic of this mixture was that it could operate at any temperature between 5°C and 40°C, and much of the work reported was carried out at 30-35°C. The voltage range was 20-40V and the current density 1.5-3 A/dm^2. Hardness values of 375-400 Vickers were obtained.

Japanese work has been carried out with sulphuric acid and magnesium sulphate electrolytes,[53] and sulphuric acid with 1-10 g/l potassium sulphate added.[54] In another development[55] 250-300 g/l aluminium sulphate, 30-40 g/l oxalic acid and 20 g/l glycerol are used as the basis of a hard anodizing electrolyte. This electrolyte can be used at IO-25°C and a current density of 2.5-3.5 A/dm^2. Very thick films in excess of 100 microns are said to be readily produced and film hardnesses are in the range of 400-500 Vickers.

Lichtenberger and Holló[56] have also investigated a formic-oxalic acid bath containing:

formic acid	50 g/l
oxalic acid	80 g/l

The properties of these coatings vary with the operating conditions, but at the comparatively high voltages used, up to 50 volts, barrier film thicknesses may be up to 540 Å and the coatings are substantially less porous, e.g. 1-2 x 10^{10} pores per cm^2, than coatings produced by other methods. The cell diameter is correspondingly larger in coatings formed in the formic-oxalic acid bath.

Sulphonic acids

Earlier still, in Germany, the same reasoning, that harder and more compact films could be obtained by weakening the aggressive sulphuric acid electrolyte, was being applied by using sulphonated acids with the general formula $H_2SO_3.X$, where X is an aromatic radical, to replace part of the sulphuric acid. This resulted in the patents of Schering A.G.[57] of 1938 for producing very hard wear-resistant films at room temperature, and although these were not much used for hard anodizing, the same electrolytes were to emerge in the post-war era under the guise of integral colour anodizing methods, where the emphasis was more on colour than wear resistance, though naturally the latter advantage was not ignored. The wear resistance of coatings produced in many integral colour anodizing electrolytes at temperatures of 30°C or more is in fact equivalent to what can be produced in sulphuric acid at sub-zero temperatures, and often with a great deal less tendency to 'burning'. These electrolytes generally have a high organic acid

content with a low sulphuric acid level, but more recently Woods[58] has claimed benefits for the addition of small amounts (0.5-5 g/l) of lignosulphonates to a 250 g/l sulphuric acid electrolyte.

Integral colour electrolytes

To render this Chapter complete one should therefore repeat all the electrolyte types that have already been described in Chapter 8, pages 631 to 669, since for the most part they can be classed as mixed acid electrolytes suitable for hard anodizing. There is this important difference, however. that while the integral colour depends on close control of the sulphate and dissolved aluminium, both of these can be raised considerably with no detriment to the hardness of the coating, although the colour will tend to become very much lighter. Control of the electrolyte is therefore a great deal less critical when using mixed acids for hard anodizing than for colour anodizing. The electrolytes are more tolerant of alloy variations than sulphuric acid. It might be wondered therefore why such electrolytes are not used more frequently for hard anodizing. Some operators who have them installed do in fact process large components or difficult alloys by integral colour processes, because the tank dimensions and rectifier capacities are large. However it would appear that no systematic survey has been published on the operating limits of mixed acid electrolytes for hard anodizing, and how they compare with ordinary sulphuric acid hard anodizing. However hard anodizing electrolytes and processing conditions have been summarised by Kape[59] and are shown in Table 9-12.

TABLE 9-12

Sulphuric acid based processes used for hard anodizing[59]

Process No	*Basic Electrolyte*	*Process ref.*	*Temp Range*	*Current Form*	*Voltage Range V*	*CD Range A/dm²*	*General Characteristics*
1.	0.5% - 2.5% vol H_2SO_4	Czokan	−5°C-10°C	d.c.	20 - 100	2 - 10	Rough coating
2.	10% ± 2% vol. H_2SO_4	Alumilite	0° to 5°C	d.c	15-70	1.5 - 3	Normal, not Cu alloys
3	15% ± 1% H_2SO_4 by vol. + CO_2	M H C	0° to 5°C	dc.	15-80	1.5 - 3.6	Normal, not Cu alloys
4	20% ± 2% vol H_2SO_4	(MOD.)	0° to 10°C	dc.	15 - 120	1.5 - 4.8	Normal, softer Cu Alloys acceptable
5.	7 - 20% vol. H_2SO_4 + 10 - 20 g/l Oxalic Acid or Glyoxylic Acid	Alumilite 226 Duranodic 100	−5°C to 10°C	d.c.	20 - 100	1.5 - 3.6	Normal, harder
6.	10 - 20% vol. H_2SO_4 + 10 - 50 ml/l "Sanfran" contains Mellitic Acid	Sandford	0°C to −5°C	d.c.	15 - 70	1.5 - 4 8	Normal. Cu Alloys acceptable

TABLE 9-12 *continued*

Process No	Basic Electrolyte	Process ref.	Temp. Range	Current Form	Voltage Range V	CD Range A/dm²	General Characteristics
7	10 - 20% vol. H_2SO_4 + 2.5 to 10% vol. Glycerol and/or Triethanolamine	–	0" to 10°C	d c. 100	20 - 3.6	1.5 - 4.8	Very smooth coatings
8.	10 - 20% H_2SO_4 + 5-50 ml/l Nitric Acid	Acorn	–5° to –10°C	d.c.	20 - 120 lower V for given CD	1.5 - 4.8	Rapid film growth. Cu Alloys acceptable
9.	As 1 - 8	Hardas	0" to -5°C	a.c. + d.c.	10 - 90	1.0 to 5.0 d.c. 0 5 to 2.5 a.c.	Rapid film growth V. Thick coatings
10.	As 1 - 8	Constant Wattage HDA	–5" to 10°C (mainly 10°C)	* see footnote	* see footnote	* see footnote	Rapid film growth
11.	As 1 - 8, mainly Sul-Oxalic Acid	Low Voltage Sandford Plus	0" to–5°C	a.c. + d c	24 V	1 - 5	Uniformity of coating
12.	As 1 - 4, mainly H_2SO_4 + special additives	–	–5° to 20°C (mainly 10°C)	a c	20-70	1-10	Very rapid film growth on most alloys

* Constant Wattage process: $A/dm^2 \times V$ remain constant within range 600 - 3600 W/ft^2 (60 - 360 W/dm^2).

Sulphuric acid-nitric acid[60,61]

In one process it has been proposed to add to the sulphuric acid electrolyte either nitric acid or a compound producing nitrate in an amount equivalent to 1-45 g/l of HNO_3. This, it is claimed, enables anodizing to proceed to an equivalent thickness with a lower voltage, less voltage rise during anodizing, a reduction in electrical energy, less cooling and hitherto difficult alloys can be anodized more readily. Compounds which can be used for this purpose include nitric acid, ammonium nitrate, aniline nitrate, cupric nitrate, guanidine, m-nitrobenzoic acid, *m*- or p-nitrophenol, urea nitrate. The benefits of small amounts of nitric acid, ammonium nitrate or hydrochloric acid, added to sulphuric acid or sulphuric acid/oxalic acid electrolytes, have also been described by Sharma et al.[62] In particular they found benefit in overcoming the presence of Al (FeMn) Si particles in DTD 5124 alloy. Similar concerns with the presence of these particles in 7075 alloy extrusions, were overcome by other workers in India[63] using a sulphuric acid, oxalic acid, hydrochloric acid electrolyte to dissolve them during the anodizing process.

Sulphuric acid-hydrochloric acid[64]

With a similar object in mind of reducing the anodizing voltage, Isawa *et al.* carried out hard anodizing in sulphuric acid with additions of hydrochloric acid. By adding 0.5% of HCl the anodizing voltage was reduced by about 8%, and with 1% HCI the voltage was decreased by about 14%, while the 'coating ratio' of the films was reduced by only 0.02 and 0.11 respectively. The same effect was obtained by additions of magnesium chloride. The economy in electrical consumption amounted to 20-30%.

Oxalic or glyoxylic acids[65]

Hard anodizing may be carried out in a binary acid electrolyte containing the following acids.

(1) Oxalic acid or glyoxylic acid at 1-100 g/l.

(2) From 10 g/l to saturation of dibasic or polybasic acids excepting oxalic, maleic or any acid which liberates nitrate or chloride ions. (Glyoxylic, malonic, tartaric, citric, diglycollic, malic, succinic, glutaric, itaconic, pyromellitic. trimellitic, citraconic, thiomalic, thiodiglycollic, acetylene dicarboxylic, aconitic, glyoxylic, phthalic acids.)

Some examples of these electrolytes along with the abrasion resistance obtained on 20-30 μm films have been quoted on page 659, and some of these coatings appear to be extremely hard even after effective sealing.

Sulphuric-sulphamic acids + Ni/Co[66]

Hard anodizing can be carried out in sulphuric acid to which salts of nickel or cobalt have been added by using interrupted or periodically reversed current. For example, using 250-290 g/l sulphuric acid with 25-30 g/l of nickel or cobalt, the current is interrupted for 4 seconds in each 20 seconds.

Sulphamic acid may also be present in this process; for example, using sulphuric acid 50-150 g/l, sulphamic acid 10-100 g/l, nickel or cobalt 25-35 g/l the work is made anodic for I20 seconds and cathodic for 60 seconds, this cycle being repeated.

Reynolds multipurpose electrolyte[67,68]

The Reynolds niultipurpose electrolyte has already been mentioned in connection with both bright anodizing and architectural anodizing but its third use is as a hard anodizing electrolyte. It consists of a 14-24% (wt) sulphuric acid electrolyte with additions of 2-4% (vol) of the MAE additive (2 parts glycerine to 3 parts of 70% glycollic acid). For hard anodizing purposes it is used at a temperature of 15-21°C, a current density of 2.4-6 A/dm^2 and an aluminium content of 4-8 g/l. The high acid concentration is particularly required when

treating 2000 series alloys. One of the particular benefits described[68] is the small increase in surface roughness during hard anodizing, even when producing coatings of 100 microns or more.

Tartaric acid based electrolytes

Tartaric acid based hard anodizing electrolytes have been developed in Japan, particularly by Fukuda.[69 70 71 72] These electrolytes are based on tartaric acid, malic acid or malonic acid (1 mole/l) with additions of 0.15-0.2 mole/l of oxalic acid. These baths were used at high temperatures (40-50°C), and voltages of 40-60 V produced current densities of about 5 A/dm^2 and films with Vickers hardness values of 300-470.[71]

Cooling and agitation

As all the hard anodizing processes are used at low temperatures, cooling is of great importance at the high currents and voltages used. At these temperatures water cooling is obviously not possible and some type of refrigerant must be used, and accounts of particular systems have been published.''

Cooling of hard anodizing installations is an expensive operation which requires considerable thought in order to achieve the most economic system. At the temperatures used for hard anodizing in sulphuric acid, chilled water is not suitable and it is customary to use brine, ethylene glycol plus water (anti-freeze), or to circulate the refrigerant Freon through the cooling coils. Probably the most trouble-free system is that based on the use of a reservoir of ethylene glycol maintained at between -15 and -10°C, which is pumped on demand through the cooling coils of the anodizing tank, a thermostat controlling the pump. The coils may be of lead, copper covered with lead, or titanium. Titanium is not much more expensive than lead because thin gauge tubes of excellent heat transference can be employed, but pure titanium is attacked by sulphuric acid unless positively polarized. It is said that the alloy Titanium-330 is safe for use in dilute sulphuric acid.

The compressors can be of the rotary, reciprocal or centrifugal type. Rotary compressors are for small scale work involving up to 10 tons of refrigeration (120,000 Btu/h), while the centrifugal compressors are generally for high capacity work and become very inefficient if used at low output. Since the demand of an anodizing plant is frequently very variable it may be more economical to use two multi-cylinder reciprocating units than one larger centrifugal compressor.[74]

Plate-type heat exchangers have been used in place of coils. These occupy less space at the tank sides and can also serve as cathode plates,[75] and external heat exchangers are increasingly used.

An effective system employed in France uses external cooling by means of a double system of tubes in lead and copper sheathed lead, arranged so that the sulphuric acid is pumped through one circuit and the refrigerant in the opposite direction through the associated circuit. Pumping the anodizing electrolyte through

external stainless steel or carbon block heat exchangers is also frequently used (see p. 461).

As heat is produced largely within the anodic coating itself, it is necessary to provide efficient agitation to keep the work at the required temperature. At the high current density used in the Hardas process, air agitation is not sufficient to ensure that heat dissipation is sufficient to maintain the required hardness (800-1,000 VPN depending on alloy composition). Additional agitation can be provided either by a paddle or by pumping the electrolyte through an external heat exchanger which thus combine:, cooling with agitation.

Fig. 9-9 shows the relationship between the a.c. used. the section of the sheet, and the minimum rate of agitation. When agitation is increased the a.c. component can he reduced without burning resulting. As would be expected, the thinner the sheet the more agitation is required to avoid burning. General descriptions of equipment for hard anodizing have been provided by Johnston[7"] and Bennett.[7"]

Electrical equipment

In its simplest form hard anodizing can be carried out using a normal rectifier with appropriate voltage and current capacity and suitable current or voltage controls. However the increasing use of more complex power systems, particularly for providing a.c. superimposed on d.c. or pulsed waveforms, has already been mentioned. One such power supply has been developed by Frusztajer and Lerner.[78] A form of this is illustrated in Fig. 9-10.

In this case a 2-phase transformer secondary composed of two windings (1 and 2) with a centre tap (3) is in circuit with two diodes or thyristors (4 and 5). These diodes or thyristors have a common point (6) which is a first output terminal of the rectifier system. A load (7) is connected by its first terminal (8) to the first output terminal and by its second terminal (9) to the centre tap (3) of the transformer secondary. A capacitor (10) with its first terminal (11) and a second terminal (12) is connected respectively to the first load terminal (8) and to the centre tap (3) of the transformer. As long as the second load terminal and the second capacitor terminal are connected to the transformer centre tap only, direct current with a ripple dependent on the value of the capacitor (10) will flow through the load. In this case the a.c. voltage component across the load is minimal and the a.c. potential of the load terminals may be considered as being balanced.

An additional a.c. voltage component is introduced across the load (7) when the second load terminal (9) is moved from the centre tap and is connected to different points along the transformer winding, whereas the second capacitor terminal is still connected to the centre tap (indicated schematically in Fig. 9-10 by dotted arrows). This gives an unbalanced winding of the transformer which changes the a.c. potential of the second load terminal and also supplies voltage to the diode or thyristor. If the capacitance of the capacitor (10) is large and a sine wave voltage is applied to the input of the transformer, the waveform of the additional component across the load is sinusoidal too.

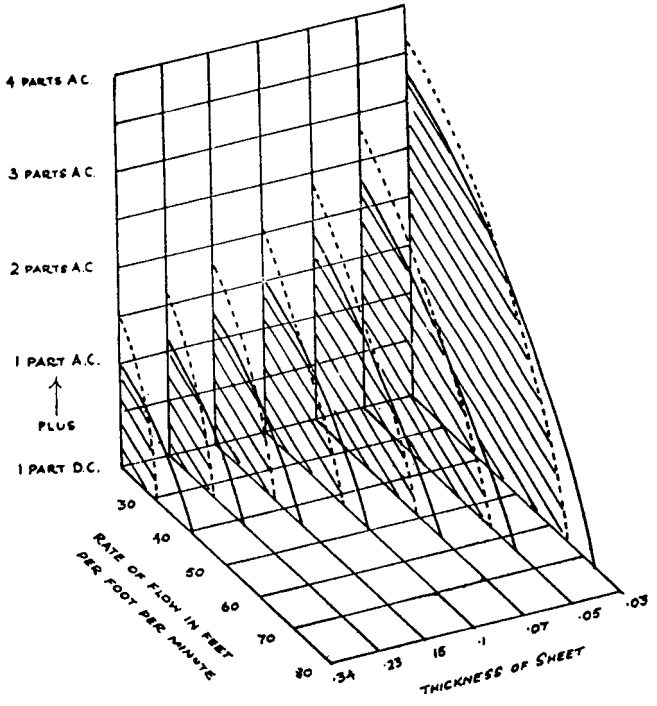


Fig. 9-9. Diagram showing the relation between sheet thickness, proportion of a.c. component and speed of agitation in the Hardas process. The solid and dotted curves show the relation between speed of agitation (in terms of rate of flow in ft per min per ft of anode surface). When agitation is increased the a.c. can be reduced. The increase of the shaded area to the right represents the tendency for thinner sheet to burn[18]

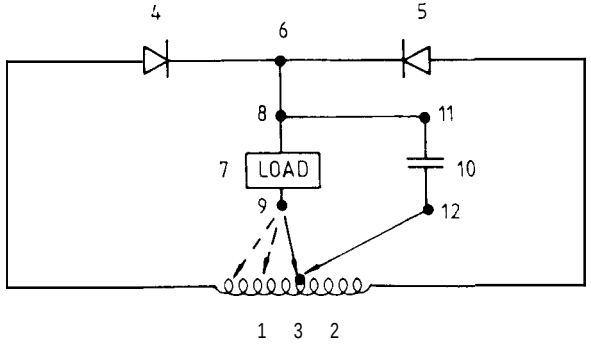


Fig. 9-10. Method of providing a.c. superimposed on d.c. for hard anodizing"

A more conventional type of power supply is illustrated in Fig. 9-11. Here an inductance (3) blocks the flow of a.c. into a d.c. source (1), whilst a capacitor (4) prevents an a.c. source (2) from short-circuiting the d.c. power supply. This provides a.c. superimposed on d.c. to the load (5). For the supply of very large currents, the values of inductance and capacitance required make this system expensive.

Another circuit which can be used for anodizing with d.c., a.c. or superimposed a.c. on d.c., is that described by Tajima *et al.*[79] for use in a sulphamic acid anodizing plant. As previously indicated pulsed current rectifiers have been described by Colombini.[28,29]

In Russia a quite different technology of micro-arc oxidation has been developed[80] and used for hard anodizing, and coatings up to 160 microns with a microhardness of 1200 Vickers have been produced.

Low pressure anodizing

Anodizing at low pressures, e.g. at 10 mm mercury, has been attempted on a laboratory scale by Stalzer.[81,82] This prevents the accumulation of heat in the coating and enables the use of higher current densities for short periods. Stalzer, who has suggested the possibilities of using this technique for hard anodizing complex shapes as well as for basket anodizing, points out, however, that in order to maintain the low pressure it is necessary to prevent hydrogen evolution at the cathode, e.g. by using a diaphragm system with the cathode compartment filled with copper sulphate solution.

Jigging arrangements

Even more than in normal anodizing, it is essential to provide good electrical contact in hard anodizing, and clamps and jigs must be sufficiently sturdy to hold the work rigidly in view of the swift flow of the solution.

Two types of clamp are preferred, the screw-pressure type and the bolted lever. With the former, only a minimum area of the clamp should be immersed, as if the screw thread is anodized the work cannot subsequently be removed without damage to the clamp. For this reason plastic clamps are increasingly used. The bolted lever type of clamp may be immersed in the solution more readily, but at least the bolt threads and hinge should be stopped-off. Spring clips made from bent flat bar or rod and tightly wired to the anode can be used for small, light articles.

Contacts should be made of aluminium or, where this is too weak, an aluminium-magnesium alloy (5154A or 5083) or 6063-T6 (a heat-treatable Al-Mg-Si alloy)[8] may be used. In this case, the lower electrical conductivity of the alloy, which in the case of 5056A is less than half that of pure aluminium, must be taken into account.

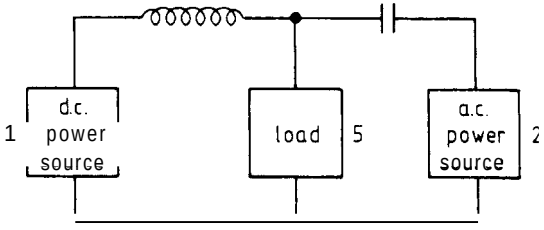


Fig. 9-11. Simple power supply arrangement for producing a.c superimposed on d.c.[79]

Titanium has also been found useful for hard anodizing; it is particularly suitable for screw pressure and bolted-on jigs. Leopold[83] has described the fundamentals for design of titanium racks for hard anodizing. He indicates that the rack must give positive, firm contacts, that the current density from the clip to the racked piece must not exceed 24 to 36 A/ft^2 (2.4-3.6 A/dm^2) of aluminium surface, and that the solution temperature should be within the range of 32-50°F (0-10°C).

Even more so than with normal anodizing, it is important to see that the jig material is compatible with the work. This is automatically ensured by using identical alloys for both. It becomes essential when hard anodizing an alloy of high silicon content, such as an LM2 casting, which has a pronounced rising voltage characteristic and may require as much as 90 or 100 volts to maintain the current density. Under these conditions a jig of 6063 material (Al-Mg-Si) would carry a large proportion of the total current and break down long before this voltage was reached. In such a situation titanium would be an ideal jig material.

Jigging is a very important feature of the art. Many applications arise where the whole operation becomes an exercise in engineering ingenuity such as when anodizing the bore of a long narrow tube, or the inside of a deep blind hole.[84] Campbell has patented a method[X5] for anodizing the exterior surface of large diameter cylinders by rotating them in a shallow tank of acid, an essential part of the operation being the high speed flow of electrolyte through an annular passage defined by the periphery of the rotating article and the inner wall of an actuate baffle whose radius can be adjusted to match the diameter of the article being anodized. Fig. 9-12 illustrates this treatment in progress. As in normal anodizing, clamps should be arranged at hidden parts of the work where possible.

Stopping-off

Stopping-off is relatively simple. Wax or the usual P.V.C.-type compositions or tape may be used, as in electroplating, while chromic acid anodizing has also been used as a stop-off.[86] Whether it is cheaper to stop-off will generally depend on the current required for the excess areas or, more rarely, on the appearance, which is a dark grey-green on the hard anodized surface.

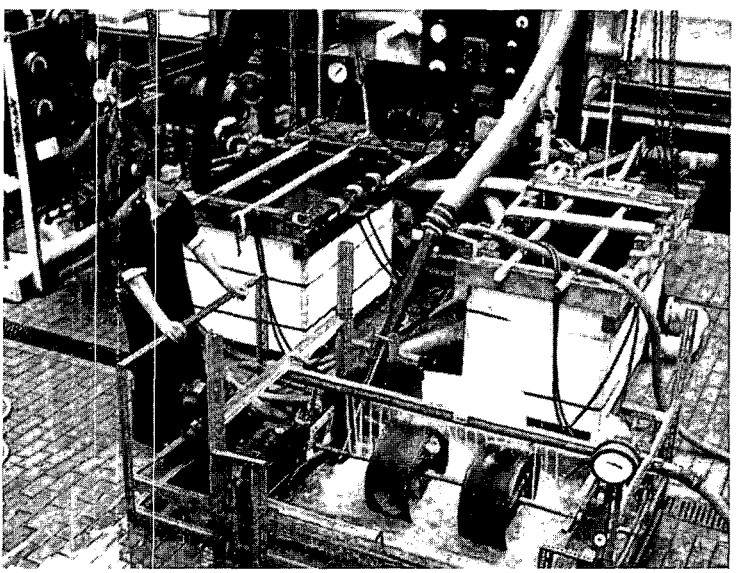


Fig. 9-12. Patented method of hard anodizing the exterior surfaces of large diameter cylinders[85]

[Courtesy Acorn-Hardas Ltd.]

Chromic acid anodizing is more commonly used as a stop-off before hard anodizing than sulphuric acid anodizing, mainly because many parts contain recesses or are already assembled before treatment.

There are a number of methods in use for this technique, of which the following are typical:[14]

A. Mask areas to be coated with hot wax (by dipping or brushing) or with vinyl tape or lacquer, and plug holes with rubber or hardwood. Alternatively, use a stop-off fixture.
Chromic acid anodize.
Strip the mask.
Hard anodize.

The main disadvantage of this method is the lack of adhesion of the wax on bare aluminium, which may cause trouble at the edges.

B. Chromic acid anodize and seal.
Apply mask.
Chemically strip areas to be hard anodized.
Hard anodize.

A phosphoric acid stripping solution is used at 82°C to minimise the inevitable roughening of the surface caused by stripping the chromic acid film, which is particularly pronounced with casting alloys containing silicon. Even *so*, the method is unsuitable where a fine surface finish is required.

C. Chromic acid anodize and seal.
Machine areas to be hard anodized.
Hard anodize.

This method is cheaper than B. Machining replaces chemical stripping and no masking material is applied. The chromic acid anodizing step thus becomes very important, and adequate sealing at 99-105°C in deionised water or in nickel-cobalt acetate or dichromate solution is essential.

A protective lacquer is sometimes applied to the sealed coating to avoid mechanical damage in handling before hard anodizing.

D. Chromic acid anodize and seal.
Machine areas to be hard anodized.
Mask anodized areas.
Hard anodize.

In this method masking is used as an additional safeguard over method C and it is, therefore, more expensive.

The use of chromic acid anodizing for stopping-off has been the subject of a patent application.[87]

Alternatives to wax are increasingly used[27] and these include masking lacquers applied by dip, brush or spray, and silk screens or photo-sensitive resists for high accuracy. Tapered neoprene bungs are used for masking holes, and purpose-made silicone rubber shapes for irregular holes. Blanked-out discs and shapes in adhesive vinyl are used for local masking.

Local hard anodizing can be carried out using the equipment described in Chapter 7 (page 570), and this practice has been described by Roberts.[88] Examples given are the need for hard anodizing on local slide or bore areas, and the local build-up of over-machined components.

Pretreatment and structure

The structure and also the appearance of anodic oxide coatings vary considerably with the basis metal composition, i.e., with the presence of AlFe, Al_2Cu, Al_6Mn and other intermetallic compounds. Streaky coating may be due to structural deformation in cold working, while the dendritic structure of some castings may be reproduced in the anodic oxide coating.

Surface preparation also affects the appearance and quality of a hard anodic coating. Experiments carried out by Csokán[89] showed that while untreated aluminium produces uniform but slightly rough coatings, mechanical polishing before anodizing gives a fine-grained smooth and more attractive film. Electropolishing on the other hand may give rise to a non-uniform structure showing glassy oxidation zones with fine lines between the primary nuclei of the anodic coating, explained by Csokán as due to the thin oxide film left on the surface by electropolishing.

TABLE 9-13

Selection of alloy pretreatment[16]

Material condition	*Mechanical or solvent treatment*	*Comments*	*Chemical treatment*
Machined component, light soil and oil.	Vapour degrease	Vapour degrease may alone be sufficient.	1 min hot acid clean plus desmut.
Extrusion and sheet. Mill finish.	–	Prolonged etch tends to smooth out die and roll lines.	1 min hat acid clean, 6-8 min caustic etch desmut.
Taped pans (adhesive tape)	Solvent clean by hand, vapour degrease. May have to be repeated after chemical treatment.	Adhesive tape residues are transparent and difficult to see. Paper backed masking tape is difficult to remove.	As above but may have to be repeated.
Cast surfaces	Vapour degrease.		1-5 min hot acid clean. Desmut.
Lapped, vapour blasted, sand blasted and barrel polished or deburred.		Prolonged treatment required to remove passive layer.	10 min hot acid clean. Desmut.
Parts masked with wax or paint.	Scour areas to be anodized with wire wool, pumice, wetting agent and water.	To remove excess maskant and overspill.	Cold acid etch Desmut.
Large components.	Scour with wire wool, pumice, wetting agent and water.	Parts too large for pretreatment tanks	None
Engineer's blue identification paint	Suitable solvent. Meths, acetone, MEK.	Mechanical treatment may be required.	May be any or combination of those above.

Similarly, etching in a nitric-hydrochloric-hydrofluoric acid mixture before hard anodizing produces an etched appearance after anodizing, possibly due to the presence of a fluoride film on the basis metal which causes the formation of a non-uniform, thin anodic coating.

After the normal pretreatment, it may be necessary to remove a passive layer by scouring with pumice or steel wool before hard anodizing.

A useful summary of pretreatment problems experienced with hard anodizing has been provided by Thompson[''] and is shown in Table 9-13.

Markowitz[90] has studied the effect of surface preparation methods prior to anodizing on the blistering and porosity of hard coatings produced on 7075-T6 cylinders. He found that mechanical cleaning produced the best hard anodic coating, with non-chromated deoxidizing producing the worst blistering. Chromated deoxidizers produced an intermediate result, but chemical etching prior to hard anodizing was not recommended, because of differential attack on intermetallic compounds in the alloy. Incorrect mechanical treatments, such as the use of tools contaminated with other metals, shot peening residues in the surface or oil contamination, could also lead to blistering problems.

Where dimensional tolerances are close it may be necessary to prepare the work by machining. Where no smoothing operation is applied after anodizing, machining may also be desirable because the roughness of the surface is increased by hard anodizing. Machining to 4-8 micro-inch (0.1-0.2 μm) finish is normally suitable. The component will increase in thickness by something like SO% of the coating thickness. As this, however, depends on the alloy composition and operating conditions. the precise amount will have to be determined by experiment.

According to Acorn-Hardas Ltd.[91] hard coating up to 75 μm (3 mil) thick can be produced on all aluminium alloys now commercially available as sheets, plates, forgings, extrusions: sand castings or gravity die-castings. These include alloys containing up to about 18% of other metals. Pressure die-castings may also be hard anodized but the coating rarely averages more than 25 μm (1 mil) thickness. The presence of other metals in an alloy at maximum commercial levels affects the properties of the coating as follows:[91]

	Thickness	*Hardness*	*Adhesion*	*Dimensional Change*
Magnesium	+	–	–	50%
Copper	=	–	=	43%
Silicon	–	–	=	38%
Manganese	=	=	=	50%
Zinc	–	=	–	43%
Nickel	–	–	=	43%

\+ better than average = average – less than average

Dimensional change is the dimensional increase per surface expressed as a percentage of the applied coating thickness.

Sealing

After anodizing, the parts are rinsed thoroughly and may then be sealed in boiling distilled water, 5% dichromate solution, dewatering oil or wax (80°C, 15-30minutes). Dichromate sealing improves the fatigue properties but. in common with other aqueous sealing solutions, decreases the abrasion resistance and insulating properties to some extent. For this reason, aqueous sealing processes are not normally used where high wear resistance is required. The effect of sealing on jet abrasion values has been measured by Hitchcock[92] and is shown in Table 9-14.

Hard anodized coatings may be impregnated with oils, silicones or dry lubricants such as colloidal graphite and molybdenum disulphide for the improvement of anti-friction properties. The use of solid film lubricants has been described by Brace and Faul.[93,94,27] They cover PTFE, molybdenum disulphide, graphite and allied systems, and they report their coefficients of friction and stick-slip properties. They indicate that fluorcarbons are normally applied by dip or spray, and dry molybdenum disulphide lubricants by tumbling the part in the pigment powder.

Air-dried resin-bonded lubricants have the best lubricating characteristics but generally lack wear resistance, whereas phenolic thermosetting types are good general purpose film lubricants. They have reasonable lubricity, while giving greatly increased corrosion, solvent and chemical resistance in comparison with the air drying formulations. Epoxy-phenolic thermosetting materials are better at resisting environmental conditions than lubricating a surface, whilst inorganic bonded lubricants have better lubricity than any organic bonded materials. The latter are compatible with liquid oxygen and high vacuum conditions, but give little enhancement of corrosion resistance. They are degraded by many solvents and must be evaluated carefully for sensitivity to specific chemical environments.

PTFE coatings are not easy to apply but General Magnaplate Corporation have described and patented an anodizing method which allows the aluminium oxide layer to be impregnated and coated with a layer of Teflon in an aqueous resin tank to provide a hard coated surface which is well lubricated, with excellent dielectric properties and weather resistance.[95,96] The production of Teflon coated parts in America has been described by Cassidy,[97] and in the U.K. by Nimet.[98]

TABLE 9-14

Effect of sealing on jet abrasion resistance[92]

Alloy	*Unsealed*		*15 Minute seal (0.5 min/μm)*		
	Abrasion (g/μm)	*Seal Value (μS × μm)*	*Abrasion (g/μm)*	*Change (%)*	*Seal Value (μS × μm)*
2024-T3	24	>8,400	22	–8	7,000
6061-T6	59	>7,500	49	–17	2,500
7075-T7	48	>8,100	47	–2	1,890

TABLE 9-14 *continued*

30 Minute seal (1 min/μm)			*60 Minute seal (2 min/μm)*		
Abrasion (g/μm)	*Change (%)*	*Seal Value (μS × μm)*	*Abrasion (g/μm)*	*Change (%)*	*Seal Value (μS × μm)*
21	–13	840	15	–38	448
44	–25	500	41	–31	325
42	–13	351	32	–33	270

Note: (1) Seal value of 500 is considered maximum for good corrosion resistance (See BS 1615).

Workers at UMIST[99] have studied duplex anodizing processes, developed in Japan, where work is first anodized in sulphuric acid, and then anodized in an ammonium tetra-thiomolybdate electrolyte to produce molybdenum disulphide in the pores. A related Japanese process[100] consists of cathodic deposition of molybdenum oxyhydroxide on aluminium from an ammonium molybdate solution, followed by anodizing in a sulphosuccinic acid electrolyte. Such films gave microhardness values of about 700 Vickers.

The effect of sealing for 30 minutes in boiling deionised water on a number of hard anodized panels is shown in Table 9-15. These were of 99.0% aluminium anodized at 5°C and 4.3 A/dm^2 (40 amp/ft^2) in sulphuric acid at three concentrations, and the specific abrasion resistance was determined by Appendix L of BS 1615 : 1972 in terms of grammes of SiC per micron of coating required to penetrate the film. (These values are comparative and should not be compared with any others made on a similar but not identical apparatus.)

TABLE 9-15

Effect of sealing on abrasion resistance of hard coatings[101]

Acid strength (g/l)	*Anodizing time (min)*	*Film thickness (μm)*	*Abrasion Resistance*		*Ratio Sealed/ Unsealed (%)*
			Unsealed (g/μm)	*Sealed (g/μm)*	
45	80	112	27.7	17.9	64.6
90	80	124	25.6	17.9	70
180	80	109	24.0	18.0	75
45	40	60	21.6	14.6	67.6
90	40	55	22.4	13.9	62
180	40	57	25.6	18.5	72.3

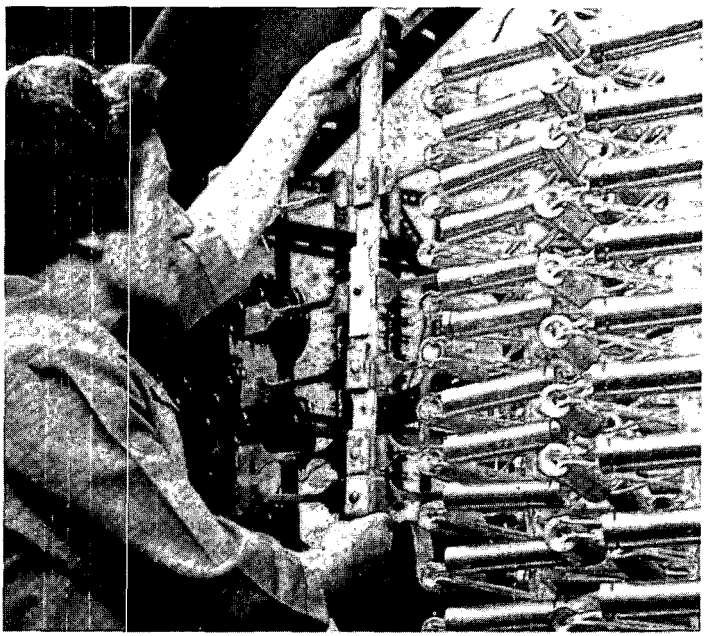


Fig. 9-13. Jigging of components for hard anodizing. On the left are waxed parts

[Courtesy Acorn-Hardas Ltd.]

In tests of a similar nature with a Haueisen Abrasionmeter, Oechslin'' found that sealing for 30 minutes in boiling water reduced the abrasion resistance of a 62 μm coating from 4.20 to 2.67 g/μm (63.6%), and of an 18 μm coating from 2.10 to 1.55g/μm (73.9%). The marked differences found in films of different thicknesses he attributed to the different internal stresses in the coatings which change from compression to tension as the film grows, as demonstrated by Arrowsmith.[102]

However Japanese workers'''' have found that boiling water sealing for 30-45 min improves wettability for lubricants and, as a result, friction forces and wear rates were reduced. This depended on the viscosity and surface tension of the lubricant, with wettability improving as these factors were reduced.

Honing and grinding

Many engineering components are honed or ground after hard anodizing (see, for example, Table 9-5). Thus Campbell reports'''' grinding small valves with 60 or 80 J Aloxite- or Alundum-shellac wheels with Sal Soda coolant, while 15 cm diameter bores have been ground with VBE (38.A.60K.5) wheels at 10,000 rpm

with paraffin coolant. An example of honing methods given by Campbell'includes the use of a single pad 600 grit graphite-impregnated rubber-bonded wheel which removed 1-1.5 mil (0.025-0.037 mm) diameter from a 1.125 inch (28.6 mm) diameter bore in 15-20 minutes for a 3 microinch (0.076 μm) finish. Diamond compound used on a Tufnol wheel has also given good results.

Acorn-Hardas[91] recommended silicon carbide wheels with 60 to 120 grit abrasive for fast stock removal to give finishes of 10-2 microinches. Grinding should be done wet with free use of a good water soluble cooling oil. Grinding wheel specifications, as described in B.S. 4481, Part 1: 1969, are as follows:

Surface grinding
C60 JV for finishes of 6-10 microinches
C120 HV for finishes of 2-3 microinches

Cylindrical grinding
C120 JV

Internal grinding
C100 JV

For polishing and lapping, a boron carbide abrasive mixed with a carrier of heavy oil or petroleum jelly gives fast and satisfactory results.[101] Grit sizes in the range of 400 to 1200 should be used.

In general, it is not difficult to machine or grind to close tolerances. Johnson[14] obtained the best results by applying the coating oversize by 1-1.5 mil (25-37.5 μm) and then lapping or honing.

Sharp edges, e.g. on valve parts, may cause chipping on drilling or honing, and spark- and ultrasonic-machining have proved satisfactory for such parts.[105]

3. PROPERTIES OF HARD ANODIC OXIDE COATINGS

Appearance and uniformity

The effect of alloy composition on the growth of an M.H.C. hard anodic coating is seen in Fig. 9-14. On the whole, all of the alloys show uniform growth equal to approximately half the coating thickness. The colour of the coatings depends on the alloy and the coating thickness. 6061 and 2024 have a tan or grey colour which darkens to jet black at 3 mil (75 μm). The coating on 7075 alloy turns black at 1 mil and subsequently turns lighter again through blue-grey to almost white at 9 mil. As would be expected, the coating on 99.99% aluminium is colourless at 1 mil and slowly turns light brown up to 5 mil. Coating thickness is

determined by the methods described in Chapter 12, and the eddy current method (EN ISO 2360), the gravimetric stripping method (ISO 2 106: 1982), and the microsectioning method (EN ISO 1463) are all suitable.

The somewhat rapid reduction in image clarity under hard anodizing conditions as compared with conventional anodizing in sulphuric acid is no doubt due to the higher anodizing voltage which is required at the lower hard anodizing temperature.[106]

In hard anodized coatings, fine failure cracks may be present when the component is withdrawn from the bath and these increase as the surface warms up after withdrawal, This type of crazing is seen in Fig. 9-15. If held against the ear and flexed, the cracking is clearly audible. In the case of some alloys, notably 2024 Alclad, the coating may blister. This is liable to occur when the thickness of the coating exceeds that of the cladding.

Surface roughness is generally increased by hard anodizing, particularly on bar. The usual practice is, therefore, to anodize oversize (allowing also for the growth of the metal) and to lap down to the final dimension. George and Powers[48] have indicated the degree of increase in roughness and their values are shown in Table 9-16.

At times it has been noted that a hard coating does not form satisfactorily at corners. This 'corner' defect"" is due to the fact that the corner cannot expand in three dimensions, and a void occurs. This is illustrated in Fig. 9-16 and is more pronounced in the thicker coatings. The number of cracks in relation to the radius as shown on rods of different diameters is shown in Table 9-17 and Fig. 9-17.

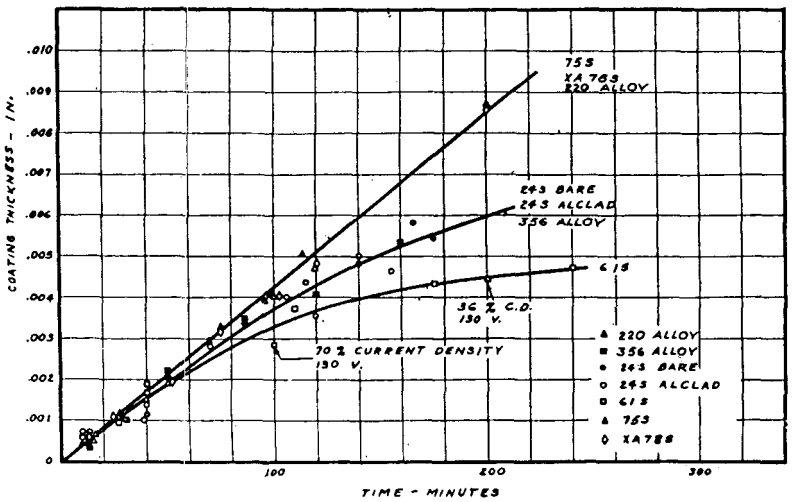


Fig. 9-14. Time versus coating thickness on a number of U.S. aluminium alloys treated by the M.H.C. process.[107] 0.001 in = 25 μm

TABLE 9-16

Surface smoothness before and after hard coating[48]

Aluminium alloy	*Coating thickness (mil)*	*Surface smoothness (μ in, RMS)* *Initial*	*Final*
7075-T6	1.2	5-7	10-20
2014-T6	1.3	5-8	50-60
43	1.1	8-10	60-70
356-T6	1.3	5-7	60-70
A214	**1.1**	6-10	40-45

It is seen that even the fairly large radius of 3.2 mm (6.4 mm diameter) results in more than twice the number of cracks as compared with a straight section. However, the coating on even the 1.6 mm diameter piece was quite adherent. Nevertheless, the radii should be as large as possible and this fact must be taken into account in design. Radii recommended by the Aluminum Co. of America for different thicknesses of hard anodic oxide are:

Coating thickness		*Radius*	
mil	*μm*	*inch*	*mm*
1	25	0.032	0.82
2	50	0.062	1.6
3	75	0.125	3.2

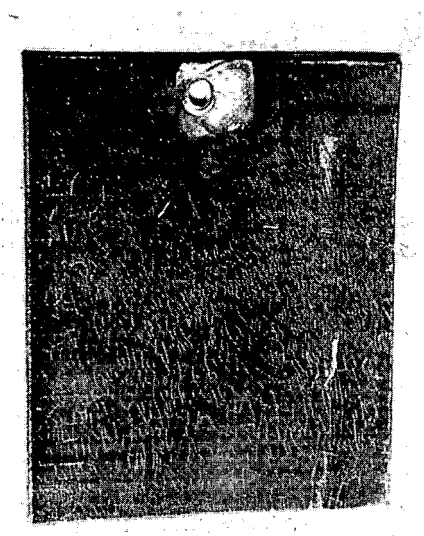


Fig. 9-15. Commercially pure aluminium sheet with 3 mil (75 μm) hard anodic coating. The crazed pattern is due to differential thermal expansion. Some of the cracks were present when the piece was withdrawn from the bath[107]

TABLE 9-17

Influence of radius on cracks in M.H.C. coating

Diameter		*Circumference*		*No. of*	*Cracks per*	
(in)	*(mm)*	*(in)*	*(mm)*	*cracks*	*(in)*	*(mm)*
1/16	1.6	0.196	5	36	184	7
1/8	3.2	0.393	10	28	71	3
5/16	4.8	0.590	15	25	42	1.7
1/4	6.4	0.785	20	27	34	1.3
Straight section		1.125 in (28.6 mm) long		12	11	0.4

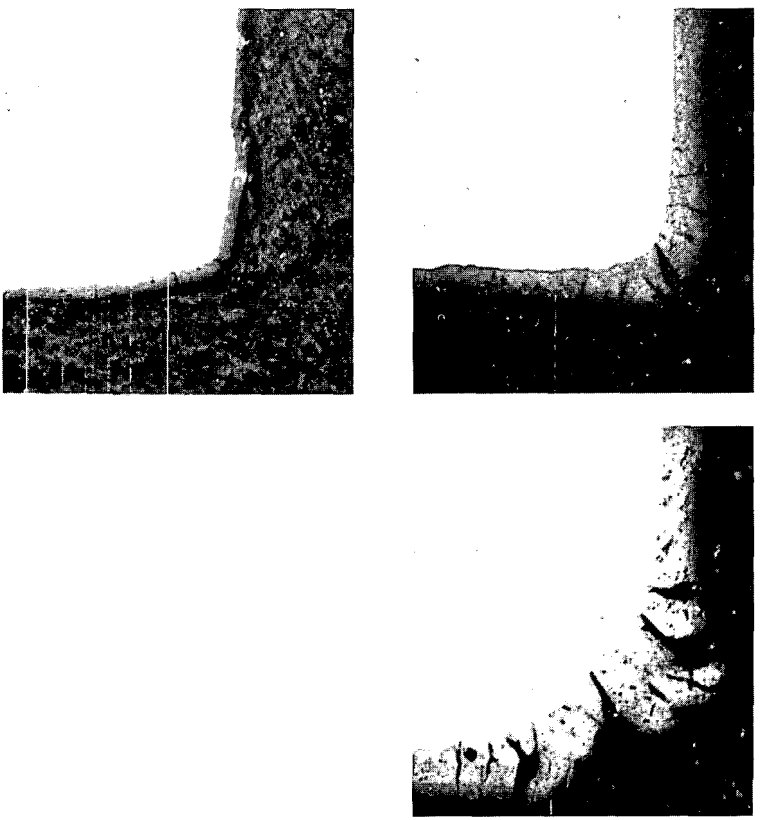


Fig. 9-16. 'Corner defect' which occurs due to the mechanism of the coating process. The defect becomes accentuated as the coating thickness increases[107]

Fig. 9-17. Cracks in a 3 mil (75 μm) hard anodic coating formed on $^{1}/_{16}$ in. (1.6 mm) diameter rod.[107] Unetched (X 300)

A more recent SEM study of corner cracks by Levine[108] shows that this effect can be influenced also by the process used.

Ostermann and Walker[""] point out that alloys with a higher proportion of silicon or copper give a greater film thickness variation during hard anodizing than other alloys. The influence of component geometry is also important and film development becomes non uniform if internal or external radii are too small, as may frequently be seen on screw threads.

The throwing power of the M.H.C. process was tested by Gillig[107] and was shown to be excellent. Results on a tube of 6061-T6 alloy 5 inches (125 mm) in length and of dimensions 0.375 inch (9.6 mm) diameter by 0.049 inch (1.25 mm) wall are shown in Table 9-18. On the other hand there is evidence that the throwing power may be highly dependent on the rate of solution movement.[82]

TABLE 9-18

Throwing power of M.H.C. solution[107]

	Outside coating thickness (mil,	*Inside coating thickness (mil,*
Open end	2.5	1.7
Centre	2.5	1.6
Closed end	2.5	1.0

Hardness and wear resistance

The wear characteristics of hard anodized aluminium are most favourable at low loads where the metal may compare favourably with hard tool steel. In practice a useful qualitative hardness test is carried out by rubbing a fine emery paper or cloth, of grade 00, two or three times over the surface. If the coating is satisfactory the paper should skid over the surface and should not abrade the coating more than is shown by a faint trace of whitening of the emery. This is the principle of the simple Clarke paper abrasion test described in BS 6161:Part 18:1991.

Micro-hardness tests have been carried out on a number of hard anodized surfaces, and have shown hardness values of 500 V.P.N. for the Hardas film[18] and 530 V.P.N. for a coating produced by the M.H.C. process on 6061-T6 alloy (H20WP).[110] These measurements are carried out on mounted and polished cross-sections of the anodic film using a diamond indenter and a very low load. Tests carried out by the Aluminium Development Association have been reported by Brace"' (see Table 9-19). These results show that the values obtained are not independent of the load and of the hardness of the basis metal. The low values obtained for LM10-W are stated to be due to the presence of magnesium oxide in the coating, and similar low values have been obtained in the U.S.A. with 2024-TI. However the most comprehensive study, with regard to alloy effect, has been carried out by Hitchcock,[49] as described earlier in Tables 9-8 to 9-11.

TABLE 9-19

Microhardness values of Hardas coatings[111]

Material	*Cona'ition*	*Nominal composition*	*Microhardness (V.P.N.) load (g)*			
			7.5	***15***	***30***	***45***
1200	½ Hard	Commercially pure **AI**	353	481	496	357
5056A	½ Hard	Al-5% Mg	440	460	452	363
LM10	Solution heat-treated	Al-10% Mg (cast)	301	282	312	336

Sautter[112] has shown how the microhardness of normally anodized coatings varies across the thickness of the anodic coating, the layers adjacent to the metal being the hardest with a progressive decrease as we proceed from the metal to the surface (Fig. 9-18). As the anodizing temperature is reduced this effect becomes less until at 0°C the hardness of a 25 μm film is practically uniform across its whole thickness.

A note of caution is often sounded about the significance of these tests because, when it comes to wear resistance, the hardness measured by micro-indentation methods does not always represent the performance of the material. Thus, according to Campbell,[104] a hard coating registering 450 V.P.N. will have the wear resistance of a tool steel of 950 V.P.N., and even an anodic coating on a high copper alloy such as L65, which registers 250-280 V.P.N., will often offer as much resistance to wear as tool steels.

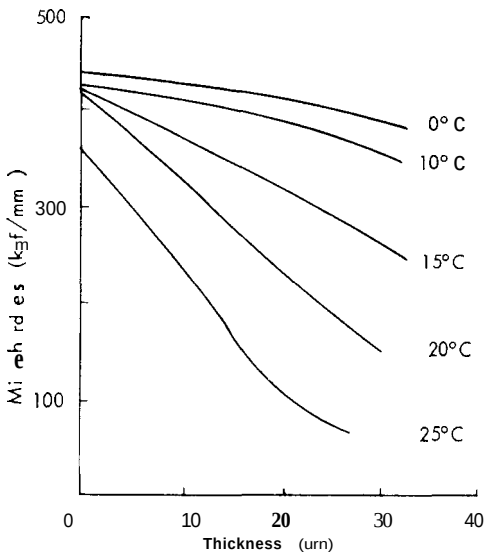


Fig. 9-18. Influence of electrolyte temperature on the microhardness of d.c. sulphuric films formed on AlMgSi 0.5 alloy at 1.5 A/dm^2 [112]
1 kgf/mm^2 = 981 N/m^2 25.4 μm = 1 mil

It is generally considered, therefore, that a better guide than hardness values is provided by tests showing the wear-resistance of the coatings directly. In a number of tests carried out by the Aluminium Development Association using the Schuh and Kern (abrasive jet) method (see Chapter 12), a 5.1 mil (130 μm) coating on the 5251 alloy (Al-2% Mg) gave a result of 1,026 g (weight of abrasive required to penetrate the coating), compared with 615 g for a 2.7 mil (69 μm) M.H.C. coating on 7075-T6, corresponding to specific abrasion resistances of 201 and 227 g per mil respectively.' These are relative values very much dependent on the particular piece of apparatus used and cannot be compared with the rather lower values reported by Vanden Berg[113] whose results for coatings produced by the M.H.C.

process, the Alumilite hard anodizing processes and the Alumilite normal anodizing process are given in Table 9-20 for different alloys. These results were obtained by blasting 180 grit emery through a 11/64 inch (0.44 mm) diameter orifice at 5 lb per square inch (34 KN/m^2) pressure.

In a comparative test with cyanide-case-hardened steel, the same author reported that approximately half the amount of wear was shown by the M.H.C. hard anodized aluminium after 50,000 cycles in a Taber abrasion tester.

TABLE 9-20

Specific ,abrasion resistance of M.H.C. and Alumilite 226 hard anodized coatings compared with that of conventional anodic coatings (Alumilite 204)[113]

Alloy	*Type of coating*	*Thickness of oxide coating (mil)*	*Weight of abrasive to penetrate coating (g)*	*Weight of abrasive per mil of coating (g)*
1200	Alumilite 204	0.47	35	75
	Alumilite 226 *	2.24	387	173
	M.H.C.	2.27	405	146
3103-HI8	Alumilite 204	*0.53*	33	62
	Alumilite *226* *	*2.33*	*368*	158
6061-T6	Alumilite 204	0.46	41	89
	Alumilite 226 *	2.15	364	169
	M.H.C.	2.31	390	169
7075-T6	Alumilite 204	0.45	46	102
	Alumilite 226 *	2.13	357	168
2024-T3	Alumilite 204	0.41	22	54
	Alumilite 226 *	2.10	142	58
	M H.C.	2.48	163	68

* Alcoa hard anodizing process.

Results showing comparative wear-resistance with hard chromium deposits and cyanide-hardened and heat-treated steel are shown in Fig. 9-19.[114] Although hardness tests of hard anodized coatings give comparatively low values in comparison with high speed steel and hard chromium (400-500 VPN as compared with 950-1 100 VPN),[104] the wear-resistance is normally equivalent or better, according to Campbell,[104] who has described an instrument for measuring the wear-resistance by the width of repeated overlaid diamond scratches.

Many of the abrasion results quoted, particularly from North America, are based on measurements with the Taber Abraser. Whilst this method is widely used, problems have been reported in terms of reproduceability. Difficulties with different types of wheel are described by George and Powers,[48] who found that the H10 (vitrified) wheels gave better results than the H38 wheels (800 grit), the 200 grit finish on the former being easier to maintain. Lerner[115] reports seasonal fluctuations in abrasion resistance measurements, due to changes in humidity at the time of measurement, a fact also found important in the jet-type abrasion tests. Investigations in France[116] have also covered this method of abrasion testing, but the concerns on reproducability were the main reason that this method was not standardised within ISO. There is general agreement outside the aerospace industry that the improved jet abrasion method (ISO 8252:1987, EN 12373:Part 10:1999) and the abrasive wheel test (ISO 8251:1987, EN 12373:Part 9:1999) provide more consistent methods of abrasion testing, and they are increasingly being included in hard anodizing standards and specifications.

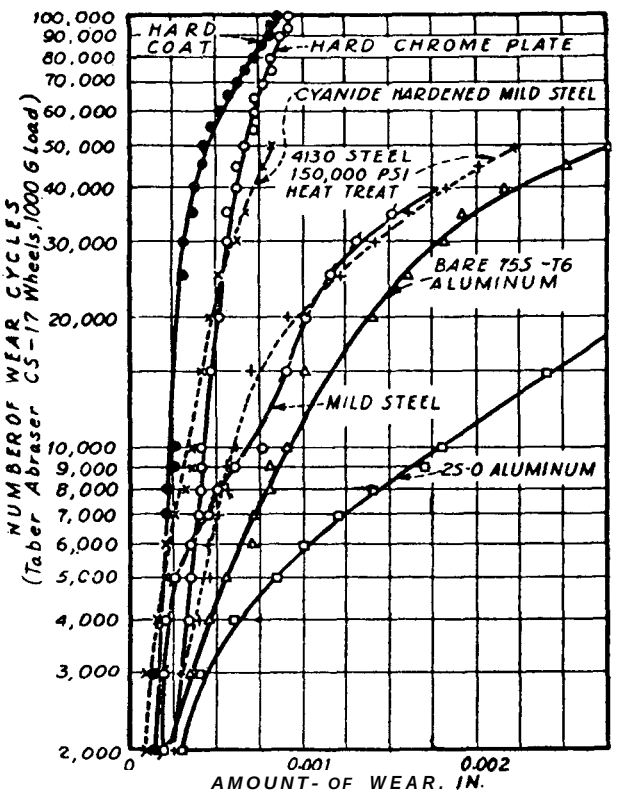


Fig. 9-19. Comparison of wear-resistance of M.H.C. hard coating with that of other materials and coatings[114]

Of possibly greater importance than the values for abrasion resistance obtained directly after hard anodizing is the extent to which the abrasion resistance is reduced in time under the influence of atmospheric exposure. This is shown by tests carried out by Gillig,[107] whose results for M.H.C. coatings for several alloys are reproduced in Figs. 9-20, 9-21 and 9-22.

These examples show that decrease in abrasion resistance over six months' exposure to the atmosphere can be quite pronounced and will depend to some extent on the alloy, e.g. the reduction in abrasion resistance on 6061 (H20) is lower than on clad Al-Cu-Mg-Mn alloy, while on bare alloy, the abrasion resistance, which is initially rather low, rapidly becomes even more unsatisfactory on exposure. Excellent abrasion resistance was shown by the hard anodized casting alloy Alcoa 356 (Al-7% Si-0.3% Mg), due in part to free silicon being entrapped in the coating. This deterioration of abrasion resistance is largely a function of the humidity, and at its greatest is similar to the fall in abrasion resistance produced during a norinal hydrothermal sealing as noted by Harris (Table 9-15). In investigating the effect of various sealing treatments, no very pronounced improvement was found.[19] Where good abrasion resistance is essential, no oil must be applied to the coating.

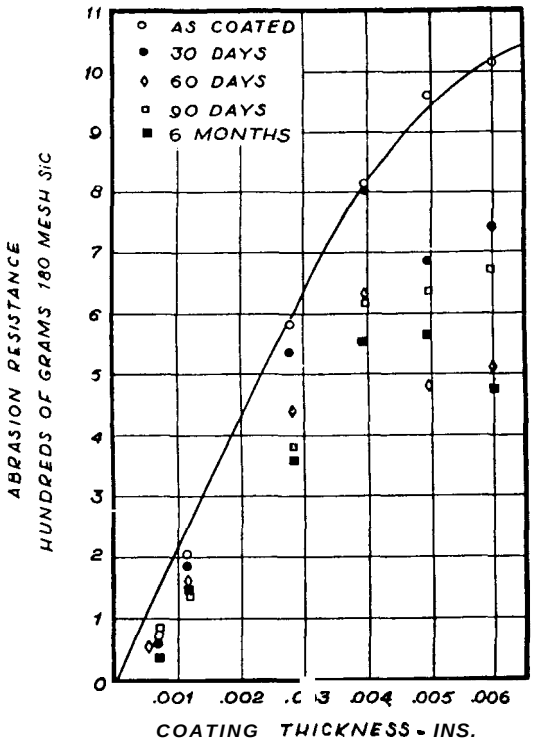


Fig. 9-20. Influence of atmospheric corrosion and coating thickness on abrasion resistance of M.H.C. coating on 2024 Alclad.[107] 0.001 in = 25.4 μm

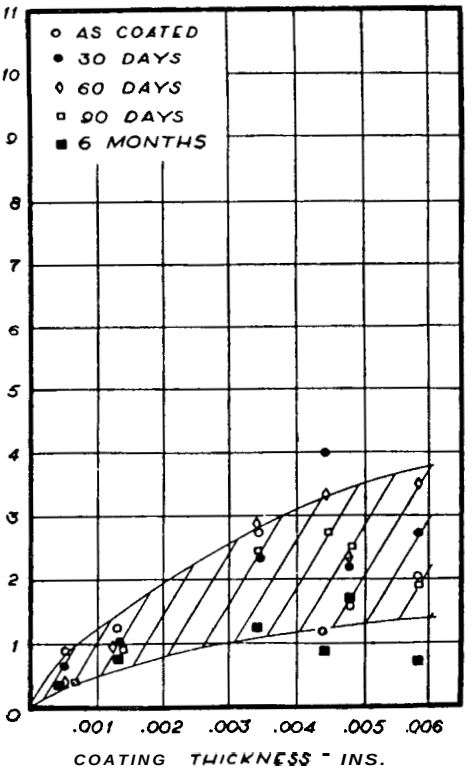


Fig. 9-21. As Fig. 9-20 but on bare 2024 (Al-Cu-Mg-Mn) alloy[""]

Measurements of wear resistance or hardness by micro-indentation tests, abrasive wheels or abrasive jets may not be an accurate guide to the behaviour of hard anodized surfaces when subjected to friction or movement in contact with other materials. Dettin and Sacchi[117] studied the wear on hard anodized plates in contact with rotating wheels of steel or aluminium 40 mm diameter by 8 mm rotating at 260 r.p.m. under various conditions of pressure and lubrication. In the case of a steel rotor under 18.5 kg/mm^2 they found that there was a period of 120 hours with scarcely any wear, followed by a period of rapid erosion up to 180 hours during which time about 10 μm of coating was removed, and then a further stable period with very little wear. The period of rapid wear was due to minute particles of aluminium oxide becoming embedded in the steel so that it constituted an abrasive medium; others have noted similar effects when abrading hard anodized aluminium with nylon or rubber when the loss of weight is higher than one would anticipate. When the rotor was made from hard anodized aluminium (Anticorodal),

at 24 kg/mm^2 the surface wear began after 30 hours and continued up to 200 hours when the 70 μm coating was penetrated up to 15 μm, but there was scarcely any change for the next 100 hours. When the pressure was raised to 28 kg/mm^2 the wear was very rapid with complete removal of the coating.

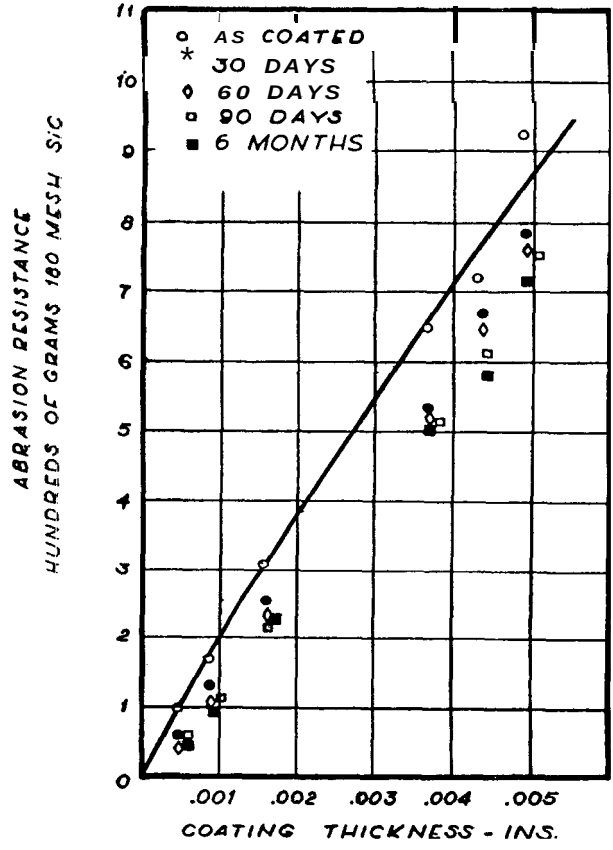


Fig. 9-22. **As** Fig. 9-20 but on 6061 (Al-Mg-Si) alloy[107]

Vandelli[118] examined the behaviour, when hard anodized, of the alloy P-AZ 7.8 GC UNI 3737 (1.5-1.7% Cu; 2.3-2.7% Mg; 7.5-8.1% Zn) using a 'pin and ring' type apparatus in which an 8 mm by 12 mm long 'pin' rested under a load on the cylindrical surface of a 50 mm diameter wheel rotating at a surface speed of 0.5 m/sec. Measurements of wear could be carried out when either or both components were hard anodized (Fig. 9-23), and curves were plotted relating the

time for penetration of the coating with the applied pressure. He also measured the coefficients of friction and the temperature rise as a function of time during testing.

Oechslin[15] has also measured the coefficients of 'wear', and compared hard anodized aluminium with tempered steel as an ideal material for bearing surfaces between which the pressure is low. Ueda and Hasunuma[119] in Japan have also reported on the wear resistance properties of hard anodized coatings on aluminium, and studies in Russia have been noted.[120]

An extensive survey of wear resistant coatings on aluminium has been carried out in Sweden."' These workers looked at a wide variety of surfaces including hard anodizing, with and without lubricants, hard chromium plating, electroless nickel plating and a range of applied polymer and particle-reinforced coatings. They then tested these using the Taber Abraser, the pin on disc test (DIN 50321), and a reciprocating adhesive wear test. They also tested the coatings in applications such as a rotating sleeve with PTFE sealing, a food packaging machine, and a yarn feeder system. Typical results are shown in Table 9-21. In general hard anodized coatings performed well in these tests.

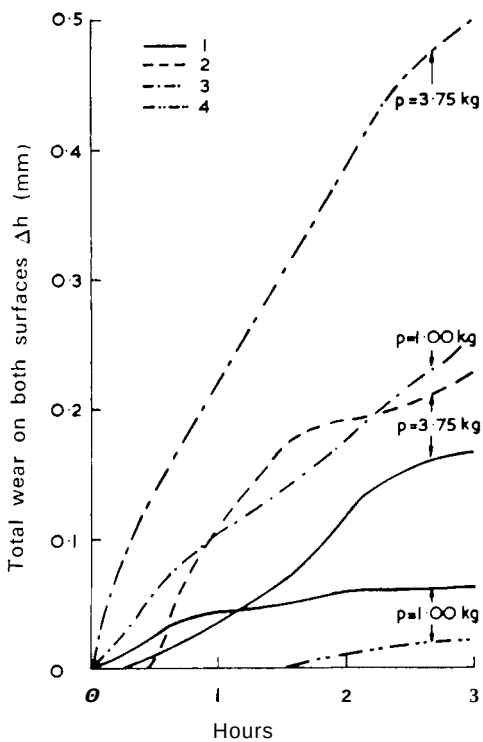


Fig. 9-23A. Rate of wear between a rotating wheel and a fixed pin or rod in Al-Cu-Mg-Zn alloy

1. Both surfaces not anodized
2. Both surfaces hard-anodized 25-30 μm at 4 A/dm^2, -5°C in 12% sulphuric + 1.5% oxalic acid
3. Wheel anodized: pin not anodized
4. Wheel not anodized; pin hard anodized

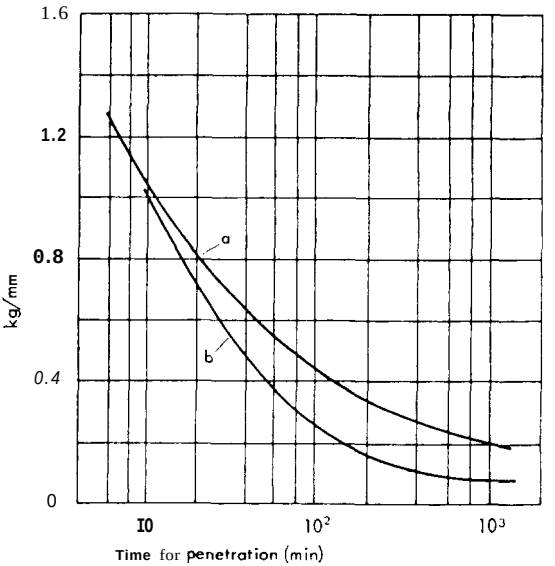


Fig. 9-23B. Wear resistance of hard-anodized 8 mm dia. rod in Al-Cu-Mg-Zn alloy when abraded by a cast iron 50 mm dia. wheel rotating at 0.5 m/sec. Dependence of time for penetration of coating on pressure per mm of contact
(a) 20 μm coating formed at 2 A/dm² and -5°C
(b) 74 μm coating formed at 2 A/dm² and -5°C
Same electrolyte as in Fig. 9-23A

TABLE 9-21

Overview of results from laboratory and application tests with respect to the observed system wear[121]

	System wear – laboratory rests			*System wear – field application*		
Coating type	*Taber*	*PoD (dry)*	*RAW (dry)*	*PTFE sleeve AA7075*	*Conveyor links SS4425*	*Yarn feeder SS4250*
Hard anodizing SS4212	Low	Low	Low	Low	Low	–
Hard anodizing SS4250	Low	Low	Moderate	–	–	Low–High
Kepla-Coat	Moderate	Low	Low (Anodizing) High (Steel)	Low	Moderate High	(Low)
Hard chromium	Low	Low	Low–Moderate	–	–	Low
Electroless Ni	High	Low	Low– High	Low	Moderate	(Low) Moderate
Particle disp	Low	Low–Moderate	High	High	Moderate	–
PVD	Low–High	Moderate–High	High	High	Moderate	–
Ion implantation	High	High	High	High	–	–
Thermal spray (hard part)	Low	Low–Moderate	Low–Moderate	Moderate	High	–
Thermal spray (metallic)	High	Moderate	Moderate	Moderate	Moderate High	–
Polymer	High	Low	Low	Low	–	Moderate

In one process patented in Russia it has been proposed to improve the wear resistance and coefficient of friction by anodizing an article twice with an intermediate heat treatment. The coating may be finally impregnated with an antifriction substance.[122]

A recently announced process which produces coatings of both aluminium and silicon oxide is said to give hardness values of up to HV 2,300.[123,124] Wear resistance is said to be better than that for conventional hard anodizing and electric insulation values are high. The process involves anodizing at up to 800V ac in an electrolyte containing silica and fluorides. The aluminosilicate coating produced can attain a thickness of 60 microns in about 40 minutes, and components so coated can be used at a temperature of *350°C* for extended periods. The process has been developed by a French company called Almag.

Surface finish

The resistance to wear of an anodic coating will be closely related to the surface finish. The effect of surface roughness will be for minute particles of oxide to be fractured from sharp edges or prominences under the high local pressures, and these can cause rapid deterioration if trapped between the sliding surfaces. It is important therefore to keep surfaces as smooth as possible before anodizing, and they will need to be rather better than the final finish required because of the tendency for the surfaces to become slightly rougher during hard anodizing.

Under normal hard anodizing conditions the natural roughness will increase by about 10-20 microinches (0.25-0.5 μm) for wrought alloys, while for casting alloys this increase in roughness may be between 50 and 100 microinches[15] (see also Table 9-16). Where a fine finish is required it is customary to hone to the desired finish.

In some cases the requirements of surface finish may take priority over hardness, and a range of semi-hard coatings may offer an adequate performance. The internal bores of hydraulic tubes are a case in point where smoothness and diinensional tolerances are important, and such cases are beginning to highlight the benefit of a standard specification for hard anodized coatings.

The properties of hard anodized aluminium as a bearing material are good and may be further improved by impregnating the coating with lubricants such as protective oils, molybdenum disulphide or graphite. Nylon and Teflon have also given good results for this purpose.[14]

Effect of basis metal composition

Alloy composition can significantly affect the properties of hard anodic oxide coatings. Taber abrasion tests using a CS-17 Taber wheel at 500 g load and 10,000 revolutions at 70 r.p.m. showed[125] that hard coatings on 6061-T6 alloy performed significantly better than on 2024-T3. Similar results were also obtained in

indentation resistance tests measured on a Knoop indenter. While, on 2024-T3 alloy, the depth of indentation increased with coating thickness up to the value for the uncoated alloy at a thickness of 4 mil (100 μm), coating thickness had no significant effect on the indentation resistance of 6061-T6. A similar pattern has also been observed in salt spray test results which showed a marked superiority for hard anodized 6061-T6. It is noteworthy that this effect is independent of coating thickness but is connected with the better continuity of the coating on the 6061 alloy (cf. Figs. 9-24 and 9-25).

The better wear resistance after hard anodizing of some heterogeneous aluminium alloys is no doubt due to inclusion of intermetallic compounds in the coating, while the somewhat higher porosity of films on homogeneous alloys gives rise to lower wear resistance.[126]

Oechslin[15] has reported in considerable detail the Vickers hardness values of a wide range of alloys hard anodized to various film thicknesses. However once again it is the recent work of Hitchcock[49] that provides a good picture of the effect of alloy (see Tables 9-8 to 9-11).

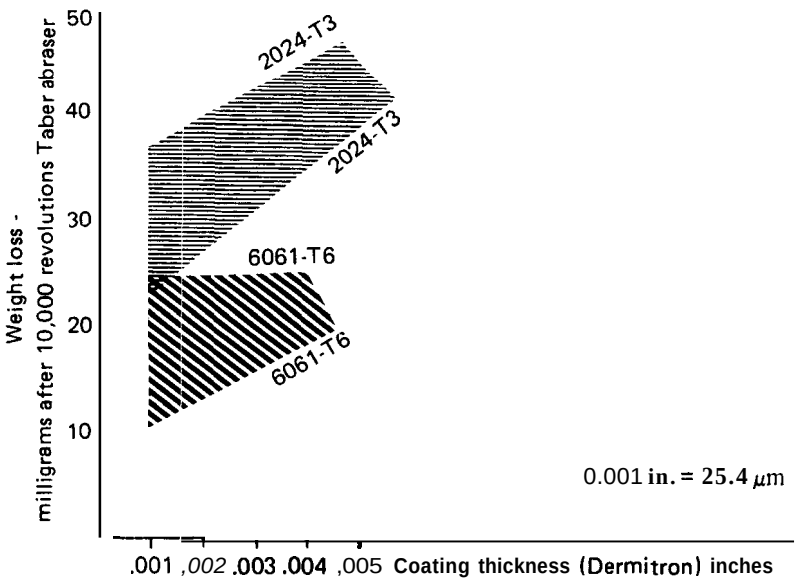


Fig. 9-24. Taber Abraser weight loss v coating thickness.[125]

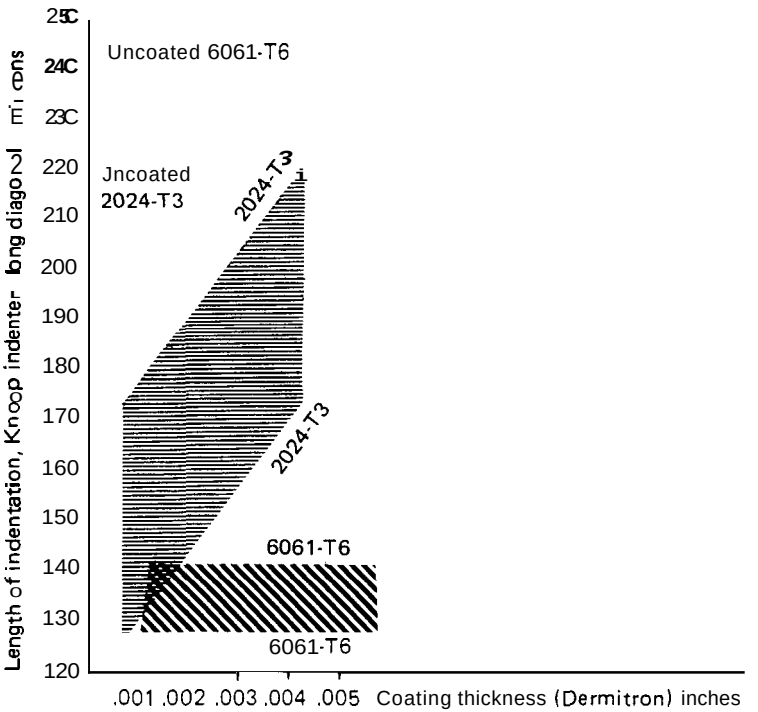


Fig. 9-25. Coating thickness v Knoop Indenter values[111]

For the best resistance to wear and abrasion it is preferable to use pure aluminium or alloys with the lower values of alloying additions. It is usually necessary however to couple the hard surface with a higher mechanical strength and hardness in the basis metal than is possible with pure aluminium, and the preferred alloys are the AlMgSi alloys (6063, 6082). AlZnMg alloys are very suitable for hard anodizing, and copper up to 2% may be present, but if copper is higher there are limitations to both the thickness and hardness of the coating that can be obtained. Alloys with high silicon may be hard anodized but high voltages are necessary to maintain the current flow.

Because of the variable response to anodizing of the different alloys it is more important than in normal anodizing to avoid mixed batches, or assemblies containing different alloys, or mixtures of cast and wrought materials. It is also necessary to ensure that the jig material is compatible with the work being treated, particularly in the case of alloys which have the rising voltage characteristic, since the jig material may consume far too much current or break down. Titanium is usually an ideal jig material for these alloys, but very firm contact to the work must be made, preferably through a bolted-on or screwed-in contact.

The alloy being treated also has an effect on tendency to burning. With the high current densities and high voltages involved in hard anodizing, any weak point in the film may allow a very high proportion of the available current to flow at that point. Enormous local current densities are achieved and the high temperature produced means that the film is dissolved as fast as it is formed, and rapid dissolution of the basis metal takes place. Indications of burning include a rise in current which shows no tendency to fall off. Among a list of reasons why burning occurs Thompson[''] suggests that alloys mixed on the same load, components in a high copper alloy usually of thin section, and free machining alloys (2011 type), particularly where segregation is pronounced or where thin sections are involved, can all cause problems. According to Scott[''] such thin materials are best anodized at a higher electrolyte temperature and lower current density than normal, in order to avoid burning. The causes of burning have also been addressed by Pernick[127] who cites high starting voltages, poor bath agitation, electrical contact problems, and thin-walled parts.

A further limitation with high zinc or high magnesium alloys is the inherently lower cohesion of the oxide film, which makes it chip more easily than the homogeneous coatings on pure metal. Such alloys are not suitable where the component is subject to impact loading in service, but one would need to be cautious about using any hard anodized aluminium under such conditions.

Heat resistance

The anodic oxide coating is a good insulator and this may be a disadvantage in mechanical applications where good heat dissipation is an advantage. On the other hand, hard anodized aluminium shows a good heat resistance. According to Campbell,[104] a dense 3 mil (75 μm) hard anodic oxide coating has better heat resistance than a softer 6 mil (150 pm) coating and withstands short exposures to temperatures of the order of 2000°C. It is thus suitable, for example, for rocket venturis. Of specimens treated by the Hardas process, heating to 300°C six times for 10 minutes, each cycle had no effect on commercial aluminium and LM1-M casting alloy, while 5056A (Al-5% Mg) showed progressive crazing with each successive cycle, though this did not occur at 200°C. Casting alloys such as LM2-M and LM6-M (similar to L33) blistered at 300°C, while LM10-W (L53) crazed heavily and developed warts at 150°C. Crazing seems to occur alternatively to exfoliation of the coatings and, in fact, crazing does not seem to have an adverse effect on the running of hard anodized aluminium alloy pistons. The benefit of hard anodizing on the base of pistons has also been reported by Rohrie.[128] It is claimed to improve the resistance of the piston to temperature changes, and so prevent or delay the formation of cylinder rim or bottom cracks.

The crazing of the coating which accompanies heating of the hard anodized surface is not generally detrimental in any way other than to the appearance, but it has been proposed to improve the resistance to thermal shock by a conditioning

treatment in which the anodized component is subjected to a controlled slow heating and slow cooling procedure.[129] Coatings up to 200 μm (8 mil) thickness are dried and heated at a rate of not more than 3.2°C per minute either to 93-100°C or to a temperature T which is between 65-95°C at which it is maintained for at least 0.4(200–T) minutes, after which it is cooled to room temperature at a rate of not more than 3.2°C per minute. After this treatment the surface may be heated to at least 205°C in not more than 30 minutes and then cooled.

Fig. 9-26 shows the result of one of a series of heat absorption tests carried out by Gillig.[107] In this test a thermocouple was held against the back of a test piece placed 15 cm from an infra-red bulb under standard conditions, and shows that the heat absorbed increased with coating thickness.

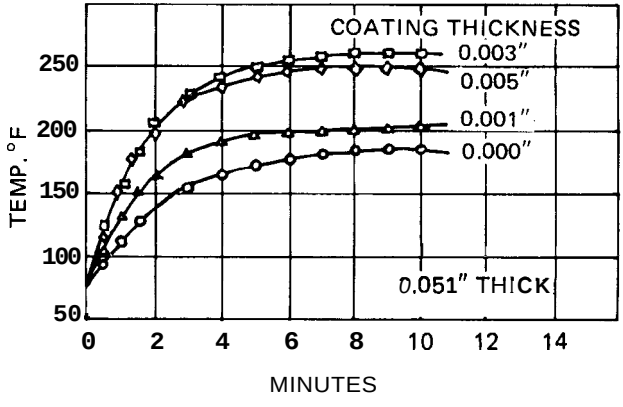


Fig. 9-26. Temperature reached by 6061 (Al-Mg-Si) alloy in relation to coating thickness.[107] 0.001 in. = 25.4 μm

Of some importance in certain applications, particularly in the aircraft industry, is the resistance of hard anodized aluminium to direct flame impingement, and some results obtained with different alloys and coating thicknesses are shown in Table 9-22.[107] The results show that in nearly all cases the time to failure increased with coating thickness. Under stress, however, it is probable that little or no improvement would be obtained.

TABLE 9-22

Resistance to direct flame impingement of hard anodized aluminium alloys (M.H.C. coating)[107]

Alloy	*Coating thickness (mil)* 1	2	3	4
	Time to failure (minutes)			
6061 (Al-Mg-Si)	0.49 0.52	0.60 0.52	0.74 0.86	0.87 0.85
2024 (Al-Cu-Mg-Mn)	0.50 0.56	0.70 0.71	0.90 0.73	0.97 1.02
2024 (Alclad)	0.55 0.55	0.64 0.79	0.77 0.76	1.10 1.02
7075 (Al-Zn-Mg-Cu)	0.48 0.49	0.66 0.68	0.78 0.82	0.98 0.94
356 (**Al-Si,** cast)	2.55	3.08	4.06	5.81
220 (Al-10% Mg, cast)	2.55	32.9	5.20	3.10

Specimens 4 in × 4 in, thickness normally around 0.05 in, except cast alloys 356 and 220 which were approximately 0.2 in thick. 1 in = 2.54 cm. 1 mil = 25.4 μm.

Thermal properties

The temperature of fusion of anhydrous alumina is 2100°C. The hydrated alumina begins to lose its water of crystallization at about 500°C.

The specific heat of the coating is:[130]

0.200 cal/g from 20 to 100°C
0.233 cal/g from 100 to 500°C

The coefficient of linear expansion is approximately five times less than that of the basis metal:

anodic coating, $a = 5 \times 10^{-6}$
aluminium. $\alpha = 23 \times 10^{-6}$

The thermal conductivity of the anodic coating is between one tenth and one thirtieth of that of aluminium:

alumina	0.05-0.015	cal/cm²/sec/cm/°C = 21-6.3 W/m "C
aluminium	0.5	cal/cm²/sec/cm/°C = 209 W/m "C

The emissivity of aluminium increases rapidly as the thickness of the anodic layer is built up, increasing to 80% for a 10 μm coating. **A** thick hard anodic coating is therefore well on the way to being a 'black-body' for heat dissipation, and there is very little advantage in dyeing it black as is sometimes done.

Electrical properties

The breakdown voltage of Hardas anodic coatings is shown in Table 9-23.[18] These results were obtained on 5154A (Al-32% Mg). As shown, the coatings are highly insulating and this property can be further improved by hot water sealing and waxing. The effect of hot water sealing by itself is inconclusive. Breakdown voltages up to 3,750 volts are quoted by the Glenn L. Martin Co.[7] According to Brace, pure aluminium or a homogeneous alloy composition must be used to obtain consistent results. These materials will also give the highest breakdown values, as impurities in the film, particularly when due to segregated constituents. will normally improve the conductivity. Where the highest breakdown voltage is of importance a high forming voltage should be used to increase the barrier layer thickness.

The great advantage which anodic coatings on aluminium possess over most other media for electrical insulation is the fact that they can operate up to temperatures of *500°C*. It is difficult to guarantee precise values for breakdown voltage because of the uncertain effects of alloy constituents, crazing of the coating and humidity, all of which affect the behaviour, and electrical breakdown is an exceedingly complex phenomenon anyway. For adequate electrical insulation it is important to exclude water or water vapour, and to avoid high local pressures which would tend to fracture or distort the anodic coating. Generally the contribution of the hard thick coating is as much due to withstanding physical or mechanical pressure as it is to offering dielectric strength.

TABLE 9-23

Breakdown voltage values for Hardas films[18]

Thicness		*Unsealed*	*Sealed in boiling water*	*Sealed in boiling water and impregnated with paraffin wax*
(mil)	*(μm)*			
1	25	250	250	550
2	50	950	1,200	1,500
3	75	1,250	1,850	2,000
4	100	1,850	1,400	2,000

Bocachard and Darnault[130] have given the dielectric constant (permittivity) of hard anodic coatings as 7.4-7.6, with a temperature coefficient of 0.06% per degree (Celsius) between 20 and 100°C. This is rather lower than the values of 8-10 which have been quoted for the compact and homogeneous barrier layers with no porous structure.

The same authors quote the resistivity of 50 μm anodic films as:

40 . 10^{14} ohm.cm^2/cm	at	20°C
8 . 10^{14}	at	100°C
1.1 . 10^{14}	at	200°C

These values are of the same order as glass and porcelain and about half that of mica. which is 90 . 10^{14} at 20°C.

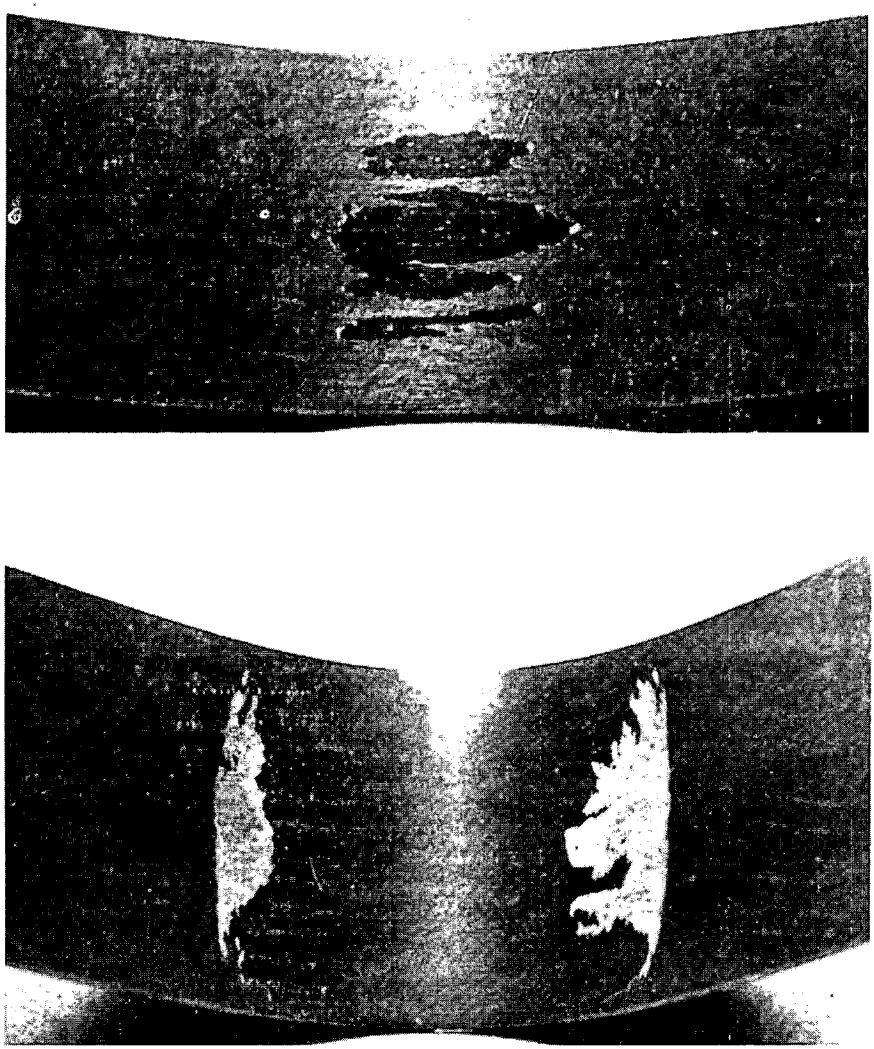
The combination of high dielectric strength and good thermal conductivity makes hard anodized aluminium superior to most other materials as an insulating mounting for electronic components. Matisoff[131] has found that the use of a hard anodized bracket in place of a mica washer lowered the operating temperature of a power transistor by 27°C. The Hardas coating used (Anochrome Corporation) has an operating temperature of 480°C, a dielectric strength of 26 V/μm and a low thermal conductivity of 3.1 W/m "C, but a thin coating on a 1.6 mm base is equivalent to an insulator of conductivity 138 W/m °C (0.33 c.g.s. units). A coating thickness of 50-100 μm is recommended.

Adhesion

A number of bend test experiments carried out by Gillig[107] gives a good indication of the adhesion as well as of the mechanical strength of the hard anodic coatings. In this test, specimens 1/16 inch thick x 1 inch wide x 8 inches long (0.16 × 2.54 x 20.3 cm) were bent in a vice and the free bend radius measured at which the coating cracked. It is interesting to note that failure always occurred in the compression side. Figs. 9-27 and 9-28 show the type of failure which takes place with two coatings differing only in thickness.

Mechanical strength and fatigue properties

Table 9-24 shows the effect of hard anodizing on the tensile strength of a number of alloys.[114] It is seen that there is a slight decrease in tensile strength with coating thickness in the case of almost all the alloys tested, but this is not normally sufficient to detract from the use of the hard anodizing process.



Figs. 9-27 and 9-28. Type of failure occurring on bending 2024-T3 (Al-Cu-Mg-Mn) specimens with an M.H.C. hard-anodic coating. (Fig. 9-27 above) A 2 mil (50 μm) coating which has peeled off in layers. (Fig. 9-28, below) A 1 mil (25 μm) coating. The outer layers have peeled off to a considerable distance. The layers in contact with the basis metal have pitted only slightly.'"'

TABLE 9-24

Mechanical properties of Hardas hard anodic coatings

Basic metal	Coating thickness (mil)	Coating thickness (μm)	U.T.S. (lb per sq in)	U.T.S. (MN/m^2)	Elongation on 2 in %
6061-T6	–	–	47,700	329	12.0
(0.32 in thick)	0.5	13	49,100	339	12.5
(Al-Mg-Si)	1.0	25	48,800	336	11.5
	3.0	75	45,400	313	8.0
	5.0	125	45,100	311	5.5
2024-T3	–	–	67,700	467	18.0
(0.32 in thick)	0.5	13	66,500	459	17.5
(Al-Cu-Mg-Mn)	1.0	25	67,200	463	15.0
	3.0	75	62,700	432	11.0
	5.0	125	58,600	404	–
2024 Alclad – T4	–	–	64,200	443	17.5
(0.32 in thick)	0.5	13	65,400	451	16.0
	1.0	25	67,000	462	14.0
	3.0	75	64,000	441	11.5
	5.0	125	58,200	401	–
7075-T6	–	–	80,000	552	8.5
(0.32 in thick)	0.5	13	80,600	556	7.5
(Al-Zn-Mg-Cu)	1.0	25	79,800	550	7.5
	3.0	75	78,000	538	7.0
	5.0	125	72,900	503	6.5*
356-T6	0.5	13	24,750	170	3.0
(0.150 in thick)	1.0	25	29,700	205	6.5
(Al-Si, cast)	3.0	75	26,350	181	4.0
	5.0	125	31,200	215	5.5

*Coating flaked off partially.

Elongation is, of course, reduced by hard anodizing and the endurance strength is also markedly reduced as seen in Fig. 9-29.

The fatigue strength was also measured by Gillig[107] on a Baldwin-Lima-Hamilton Model SF2 constant load fatigue machine, and his results on annealed 7075 (Al-Zn-Mg-Cu) specimens 0.51 inch (1.27 mm) thick, and after hard anodizing to 1, 3 and 5 mil (25, 75 and 125 μm), are shown in Fig. 9-30. A similar decrease in fatigue resistance is shown and the general conclusion is that while the coating

lowers endurance strength considerably at high stress, the decrease at low stress is comparatively small. The coating thickness has little influence, and at any rate with the unclad alloys, much the same results are obtained at above 1 mil (25 μm) thickness. The decrease in endurance strength is believed to be due to stress concentration at the micro-cracks in the coating. As is shown in Table 9-25, which summarises the effect of alloy composition, little or no difference is found in the cast alloys which have a low endurance strength in the uncoated state. Where fatigue stress is decreased considerably, this may be alleviated by dichromate sealing. Thus, on L168 alloy, treatment in sodium dichromate solution has reduced the fatigue loss to 8% at 1 million cycles and to 16% at 10 million cycles.[132] It is, however, achieved at the expense of some loss of abrasion resistance. There is evidence that hard anodizing by the d.c.-a.c. Hardas process reduces the fatigue resistance to a smaller degree than d.c. anodizing, and Campbell has given an average value of 25-30% for this reduction. Transgranular cracking of 7071 alloy beneath a hard anodic coating has been described by Forsyth.[133]

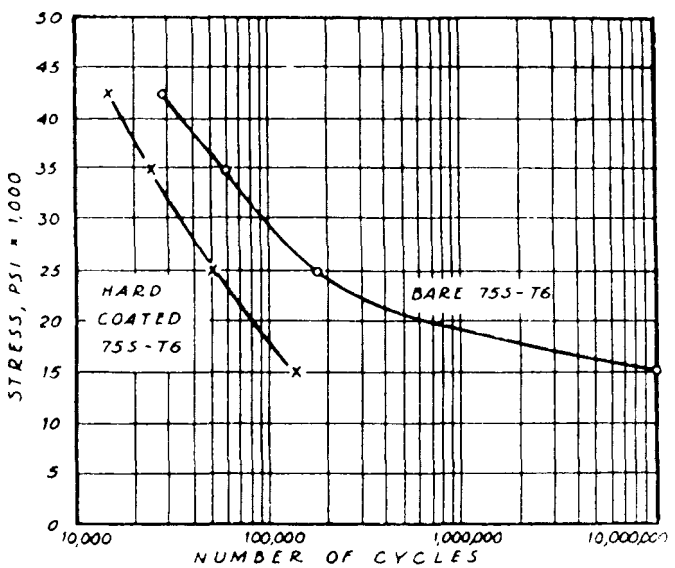


Fig. 9-29. Curve of stress/number of cycles to failure showing the marked drop in endurance limit of hard-coated aluminium.[114]
10 x 1000 p.s.i. = 68.9476 MN/m^2

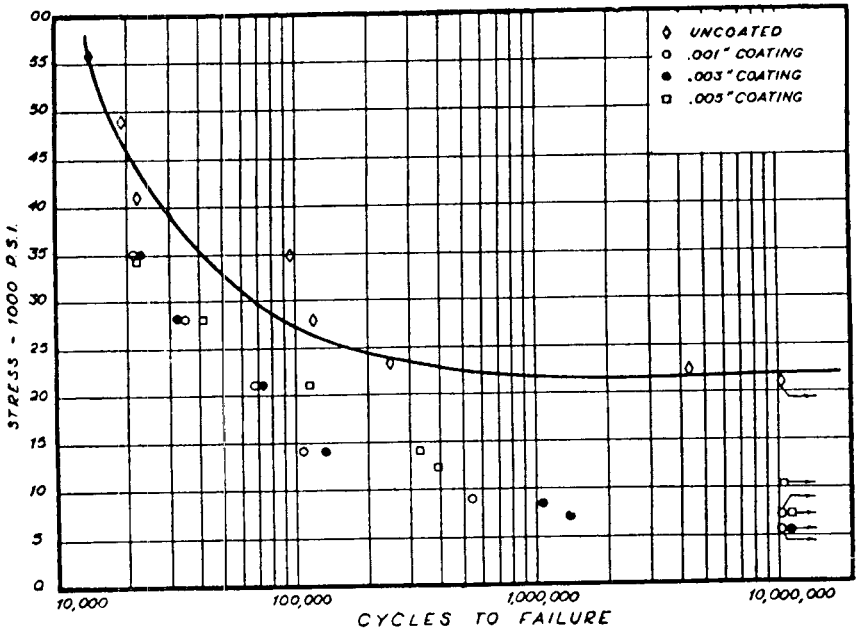


Fig. 9-30. Effect of hard coating (M.H.C.) on fatigue strength of 7075 (Al-Zn-Mg-Cu) alloy specimen? 0.51 in thick."" 0.001 in. = 25.4 μm

TABLE 9-25

Endurarice strength at 10^6 cycles of hard anodized (M.H.C.) aluminium alloys (lb per sq in)[114]

Alloy (Alcoa)	*Uncoated*	*Coated*	*% Decrease*
Alclad 2024	11,000	7,500	32
2024 bare	19,000	15.000	21
1075	22,000	9.000	59
Alclad 7075	12,000	10,000	17
7178	26,000	9,000	65
6061	15.000	6,000	60
220	7,500	7,500	0
356	8.000	8,000	0

1,000 lb/sq in = 6,89476 MN/m^2

Porosity

Miyata[134] and co-workers in Japan made a study of the porosity of anodic coatings formed in 15% sulphuric acid at temperatures from 1-30°C and current densities from 2-8 A/dm^2 by measuring the apparent dielectric constant and the apparent density, assuming that the real dielectric constant of anodically formed oxide is 8.7 and that the real density is 2.95. The porosity was also estimated by measuring the amount of transformer oil absorbed by the coatings.

Their results indicate that the porosity of the oxide film formed at 4 A/dm^2 and 30°C for 30 minutes was 24-26%, while the porosity of the film formed at 1°C was IO-14%. When aluminium is anodized at above 20°C there is always a very rapid increase in the degree of porosity.

Corrosion resistance

The effect of exposure on the abrasion resistance of hard anodized aluminium alloys has been noted above. 2024 alloy (not clad) is somewhat inferior to most other alloys and is less suitable for hard anodizing.

On the whole, there is apparently rather better protection given by hard as opposed to normal anodizing. It must not be assumed that the thicker coatings will necessarily give better protection, as in thick coatings the tendency to crack undoubtedly decreases the corrosion resistance by acting as capillaries for the entry of moisture. Moreover, hard anodic oxide coatings are frequently left unsealed in order to retain the optimum wear resistance. Nevertheless, a number of authors have reported that coatings produced under hard anodizing conditions have better corrosion resistance than 'conventional' coatings of the same thickness. Corrosion resistance is improved by sealing in a potassium dichromate solution, but at some expense in terms of loss of abrasion resistance (about 20%). To avoid this the film can be impregnated with wax, mineral oil or silicones.

In some interesting experiments on the effect of rain erosion at high velocity, undertaken to simulate the effect on leading edges of aerofoils, Gillig has shown that failure depends primarily on the alloy. The best results are obtained with 2024 Alclad, 6061 and 2024 in that order. With increasing thickness the resistance to rain erosion is decreased. Failure in the case of 2024 alloy (not clad) was shown by spalling of the coating in layers while on 6061 and 7075, failure followed the micro-crack structure.

The chemical resistance of hard anodic coatings, particularly in acid solutions, is only moderate.

Corrosion resistance is also said to be improved by PTFE impregnation[135] and this, in contrast to sealing, gives no reduction in abrasion resistance of the coating. This impregnation process, known in the U.K. as Lubrok and in the U.S.A. as Tufram, reduces the coefficient of friction of a hard anodized coating to less than 0.05. This has been used on the internal surfaces of air cylinders.[136]

4. APPLICATIONS OF HARD ANODIZING

While most hard anodizing is carried out on parts which are machined from extruded bar, castings present little difficulty, although pressure die castings may sometimes give somewhat unpredictable results. Interruption of the current must be avoided as it may lead to laminated coatings. There are now a considerable number of applications and some are illustrated in Figs. 9-31 and 9-32. Early applications[7] included hydraulic gear (e.g. pistons), screw threads of hydraulic jacks, railway wagon buffers, and aircraft under-carriage legs and cylinders. In the last the sliding surfaces are hard anodized to reduce friction.

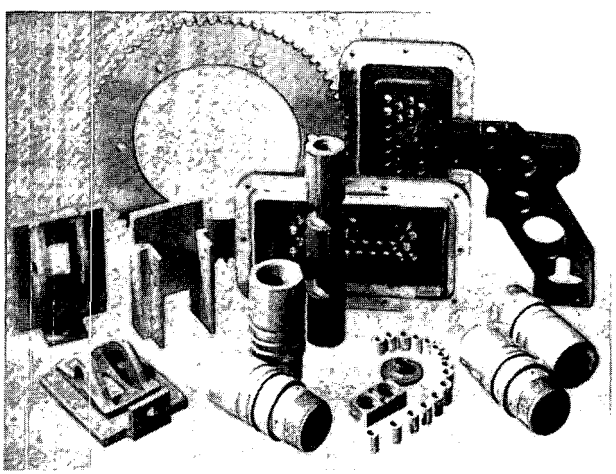


Fig. 9-31. Range of typical hard anodized components
[Courtesy of Acorn-Hardas Ltd

Fig. 9-33 shows a hard anodized hydraulic control valve. Another application is in the coating of high speed air-impellers and for the production of flame and chemically resistant surfaces in cordite cartridge containers used in a gas-turbine starter. Other successful applications for wear-resistance include the coating of a die-cast aluminium metal spraying pistol, film strip finishes on 35 mm cinema projectors, parts in cigarette wrapping machinery and aluminium rollers for a cardboard-box forming machine. In this instance, hard anodizing is stated to have superior wear-resistance over hardened steel. Aluminium gears for ticket machines, feed plates in sorting and coating machines, surgical splints, cast electric motor brush boxes[8] as well as valves, fuel- and oil-pump housings, cams, aircraft abrasion strips, bearings, clutch and brake discs, fans and nozzles, timing and mechanical computer gears, are other successful applications.'"

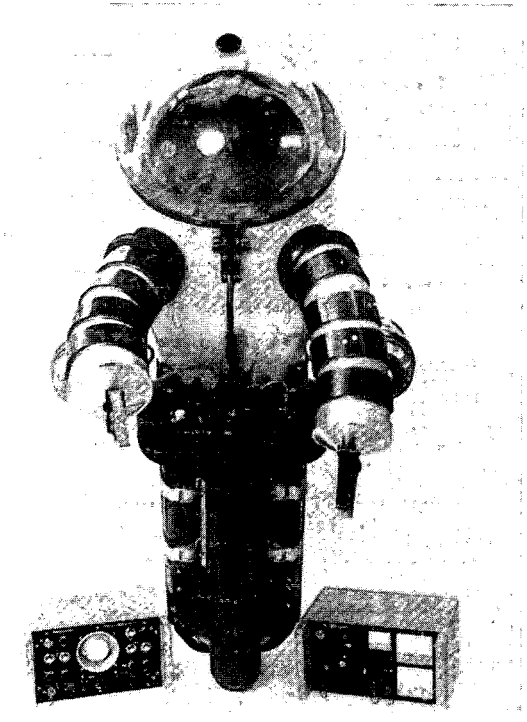


Fig. 9-32. Wasp self-propelled one-man submersible with many hard anodized parts.

[Courtesy of Acorn-Hardas Ltd.]

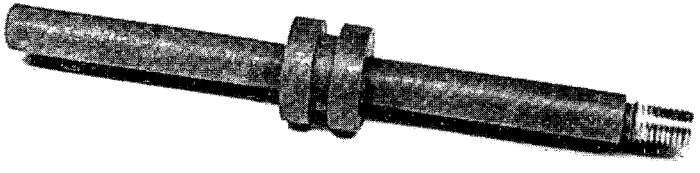


Fig. 9-33. Spool for hydraulic control valve. This valve was made from 2024 (Al-Cu-Mg-Mn) alloy and lapped to a high finish before applying a 3 mil (75 ym) coating by the M.H.C. process. Note roughness of the surface. An allowance of 0.5 mil (13 μm) was made to provide for honing to a smooth finish.[107]

Other applications listed by Campbell[104] include multiple cylinders. cam tracks, textile bobbins, grooves of V pulleys, fuel pumps and injectors, air hammer bores, ammunition guides in naval magazines, hoist guide rails, instruction plates, servo valve mechanisms, rubber drawing mandrels, sprockets of film projectors and motor cycles, disc brake cylinders and pistons, band saw tables, gear teeth. tread plates, stair nosings, pneumatic valves, wave guides, rotors and shrouds on aircraft cold air units, water pumps, torpedo hulls, piston ring grooves, toroids for coil windings and heat sinks. Use of hard anodizing for the aluminium cylinder in a high-speed non-impact page printer for mainframe computers has been detailed by Furness.[138] Hard anodizing is chosen in this application not only for its abrasion resistance, but also for its good dielectric properties. It is a critical application and the anodic coating must be of the highest quality and consistency, and must have a uniform thickness within ± 3 microns.

One of the most remarkable propositions has been to apply an anodized aluminium hard-coat to other substrates such as titanium or stainless steel.[139] This unusual end result has been achieved by adhesive bonding of a hard-anodized surface to the steel or titanium and then removing the aluminium base by machining and chemical dissolution to leave the second metal having all the advantages of anodized aluminium – electrical and thermal insulation, good corrosion and wear resistance.

It should be emphasised that, as distinct from most other finishing processes, hard anodizing rejects cannot normally be reclaimed, as stripping the oxide coating will leave the component considerably under-size. On the other hand a hard anodizing procedure has often been used to salvage expensive machined parts where too much metal has been removed and the growth entailed in anodizing can compensate for it.

The number of applications for hard anodized aluminium continues to grow rapidly and there is no doubt that any manufacturer or user of engineering equipment would be well advised to examine whether hard anodized aluminium could not profitably and advantageously replace existing parts because of its unique properties. Hitchcock,[92] in a 1988 paper, reviews some of the applications, and these are shown in Table 9-26. The number of jobbing firms who offer hard anodizing as a standard procedure has also grown steadily, while established firms have increased their investment in this business. One of the reasons for this is the relatively low cost of hard anodizing in comparison with other engineering coatings. The general field of engineering finishes has been reviewed by Bidmead and Davies,[140] and their comparison of cost factors involved in these processes is shown in Table 9-27. Nussbaum[141] also discusses cost, and, looking at the energy, material and emissions balance, he concludes that it is an environmentally friendly process, a factor of increasing importance.

TABLE 7-26

Applications for hard anodising[92]

Requirement	***Key** Properties*	*Applications*
Scratch resistance	Thickness (and toughness)	Hand-rails, covers for ticket machines, moving walkways etc.
Scuff resistance	Hardness	Keyboards, domestic trim etc.
Impingement/Erosion resistance	Thickness, surface density, jet abrasion resistance	Valve bodies, chutes, piston crowns, rocket nozzles, pumps, impellors etc.
Abrasive wear resistance	Thickness (hardness), brittleness, abrasive wheel resistance	Guide rails, pneumatic cylinders, moving parts etc. under relative high loads
Non-abrasive wear	Coefficient of friction, surface roughness	Bearings and moving parts etc. under relatively low loads
Corrosion resistance	Thickness, seal quality, freedom from cracks and flaws	Marine submersibles, torpedoes, chemical equipment etc.
Electrical	Thickness, freedom from cracks and flaws, terminal voltage, sealing quality	Heat sinks, heating elements, surrounds etc.
Thermal emissivity	Thickness, surface density	Heat sinks, solar heating etc.

Note: Many applications call for more than one requirement and some of the key properties could conflict, so a compromise will be necessary and this requires consultation with the anodizer.

TABLE 9-27

Comparison of some of the cost factors involved in engineering deposition[140]

	Costfactor					
Metal deposited	*Cost of setting-up*	*Metal & materials*	*Plating power (electric)*	*Heating or cooling*	*Effluent disposal*	*Post-plating cost, e.g grinding if used*
Copper	Low-CN * Mod-acid	Low	Low	Mod-CN Low-acid	High-CN Low-acid	Low
Nickel (elec-deposited)	Mod	Mod	Low/Mod	Mod	Low	Mod
Nickel (electroless)	Mod	High	Nil	High	Mod/Low	Can be nil
Chromium	High	Mod	High	Mod	High	High
Silver	Low	High	Low	Low	High	Low
Tin	Low	High	Low	Low-acid * High-Alk	Low-acid Low/mod-alk	Low
Hard anodizing (Al)	Low	Low	High	High	Low	Low/Mod
Cobalt	Mod	Mod/High	Low/Mod	Mod	Low	Mod
Iron	Mod	Low	Low/Mod	Low/Mod	Low	Mod

* CN – cyanide electrolyte; acid – acid electrolyte; alk – alkaline electrolyte

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CHAPTER 10

Colouring Anodic Oxide Coatings with Dyes and Pigments

After all conventional types of anodizing the anodic oxidation coating formed is minutely porous. The film is strongly absorbent and will readily stain in contact with oils, greases or colouring materials, so it is an ideal substrate for absorption dyeing. The dyeing properties of films produced in different anodizing electrolytes or under different anodizing conditions will vary, and in practice it is sulphuric acid anodized aluminium that is normally dyed, but films produced by anodizing in chromic acid., oxalic acid and even integral colour anodizing electrolytes can all be dyed to some degree. After dyeing or pigmenting it is essential to seal the anodic film to prevent the dyestuff or pigment leaching out.

The main requirements of anodic films that are to be dyed are: (1) that the coating is of adequate thickness, the precise thickness varying with the shade to be dyed, i.e., dark colour tones will require thicker coatings; (2) that it is sufficiently porous and absorptive; (3) that the coating itself has a suitable colour; and (4) that it is free from blemishes due to scratches, porosity, pits, etc., and from differences in metallurgical structure such as grain size variation or segregation. In decorative colour-anodizing it is therefore essential to use good quality metal and most manufacturing firms supply an 'anodizing quality' material. The choice of the anodizing process to be used will vary with the particular work to be treated but in addition to the factors considered in earlier chapters, special attention must be given to (a) the thickness and porosity of the coating and (b) its colour.

The main factor:: controlling the absorption of dyestuffs by the anodic coating are the thickness of the film and the area of pore wall surface available for the dye molecules to adsorb onto. This latter factor is largely influenced by the degree of

attack of the pore wall surface taking place during anodizing, so although the pore size with integral colour or oxalic acid anodized films is very much larger than that with sulphuric acid anodized films, their ability to dye is very much less. In practice, most commercial dyeing is carried out with sulphuric acid films, but films produced in other electrolytes are sometimes coloured for special purposes. With all anodizing electrolytes the precise anodizing conditions used have a strong influence on their ability to take up dyestuffs, and conditions favouring film attack will always give the best dye absorption. Thus with sulphuric acid anodizing relatively thick films (above 10 microns) produced at rather higher acid concentration and anodizing temperature than normal will give the deepest dyeings, but this must be balanced against other coating requirements such as abrasion resistance or weathering properties.

With other anodizing electrolytes, such as oxalic acid, the modified process (GXh), which is operated at 35°C to give almost uncoloured films, is preferable as a basis for dyeing. The Bengough-Stuart chromic acid coating is less suitable for colouring due to its thinness and low porosity, in addition to which its grey colour makes it suitable only for dark shades. Satisfactory dyed chromic acid coatings may, however, be obtained by the use of the constant voltage process or the concentrated chromic acid process (Chapter 7), the latter having been studied extensively by Peek and Brace.' Other coatings which are sometimes dyed include the opaque Ematal coatings and hard anodized films.

In a number of anodizing processes, attractively coloured coatings can be produced without dyeing treatments. This applies particularly to thick films produced by 'hard' or 'architectural' anodizing processes. In such cases, the colour depends on the composition of the alloy as well as on the coating thickness. As an example of this, hard anodic coatings between 37 and 125 μm (1.5-5 mil) thick on saucepans of different aluminium alloys manufactured in the U.S.A., may be produced in grey, black or bronze by the same process.' Other examples of this type are listed in Chapters 8 and 9. In addition the combination of integral colour or electrolytically coloured anodic coatings with absorption dyeing has been widely used in architectural applications. An example of these processes is the Sandalor range of finishes[3] which has been described in Chapter 8.

1. COLOURING WITH ORGANIC DYESTUFFS

Many types of organic dyes are in use, including both the acid and basic types. Alizarin dyes, complex metallic dyes, indigo dyes and even cotton dyes, diazo dyes, etc. are employed. The colour obtained is a function of the anodic film and the degree of dispersion of the dye. Dyestuffs employed must be adsorbed deep down into the coating and they must, of course, be light-fast, though the light-fastness obtained will depend also on the alloy used, the type and method of production of the coating, and the sealing operation subsequent to dyeing. The

absorption depends largely on the pH of the dye solution and the porosity of the aluminium oxide coating. As seen later, however, adsorption phenomena also play an essential part in the dyeing mechanism.

As the colour intensity and light-fastness of a particular finish depend on the amount of dye taken up by the film, as well as the particular dyestuff used, the aim in anodizing before colouring is to produce relatively thick and porous coatings. Thus in sulphuric acid anodizing, the acid concentration is often increased to 20C-220 g/l and the anodizing temperature to 22-24°C. When producing thick films (20-25 μm), however, such conditions can lead to production of a film with relatively soft outer layers, which may be unsuitable for external applications, and a compromise between absorption of dye and film quality has to be adopted. Sandoz[4] recommend a sulphuric acid concentration of 195±30 g/l, a temperature of 19±2°C and an anodizing current density of 1.5 A/dm^2 to give a 25 micron (I mil) anodic film when producing dyed finishes for architectural applications. In the dyeing process itself, saturation dyeing is achieved using long colouring times (20-40 min) at elevated temperatures, in order to get good penetration of the dyestuff into the film.

Schenkel and Speiser[5] have carried out an extensive investigation of factors affecting the dyeing of anodized aluminium. They showed that increasing sulphuric acid concentration from 170 g/l to 230 g/l increased the adsorption capacity of the film, but this was more noticeable with some dyestuffs (e.g. Aluminium Deep Black MLW) than others (e.g. Aluminium Orange GL). Increasing aluminium content in the anodizing electrolyte decreased adsorption capacity, as did the addition of small amounts of oxalic acid **(up** to 8 g/l), and again this was dyestuff dependent, In the latter case dyestuffs such as Aluminium Red RLW showed a 45% decrease in adsorption with 8 g/l of oxalic acid present in the anodizing electrolyte (190 g/l H_2SO_4), and Aluminium Deep Black MLW a 25% decrease. Increase of anodizing temperature in the range of 15-25°C increased the adsorption capacity of the film for all dyestuffs, whilst adsorption capacity showed an almost linear increase with increasing anodizing time (i.e. increasing anodic film thickness).

After anodizing, the aluminium must be rinsed thoroughly in running water before imrnersion in the dye bath. In practice an initial rinse in a relatively acid rinse bath (pH of 4 or less) followed by rinsing in a more neutral bath (pH 5-7) will ensure that gelatinous aluminium hydroxide is not precipitated in the film and give irregular dyeing. Again Schenkel and Speiser[5] have looked at the effect of rinsing time and found that it has a slight effect, with very long rinsing time (up to 60 min) at room temperature decreasing adsorption. Rinsing at elevated temperatures considerably decreases the adsorptive capacity of the film and should be avoided.

Neutralization between anodizing and dyeing is also used to eliminate any effects of the anodizing electrolyte, and dilute solutions of ammonia, sodium hydroxide, sodium carbonate or trisodium phosphate have all been used. A 5% solution of sodium carbonate was preferred by Akahori.[6] Schenkel and Speiser' examined the effects of 15-25 g/l sodium bicarbonate solutions and a 20 g/l ammonium oxalate solution and concluded that sodium bicarbonate was no more

effective than water. Ammonium oxalate helped dyeing in some circumstances particularly with long rinsing times. A short treatment (½ min) in a sodium hydrogen phthalate solution before normal rinsing also helped dye adsorption, and both the oxalate and the phthalate solutions were useful if work had to be stored for some time before dyeing. It seemed that they prevented the hydration effects occurring when the work was left in water for long periods, but if hydration had already taken place, they were not effective in reversing it. In some cases (for example in the manufacture of nameplates) work has to be dried off and stored before colouring, and in these cases it should be very carefully handled to avoid finger marks or stains, and then stored in a dry atmosphere (for example over silica gel). The reactions taking place during hydration and reactivation of anodic coatings have been described by Schenkel.[7]

Neutralization with ammonium oxalate (5-10 g/l), to which a small amount of wetting agent has been added, has been used when dyeing castings. The porosity often present in such material is a constant problem when dyeing, as sulphuric acid from the anodizing process is frequently trapped. The wetting agent used must be chosen with care, however, as it has been shown that whilst nonionic surfactants have little effect on dyeing, anionic surfactants reduce adsorption capacity considerably.[5] Short treatments in a dilute nitric acid solution (10-50% vol.) have also been used to prevent acid trapping effects. Durand and Hugenin[8] have claimed benefits for a dip in a solution containing 5 ml/l of concentrated sulphuric acid (1 min at 80°C) after storing work between anodizing and dyeing.

Dyeing is normally carried out in stainless steel, plastics, or rubber-lined tanks fitted with agitation and filtration. They are preferably covered when not in use. Tanks of mild steel or lead should not be used and aluminium or copper is not generally recommended.

The dyeing process itself is considered in the following sections of this Chapter.

Theory of dyeing

According to Giles,[9,10,11,12,13,14,15] aluminium oxide which has been treated in acid is covered with acid anions which are either bound by covalent links or are present as hydrated ions, depending on the nature of the anion:

$$>Al-OH + H^+X^- \rightleftharpoons >Al-X + H_2O$$
$$\Downarrow$$
$$>Al^+X^-$$

In dyeing, these anions are replaced by the anion of the dyestuff. The means by which the dye is adsorbed to the aluminium oxide are complex and may comprise hydrogen bonds, chelate bonds and covalent bonds as well as ion exchange."

Giles and his co-worker:; picture the sequence in dyeing as being initiated by a rapid dissolution or film etching of a surface layer of the aluminium oxide which causes an increase in specific surface area and increases the amount of dye taken up. This is followed by rapid adsorption of an external layer of dye which then slowly diffuses along the pore channels. The last (diffusion) stage can be regarded as the rate-controlling reaction as it is extremely slow and the process may not reach equilibrium for more than 10 hours at 60°C.[12] The rate of dyeing increases with temperature (see Fig. 10-1), and initially the adsorbed amount of dye is linear with the square root of the time.

A remarkable fact observed by Giles is that adsorption of sulphonated dyes by a chromic acid anodic oxide coating increases significantly with the volume of the dye bath, and this is explained by the influence of solution volume on the 'etching' effect in which the specific surface area is increased by dissolution in water.

A somewhat different theory of dyeing has been put forward by Cutroni[16] who believes that a complex ion $Al(H_2O)_4(OH)_2^+$ is formed during anodizing which links with the dyestuff. Subsequently, during sealing, the complex ion forms aluminium hydroxide:

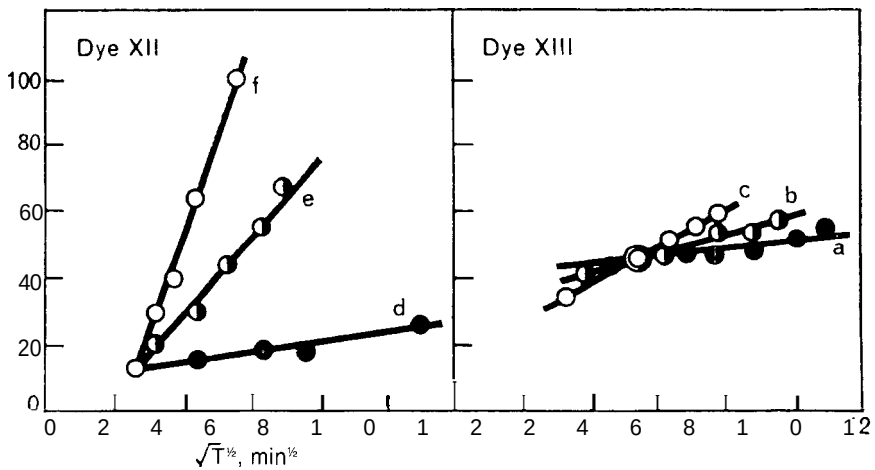
$$Al(H_2O)_4(OH)_2^+ + OH^- \rightarrow Al(H_2O)_3(OH)_3 + H_2O \rightarrow Al(OH)_3 + 4H_2O$$

Using water-soluble dyestuffs

Types of water-soluble dyestuffs

Different types of water-soluble dyestuffs are used which are distinguished by their fixation mechanism.

According to Speiser,[17] the acid and substantive dyes do not react to form a colour lake but are adsorbed physically on to the aluminium oxide. Giles believes that the adsorption of these sulphonated acid wool-types of dye is mainly by ion exchange,[15] the dye anion being attracted by the positive charge on the anodic alumina film and adsorbed either as monodisperse anions or as anionic micelles. Some covalent bonding between dye and film may also occur. Examples are the acid dyestuff Orange II:



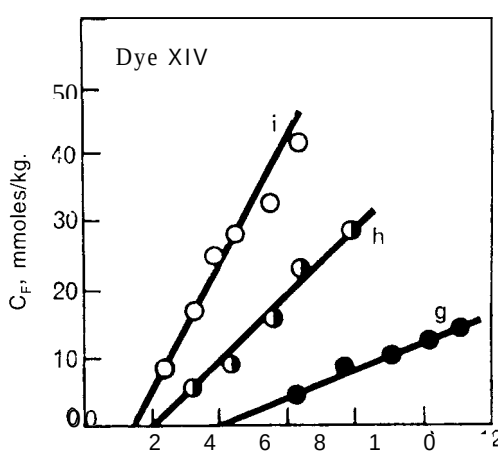
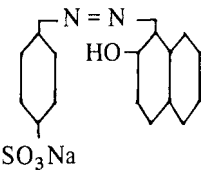
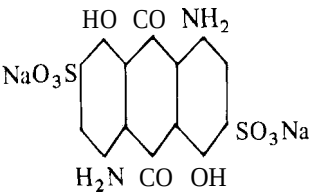


Fig. 10-1. Rates of adsorption of sulphonated dyes by the chromic acid anodic oxide film.

Dye XII (p-n-butyl homologue of XIII): (d) 35"; (e) 51"; (f) 58°C
Dye XIII (p-n-dodecylaniline→N-acetyl-H-acid): (a) 25"; (b) 49"; (c) 59°C
Dye XIV (aniline→H-acid): (g) 30"; (h) 51°; (i) 59°C[12]

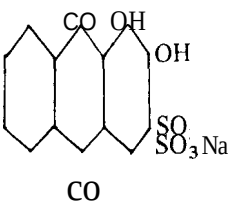


and Solway Blue BN:

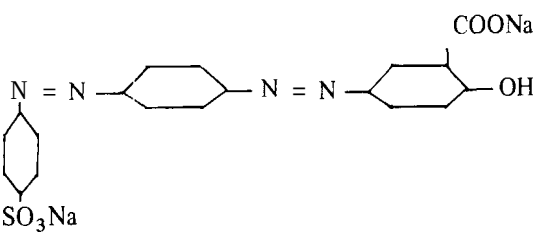


In general the light- and weather-fastness of these dyes is moderate.

According to Giles, the mordant-types of dyes form chelate complexes with the aluminium oxide." An example is Alizarin Red S:



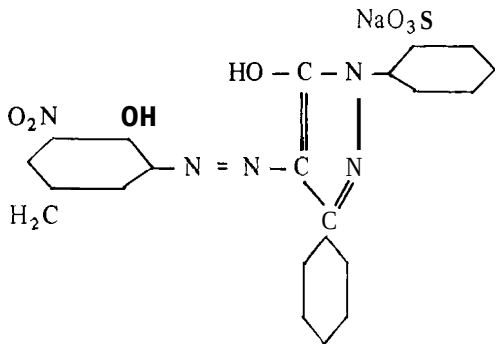
Speiser[17] gives examples of metallic and other dyestuffs which contain salicyl groups, such as Chrome Fast Orange R:



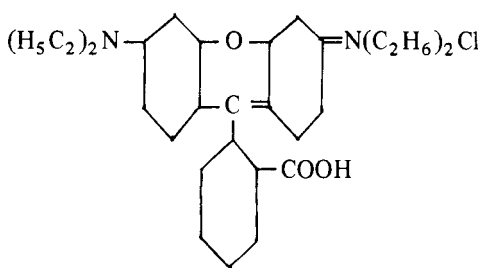
and Palatine Bordeaux RN.

In these, the complexes adhere to the aluminium oxide and may also react with the nickel or cobalt salts used in sealing.[17]

The metallized or axo type include, according to Giles,[12] such dyes as Neolan Red REG:



Finally, the basic dyes[17,18] may be mentioned. A typical example is Rhodamine B:



Others of this type are Saframine T, Auramine, Chrysoidine R and Brilliant Green B. The latter type of dye adheres to the oxide coating only when it has been treated with collagen substances before or during dyeing.[18,19] For this purpose they may be mordanted in a cold solution of, e.g., 5% potassium antimonyl tartrate or 2% sodium silicate for 10 minutes or in a tartaric acid solution. This type of dye is less frequently used in dyeing aluminium as the light-fastness is generally low.

Apart from the dyes mentioned above, modern practice has also included the use of azo dyes which are water insoluble and are formed in the film itself.[20] Their insolubility results in good water resistance and light-fastness and there is no need to seal the coating to prevent leaching. The dye is produced by diazotisation of the primary amine in ice-cooled water by means of a hydrochloric acid solution of sodium nitrite, and subsequent reaction with alkaline β-naphthol or 6-naphthylamine, etc. Modem environmental pressures mean that new dyestuffs need to be eco-friendly, and avoidance of heavy metals in this context is desirable. This has been discussed by Tscheulin.[21]

Optimum 'dyeing conditions

Temperature

The normal organic dye bath is operated hot, usually between 55 and 70°C, though in some case:; up to boiling temperature may be used. The temperature is fairly critical. Bad dyeing results if the temperature is too low as the light-fastness tends to decrease with the dyeing temperature, probably because no colour-lake is formed. On the other hand, if it is too high, there is a danger of sealing occurring before sufficient dye is adsorbed. Preferably, therefore, the bath should be thermostatically controlled.

Schenkel and Speiser[5] have illustrated the effect of dyeing temperature using a 1 g/l solution of Aluminium Black LCR at pH 4.0. The effect of temperatures from 25 to 80°C is shown in Fig. 10-2. It is particularly noticeable that, at the higher temperatures, the maximum extinction value (E), or maximum depth of shade, is reached in a much shorter time than at the low temperatures.

Sandoz[2] recommend that lower bath temperatures, even room temperature, are used for dyeings which are to be partially stripped for the manufacture of multi-colour nameplates. Such conditions can also be used for pale colours and dyestuffs that do not have good heat stability, with the lower rate of adsorption compensated by using higher dye concentrations or longer colouring times. Very high dyeing temperatures (above 80°C) are sometimes used for dyes which tend to bleed out in the sealing baths.

Time

Table 10-1 illustrates the effect of dyeing time on the light-fastness. If the time is too short, a superficial colour is obtained which is not as fast as the colour obtained by a longer time in a dye bath of lower concentration. On the other hand, too long an immersion time will not usually matter unless further dyeing stages are to follow. The normal dyeing time is 5-15 minutes but deep black colours may require up to 30 minutes, though there is no advantage in exceeding this time. The effect of dyeing time with Aluminium Black LCR is also shown in Fig. 10-2.

TABLE 10-1

Effect of dyeing time and concentration on light-fastness of Aluminium Green GLW dyed at 60°C

Concentration	*Dyeing time*	*Light-fastness*
2 g/l	20 min	**6**
7 g/l	5 sec	4-5

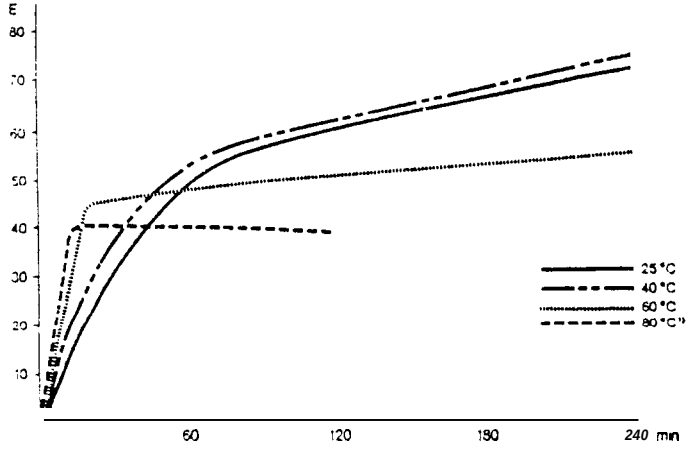


Fig. 10-2. Influence of temperature of the dyebath and duration of dyeing on extinction value[4]

Concentration

Concentration of the dye-bath varies with the dye used but increases with the colour intensity required. Typically Sandoz[4] indicate concentration levels of 0.2-0.4 g/l for light shades, 1-3 g/l for medium shades and 5-10 g/l for the darkest shades, the 10 g/l level being particularly used with black dyestuffs. In all cases the highest concentrations are used when high light fastness is required. The dye must be completely soluble in the solution, which is usually a neutral or acid aqueous solution, less often an alcoholic or acetone solution, and the pH is checked regularly. Care must be taken to keep the dye-bath free from oil and grease which might enter through unfiltered air used in agitation, as oils and grease are readily adsorbed by the coating and produce local stains. Both sulphate and aluminium ions will, in time, contaminate dye solutions, so rinsing before dyeing should be as thorough as possible. Low pH in the dye baths should also be avoided to minimise any attack of the anodic coating taking place in the dye baths. Complex-forming ions such as phosphates, silicates and fluorides are adsorbed preferentially by the anodic coating and very low levels of these contaminants will block dyeing completely." Heavy metal ions such as copper or lead can also cause problems, particularly with metal chelate dyestuffs.

Dye bath concentration can either be determined visually, by comparison of the depth of colour of diluted samples with a known standard, or by means of a spectrophotometer. In the latter case diluted samples are again used, and the extinction values measured in comparison with diluted samples of known concentration.

Acidity

As a general rule the adsorptive capacity of the anodic coating increases with decreasing pH, but a very low pH (below 4) will cause some attack of the film. The pH value can also influence the lightfastness of the finish (Tables 10-2 and 10-3) as it affects the amount of dye adsorbed (see Fig. 10-3).

TABLE 10-2

Effect of pH on light-fastness of Aluminium Deep Black MLW (concentration 10 g/l, dyed for 15 minutes at 60°C)

Dyed at	*Sealed in*	*Fastness*
pH 4.2	Water	8
	Ni/Co acetate	8
pH 6.5	Water	5
	Ni/Co acetate	5-6

TABLE 10-3

Effect of pH value of dye-bath on tone and depth of shade"

Conc.	*Dyestuff*	*pH 3*	*pH 5*	*pH 7*	*pH 9*	*pH 11*
1 g/l	Aluminium Golden Orange RLW	Very weak	Deep orange	Medium orange	Medium orange	Very weak orange
	light fastness	7-8	7-8	7-8	7-8	7-8
0.5 g/l	Aluminium Violet CLW	Deep violet	Deep violet (weaker)	Medium violet	Medium violet	White
	light fastness	5	4	4	4	
1 g/l	Aluminium Bronze G	Deep yellow-brown	Medium red-brown	Light red-brown	Light red-brown	Extremely weak red-brown. Coating pitted.
	light fastness	4-5	3-4	3	3	

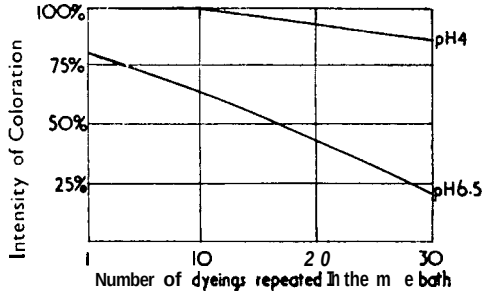


Fig. 10-3. Effect of pH value on efficiency of dye baths (10 g/l Aluminium Deep Black MLW, 15 minutes, 60°C, dyed at pH 4 and pH 6.5, sealed in water for 30 minutes at 100°C)

The optimum pH range for most dyestuffs is 5-6, but some require a pH range of 4-5 for best results. Dyes recommended for use in the pH 5-6 range are best buffered against changes of pH with an 8 g/l sodium acetate-0.4 g/l glacial acetic acid mixture. The pH level is then adjusted downwards with dilute acetic acid or upwards with dilute ammonia. However Brace[22] suggests that some of the mordant dyes behave differently and may require pH values in the range of 6.5-8.5. These come from the textile industry where fabrics may be treated with mordants containing aluminium salts, and this causes the fabric to have an alkaline reaction, which promotes reaction with mordant dyes.

Characteristics of some of the dyes commonly used in Britain and the U.S.A. are given in Tables 10-4 to 10-8. Mixtures of dyes may also be employed but care must be taken as selective adsorption may take place in the dye bath, with the result that patchy deposits may be formed, or the colour may change during the working of the bath. In general, it is recommended to obtain the appropriate single dyestuff from a reputable manufacturer. It must also be remembered that mixtures of dyes may have inferior light-fastness to the individual component.

Various additions to the bath have been proposed to improve dyeing or the light-fastness of the dye, e.g., sugar,[23] ferric hydroxide,[24] etc. Light-fastness may be tested using accelerated lightfastness equipment of the carbon arc or xenon arc type (ISO 2135: 1984). Alternatively the very severe U.V. light-fastness tests may be used (ISO 6581: 1980), but, as they effectively involve both heat and light resistance, they are too severe for all but the most lightfast dyes. In all cases, when considering the lightfastness of coloured finishes to be exposed externally, these accelerated methods should be treated as giving comparative data with samples of known durability, as the true exposure performance can only be established by actual exposure tests.

TABLE 10-4

Lightfastness of Sandoz dyeings[4]TABLE 10-4
Lightfastness of Sandoz dyeings[4]

Aluminium and Sanodal	*Lightfastness in heavy shades (Weather-Ometer exposures)*			*Lightfastness in pule shades*	*Lightfastness in hot water sealed coatings*
	Evaluated with the 8-stage Blue Scale 100 h	*Evaluated on the percentage loss in intensity 100 h*	*400 h*		
Gold 4N	8 d	0 d	0 d	<	=
Yellow G3LW	8	0	0	=	<
Fast Gold L	7-8	5	10	=	=
Yellow 3GL	8	0	5	=	=
Gold, Orange RLW	7	5	20	=	< <
Orange RL	5-6	15	25	< <	< <
Orange G	5	20	50	< <	=
Red RLW	5	20	50	< < <	< <
Red GLW	5	20	30	< <	< <
Red B3LW	7	5	20	=	=
Fiery Red ML	5	20	30	< <	=
Bordeaux RL	5	20	30	< <	=
Violet CLW	5-6	15	20	<	=
Blue 2LW	8 d	0 d	Od	=	=
Turquoise PLW	8	0	10	< < <	=
Blue G	8 d	Od	Od	<	=
Green LWN	8	0	5	< <	< <
Olive Brown 2RW	5-6	15	30	<	<
Yellow-Brown 2G	5	20	40	<	<
Red-Brown RW	4	30	70	<	<
Bronze G	6-7	10	20	< < <	=
Bronze 2LW	6-7	10	20	=	< <
Fast Bronze L	7-8	5	15	=	=
Brown GSL	5	20	50	<	=
Grey NL Liquid	7-8	5	10	=	=
Black 2LW	8	0	5	< <	=
Black CL	8	0	5	n.r.	=
Deep Black MLW	8	0	0	n.r.	=
Black GL Paste	8	0	0	<	=

= same fastness
< slightly lower
< < lower
< < < much lower
n.r. not recommended
d darker

TABLE 10-5

Heat resistance of Sandoz dyeings[4]

Aluminium and Sanodal	Dye concentration in g/l	120°C		150°C		200°C				250°C		300°C	
		hours											
		720	1500	720	1500	1	10	50	1	10	50	1	10
Gold 4N	30	5	5	5	5	5	5	5	5	5	5	5	5
Yellow 3GL	3	5	5	5	5	5	5	4	5	4	3	4	2
Yellow G3LW	2.5	3	3	2	1	3	1	1	1	1	1	1	1
Fast Gold L	2	5	5	5	4	5	5	5	5	3	1	1	1
Gold Orange RLW	3	5	5	5	5	5	5	4	5	4	4	4	1
Orange RL	3	5	5	5	4	5	5	4	5	4	4	4	1
Orange G	3	5	5	5	4	5	5	5	5	3	2	1	1
Red RLW	6	5	5	4	4	5	5	4	5	4	3	2	1
Red GLW	4	5	5	4	4	5	5	4	5	4	3	3	1
Red B3LW	5	4	4	3	2	5	4	3	4	3	1	2	1
Fiery Red ML	5	3	3	3	2	3	2	1	1	1	1	1	1
Bordeaux RL	5	3	2	2	2	3	2	1	1	1	1	1	1
Violet CLW	1.5	4	4	3	3	4	3	1	3	1	1	1	1
Blue 2LW	3.5	5	5	5	5	5	5	4	5	4	3	1	1
Turquoise PLW	5	5	5	5	5	5	5	4	5	4	1	1	1
Blue G	3	5	5	5	5	5	5	4	5	4	1	1	1
Green LWN	5	4	4	3	2	2	1	1	1	1	1	1	1
Olive Brown 2RW	5	3	3	3	2	5	2	1	3	2	1	2	1
Yellow-Brown 2G	3	3	3	2	2	s	4	3	3	2	1	2	1
Red-Brown RW	6	3	2	0	2	5	4	3	4	2	1	2	1
Bronze G	3	3	3	2	2	5	4	4	4	3	1	2	1
Bronze 2LW	1	2	2	2	1	3	2	2	2	1	1	1	1
Fast Bronze L	3	5	5	5	3	5	5	5	5	4	2	2	1
Brown GSL	5	4	3	3	2	5	4	3	4	3	3	3	1
Grey NL Liquid	1	2	2	2	2	3	2	1	1	1	1	1	1
Black 2LW	10	4	4	3	2	5	3	1	3	1	1	1	1
Black CL	6	5	5	5	2	4	3	1	3	2	1	2	1
Deep Black MLW	10	3	3	2	2	4	3	1	3	2	1	2	1
Black GL Paste	30	3	3	2	2	3	1	1	1	1	1	1	1

5 = heat stable (no visible change)
4 = slight effect on dyeing
3 = moderate effect
2 = marked effect
1 = dyeing degraded.

The test dyeings were produced as follows:
– *anodizing:* 30 min, 18-20°C, 1.5 A/dm, 12 μm, 220 g/l sulphuric acid
– *dyeing:* 15 min, 60°C, pH as in 'Optimum pH region'
– *sealing:* 30 min at the boil with 4 g/l sealing salt **AS** added

TABLE 10-6

Koppers Co. Inc. aluminium dyes*

Dye Solution		*Light Fastness*			
Conc. oz/gal	*pH*	***Excellent A***	*Excellent B*	*Good*	*Fair*
0.5	4.5		Green Gold GG Golden Yellow 3 GP	Red	
	5.0			Bright Red BB	
	5.5	Blue B	Bright Gold **AT** Roman Gold GL Bright Orange BG	Bright Red RC Dark Brown PG	
	6.0	Red S	Blue Green BG Dark Green FG Yellow Green GX		
	6.5	Yellow PM Bright Blue PT Green Blue NPT	Bright Yellow G Forest Green MBF Olive Green MBG Deep Olive MBO	Bright Yellow Brownish Orange MD Bright Orange RR Brick Red RB Crimson R Deep Pink GW Violet R French Grey CG	Violet BK
	6.8	Yellow 2G Orange 2G			
1.0	**4.5**	Black Special			
	6.5	Exterior Black New			

Rating:

Excellent **A**	Exposure 2000 hours with less than 10% loss.
Excellent B	Exposure 1000 hours without noticeable loss or damage.
Good	Exposure 500 hours with less than 10% loss or change.
Fair	Exposure 100 hours with approximately 25% loss or change.

* Compiled by Reynolds Metals Co. and published in Metal Finishing, 1969, **67,** (5), *57*

TABLE 10-7

National Aniline Division, Allied Chemical & Dye Corporation aluminium dyes*

Light Fastness

Class 8	*Class 7*	*Class 6*	*Class 5*	*Class 4*	*Class 3*	*Class 2*	*Class 1*
Canary Lake Yellow PL	Wool Fast Blue BL	Chromolan Orange GN Conc 200%	Wool Red 40 F	Salatine Yellow FF Conc	AZO Bordeaux	Chromolan Red 3RB Conc 200%	Wool Violet 4BN
Quinoline Yellow		Chromolan Black NWA Conc	Chromolan Bordeaux	Superchrome Yellow 2G	Chromolan Red 3B	Salatine Red 8BL Conc 125%	Neutral Black BSS
Salatine Turquoise G			Red Conc 133%	Wool Fast blue GL Conc 110%	AZO Rubine Extra	Croceine Scarlet MOO #90	
Alizarine Sapphire SE			Chromolan Red GRE	Alizarine Blue GRL	Lake Scarlet R Conc 125%	Wool Orange A Conc	
			Alizarol Orange 3R Conc 125%	Chromolan Grey G	Alizarine Red S Pdr Conc 110%	Metanil Yellow 1955	
			Chromolan Yellow NGR Conc 133%		Brilliant Scarlet 3R	Salatine Blue Green BFL	
			Wool Yellow, Extra Conc		Napthol Green B	Brilliant Wool Blue FFR Extra	
			Chromolan Yellow N		Chromolan Green BL Conc 125%	Chromolan Navy Blue REN	
			Chromolan Violet 2R		Chromolan Blue NGG Conc 200%	Chromolan Navy Blue RLG	
			Chromolan Brown R		Chromolan blue 3R	Alizarol Cyanine RC	
			Nigrosine 12525 Conc Crystals		Copper Shade Formulation	Resorcine Brown 3R	
						Fast Acid Violet GRF	

Note: Dyed samples anodized in sulphuric acid electrolyte were exposed in a Fade-O-meter and rated in terms of AATCC blue wool standards. Ratings indicate no more than just appreciable fading at the hours of exposure shown.

Class	*Hours of Exposure*
8	320
7	160
6	80
5	40
4	20
3	10
2	5
1	Less than 5

* Compiled by Reynolds Metals Co. and published in *Metal Finishing*, 1969, **69**, (5), 59.

TABLE 10-8

Carbic-Hoechst aluminium dyes*

Light Fastness						
Perfect 8	*8-7*	*Excellent 7*	*7-6*	***Very** Good 6*	*6-5*	*Good*
Blue LLW 3-5 g/l 2.77 pH	Yellow LLW 5 g/l 7.0 pH	Yellow GL 5 g/l 9.14 pH	Orange RL 3 g/l 8.66 pH	Golden yellow GLW 5 g/l 8.2 pH	Old Gold MRW 0.2 g/l 5.09 pH	Steel Grey BM 1 g/l 5.6 pH
Black LLW 10 g/l 3.65 pH	Golden Orange RLW 3 g/l 7.92 pH	Golden Orange 2RL 5 g/l 2.45 pH	Orange GL 6 g/l 9.61 pH	Brass Yellow MGW 0.15 g/l 7 07 pH	Red Brown RW 6 g/l 9.80 pH	
Deep Black MLW 10 g/l 4.12 pH	Black CL 3 g/l 2.79 pH	Red GLW 4 g/l 8.83 pH	Fiery Red ML 5 g/l 4.38 pH	Gold **MO** 0.3 g/l 4.0 pH	Yellow Brown 2G 3 g/l 3.38 pH	
		Red RLW 6 g/l 8.57 pH	Bordeaux RL 5 g/l 4.10 pH	Olive Brown RW 6 g/l 7.0 pH		
		Red Violet CL 6 g/l 2.86 pH	Violet CLW 1.5 g/l 3.03 pH	Brown **RL** 5 g/l 5.0 pH		
		Blue Violet LW 5 g/l 2.81 pH		Bronze G 3 g/l 2.86 pH		
		Navy BL 5 g/l 6.62 pH				
		Bluish Green MLW 5 g/l 2.96 pH				
		Green GLW 8 g/l 5.26 pH				

* Compiled by Reynolds Metals Co. and published in Metal Finishing, 1969, **67,** (5), **57.**

Whenever possible deionised water or water of low hardness should be used for making up dye solutions, as hard water will inhibit the adsorption of dyes that are sensitive to sulphate level. It may also cause precipitation and bath turbidity.

The dyeing process

The dye must be completely dissolved in the solution, and this is best carried out[4] by first mixing the required amount of dyestuff into a smooth paste with a small amount of hot water. About twenty times this amount of water (as hot as possible) is

then added to the paste with constant stirring until all the dye goes into solution. This is then added to the water (heated to dyeing temperature) in the actual dyeing vessel. If a pH buffer is to be used it should be added before the dye bath is topped up to the final dyeing volume. Finally the pH is checked and if necessary corrected, and the bath adjusted to the required dyeing temperature.

As the dye bath is used, the concentration of the dyestuff will decrease, so this must be replaced by additions of fresh dyestuff. At the same time the dyeing power of the solution will also be decreasing, owing to the drag-in of inhibiting impurities, particularly aluminium and sulphate ions from the anodizing electrolyte. This, therefore, has to be offset by increasing the dyestuff concentration to a higher level than that used initially, or in some cases, increasing the dyeing time. **As** the dye bath ages further this will become impracticable, and at this point partial dumping and renewal of the dye solution will be necessary.

The life of dye solutions can be very long (months or even years)‘ but they must be maintained carefully. In particular, suitable water must be used in their preparation, suitable dye tanks must be used, the solutions must be covered when not in use, dye bath contamination minimised, and the pH maintained at the correct level, even when the dye bath is not in use. Mould formation can occur in dye solutions and, if seen, this should be skimmed off and 0.05-0.10 g/l of a suitable fungicide such as dichlorophene G4 (Givaudan) or Preventol GD (Bayer) should be added‘ in an alcoholic solution. Many dyestuffs, however, already contain a suitable fungicide.

Although most dyeing is carried out as an immersion process, spray dyeing is often used in large architectural plants, particularly when producing the Sandalor range of combination finishes.[25,26] The main benefit is that a smaller dye volume is required, so dye change and dye storage is easier and cheaper. However the high degree of automation required in such a system is also said to give more consistency of dyeing. The importance of racking in such a system has been reported by Züllig.[27]

Faults in dyeing

As can be appreciated from the earlier discussion there are many factors which can affect the quality and consistency of dyeing operations. Batch to batch variations are most often caused by inadequate control of the anodizing, rinsing or dyeing practices, whilst changes in shade of the dyeings may be due to instability of the dye solution or uneven dye uptake from the component of a mixed dyestuff. Colour differences within the same batch may be caused by irregular anodic film thickness, or variation of alloy within the batch. It must also be remembered that the first part of the load to be immersed is the last to leave the solution, so in deep baths with slow transfer times conditions giving very fast rates of dyeing should be avoided.

However probably the most common dyeing problems are associated with localised differences within the same piece. Acid entrapment in crevices or recesses is a common problem and thorough rinsing or possibly neutralization before dyeing will be necessary. Entrapment of air can also cause lack of dyeing and, in some cases, may also have prevented adequate anodizing. Irregular, cloudy effects *on* dyeing are nearly always caused by incorrect rinsing or anodizing practice and local pale or undyed ones may be caused by inadequate degreasing or later oil contamination. Variations in appearance after etching will not usually be masked during anodizing and may well be accentuated by colouring, and welded joints, for example, give this sort of problem due to texture variations.

Porosity in castings may cause sulphuric acid anodizing solution to leach out at the high dyeing temperatures with the result that the dye will be locally decolourised. Neutralization by dilute alkalis does not as a rule prove very successful but the trouble may be avoided by alternate rinsing in warm water at up to 65°C arid cold water followed by immersion in concentrated nitric acid prior to dyeing.[28] Neutralization in ammonium oxalate (5-10 g/l) is also frequently used for castings.

Undyed areas of irregular shape which surround scratches or grooves caused either mechanically or by small strings of intermetallic compounds which form a groove during electro- or chemical polishing have been found to be caused by stray currents within the dye baths associated with the presence of impurities, particularly of chloride in the dye solution." This defect may be avoided by using non-metallic vats. Chloride in dyebaths is particularly harmful when the aluminium is coupled with more noble metals."'

Batch to batch variation in colour can also arise for many reasons, and Dixon[31] has provided a useful summary of problems and remedies. This is shown in Table 10-9.

Bleeding during sealing

Some dye!; tend to leach out during the sealing treatment and this is generally described as 'bleeding'. For this reason dyed work is often given a short (5 min) treatment in a 5 g/l nickel acetate-5 g/l boric acid solution at a pH of 6.0 and a temperature of 80°C, before conventional sealing. This 'fixing' treatment also improves weathering performance of many dyestuffs used in architectural applications. Alternatively the work may be sealed directly in nickel-based solutions. Sealing gives a greater increase in lightfastness than might be expected with many dyestuffs, and this is thought to be due to changes in their form during sealing.

Dyestuff molecules are probably gradually dissolved from the pore wall surface during sealing and then aggregate in larger micelles, which are limited by the diameter of the pores. The larger dye particles are then responsible for the improved lightfastness of the finish.

TABLE 10-9

Reasons for colour differences from batch to batch

Type of Colour Fault	*Possible Causes*	*Preventive Action*
Slow decrease in depth (over days or weeks)	Decline in dyeing capacity due to:	Add dye to correct the deficiency.
	Drop in dye concentration through consumption.	Prevent entrapment by thorough rinsing and by avoiding dripping from other solutions.
	Accumulation of deactivating contaminants in dyebath e.g. Aluminium Sulphate	Extend dyeing time. Increase dye concentration above the initial value. Part or full renewal of dyebath.
	Chemical decomposition of dye through contact with non-resistant metal parts.	Check tank and fittings for possible points of contact and insulate these points.
	Slow increase in pH.	Correct pH, buffer the bath.
Depth of shade differences	Variations in dye adsorptive capacity of anodic coating due to:	
	Varying anodising conditions.	Keep anodising conditions constant (current density, time, temperature).
	Presence of different alloys	Adjust anodising and dyeing parameters to the alloys present.
	Different time lag between anodising and dyeing (acid dip, carry-over into rinsing bath, retention time in water and air).	Keep the time interval constant. Do not suspend in anodising acid without current, rinse immediately afterwards. Do not store in water. Level out dye absorptive capacity by brief activation in acid and a neutralising rinse.
	Uneven activation in the acid dip	Keep activation time constant.
	Different degrees of bleeding in the sealing bath	Equalise or minimise losses from bleeding by: Sealing in Sealing Salt AS. Dye at higher temperatures. Immerse at highest practicable sealing temperature. Keeping sealing pH constant, buffer bath.
	Fluctuation in dyebath pH	Buffer dyeing solution
Over-heavy dyeing at beginning of production run	Increase in the anodising temperature	Do not dye the first anodising batches.
Changes of shade	Uneven depletion of constituents in dye	Correct concentrations of the constituent involved. Use homogeneous dyes whenever possible. Employ combinations of dyes with similar dyeing rates.
	Chemical instability of the dye in solution	Select dyes with higher stability in solution. Optimise dyeing conditions (lower temperature, more suitable pH, buffer). Renew dye solution at frequent intervals.

Other practices recommended by Sandoz[4] to minimise bleeding are:

dyeing at the highest permissible temperature
dyeing for relatively long times
using the best quality water for dyebath make-up
rinsing briefly between dyeing and sealing
and sealing at the boil.

Strict attention to the recommendations of the dyestuff manufacturers for optimum dyeing conditions will minimise bleeding problems, but the following treatments have also been suggested:

(1) Immersing the dyed work in boiling water for 20 seconds and plunging it quickly into cold water. This is followed by the normal sealing method.

(2) The dyed work is immersed in a 20% barium chloride solution for 5 minutes at 45°C before sealing.

Removing the dye

If it has been found after dyeing, and prior to sealing, that the desired shade has not been obtained, it is often possible to remove the dyestuff either completely or partially without damage to the anodic oxide coating. This is carried out either in nitric acid (d. 1.19; 27% wt) or in 5 ml/l sulphuric acid at 25°C. Some dyes may, however, be unstrippable, and these include particularly some dark yellows and golds, while in other cases more concentrated sulphuric acid may be necessary.

Where dyestuffs cannot be bleached in acid solutions the following methods are sometimes successful:

(1) Sodium hypochlorite 10 g/l at room temperature.

(2) Potassium permanganate 50 g/l + nitric acid concentration 50-100 g/l for 5-15 minutes at 20-30°C followed by sodium bisulphite 50-100 g/l for 1-5 minutes at 20°C.

(3) Overdye in ferric ammonium oxalate 10-20 g/l at 30°C for 1-5 minutes and then bleach in dilute nitric acid.

Removal of the dye is only satisfactory, however, where the coating has not been sealed.

Decolourising dye effluent

Another aspect of dye removal that is assuming increasing importance is the general water authority requirement that effluent from industrial plants should not be coloured. This is not normally significant in relation to the rinse waters, but decolourising and other treatments are necessary when dye solutions are dumped. The problem has been studied by Grossmann,[32] who considered the possibilities

of adsorption by activated carbon, precipitation, reverse osmosis, evaporation and incineration, catalysis, radio-activation or electrochemical oxidation, chemical oxidation or chemical reduction. Of these methods, he found that adsorption with activated carbon represented an especially suitable and economical method, particularly as it did not give rise to secondary pollution problems or problems of disposal of the solid waste. Many different forms of activated carbon are available, but Grossmann found that extruded cylinders or pellets of carbon, usually used for absorbing gas, were not suitable. Decolourisation carbon in powder form, or broken water purification carbon in granulated form, were most suitable. Types having a high proportion of macropores, a large surface area and a neutral to acid pH value gave the best results. The carbon could either be used by adding it to the solution to be decolourised and then separating it again by filtration, or by allowing the dye solution to percolate slowly through a carbon bed.

More recently Japanese workers[33] have looked at decolourizing dyes with ozone, and successful treatment of Sanodal Red B3LW is described.

Light-fastness

Fading of dyes is often due to reaction with water,[34] the reaction depending on the presence of both water and oxygen or some other reducible substance to remove the hydrogen. It is, therefore, slowed down by sealing. In the best dyes, Giles[12] believes fading is stopped almost altogether by the formation of micelles which close up the interstices remaining in the sealed pores and render them completely impermeable.

The light-fastness of dyed coatings is not an absolute physical property and the quantitative values, given from 1 to 10, express a comparison with standard dyed patterns.

The standardised methods for testing light-fastness[35] use a series of cloth samples dyed in standard colours[36] as standard patterns. These are given a lightfastness number of 1 to 6, each pattern having double the lightfastness, in exposure time terms, of the preceding one. Cuttings from these are exposed with the samples. In the case of colours of moderate or poor lightfastness, the full range of standards is used, but with lightfast colours only the No. 6 cloth standard is exposed. The samples are placed at equal distances from the light source and rotated around it. The temperature must not rise above 50°C. Half of both the exposed sample and the standard patterns are masked with opaque material to facilitate observation of fading. They are then exposed for long enough to produce a colour change equal to Grade 3 on the geometric grey scale either on the sample or on the No. 6 standard, whichever happens first. After exposure, the sample is compared in daylight with the standard patterns and is allocated the light-fastness number of the standard pattern showing the same contrast as Grade 3 on the grey scale. If the No. 6 standard fades first, it is replaced by a fresh cloth standard and the test continued. The No. 6 is replaced each time it fades until the sample under test has faded to a degree which is equivalent to Grade 3 on the geometric grey

scale. The sample is then allocated a light-fastness rating which is related to the number of times the No. 6 standard had to be replaced according to the schedule:

No. 6 standard	2	times represents a light-fastness of	7
No. 6 standard	4	times represents a light-fastness of	8
No. 6 standard	8	times represents a light-fastness of	9
No. 6 standard	16	times represents a light-fastness of	10

According to BS 1615: 1987, dyed finishes with a lightfastness number of 9 are required for external applications, whilst those with a lightfastness number of 5 are suitable for internal uses.

Some dyes have been found to darken or change their colour shade slightly after a relatively short time of exposure to the light-fastness test, although they then show little or no further change. Where the dyed work is exposed uniformly, this may be of little account.

Other methods of rating light-fastness are sometimes used. Thus, using a Fade-O-Meter, Spooner[37] proposed a rating system of from 1 to 10 denoting increasing order of merit. Using this technique, Spooner[38] found that of 115 dyes, 7.5% had 'poor' (1-2) or 'fair' (3-4) ratings, 18% 'very good' (7-8) or 'excellent', while 5 dyes had not failed after 1500 hours. The best light fastness was shown by Quinoline Yellow Conc. 180%, Alizarin, Sapphirole SE, Aluminium Black LLW and Aluminium Blue A while only slightly inferior were Eloxan Turquoise D-1, Alizarin Green G X N, Eloxan Red C-1, and Alizarin Red S Conc. 110%.

The anodizing conditions which improve light-fastness are higher coating thickness and, generally, higher anodizing temperature, though light-fastness is sometimes better when the temperature of the dye bath is kept low. Nickel acetate sealing improves the light-fastness of only some dyes; chromate sealing is useful for red dyes.

In some instances alloy composition is important. Thus, dyed aluminium-silicon alloys have by and large. an inferior light-fastness.

Light-fastness may be improved, according to Benninghof,[39] by applying colourless lacquers which contain compounds which absorb ultra violet light.

Weather-fastness

Weather-fastness is a composite property denoting the resistance of the coloured finish to factors such as light, rain, chemical attack and erosion. It should therefore not be predicted on the basis of lightfastness evaluation alone. Speiser[40] summarises the factors influencing the light and weather-fastness of dyed anodic coatings as shown in Table 10-10, and it is clear that many of these factors will not be evaluated by accelerated lightfastness and weathering tests. Real performance can therefore only be evaluated by long term exposure tests. Such tests have been reported by Speiser and Schenkel[41] after ten years exposure of a wide range of dyed finishes exposed at 13 sites around the world. A very limited range of dyestuffs was found to be sufficiently lightfast for architectural applications and

TABLE 10-10

Factors influencing the light-fastness of organic dyeings on anodized aluminium[40]

I *Dyestuffs*
- (a) Photochemical properties of molecule (chromophoric groups)
- (b) Standardising agent
- (c) Diffusion properties (size of molecule)

II *Substrate*

III *Condition of dyestuffs in film*
- (a) Quantity of dye adsorbed in film
- (b) Size and distribution of adsorbed dye aggregates

IV *Environmental influences*
- (a) Spectral composition of light (U.V., visible, I.R.)
- (b) Intensity of light
- (c) Temperature
- (d) Moisture
- (e) SO_2
- (f) Other atmospheric elements

these have been introduced by Sandoz under the 'Sanodal' name. After 6 years of exposure of the Sanodal dyes, the average loss of intensity found was as follows:

Sanodal Yellow 3GL	*23%*
Sanodal Red B3LW	3%
Sanodal Blue G	21%
Sanodal Turquoise PLW	19%
Sanodal Deep Black MLW	4%
Sanodal Gold 4N (ferrioxalate)	37%

On this basis Sandoz rate the weather-fastness of dyestuffs according to the following scale:

loss of intensity after one year	*rating*
up to 10%	perfect
up to *20%*	very good
up to *30%*	good
up to 40%	moderately good

Essential factors in obtaining adequate external exposure performance are the production of a good quality 25 micron anodic coating, the use of optimum dyeing conditions such that an adequate quantity of dye is adsorbed, and the achievement of good quality sealing. In particular dye bath activity and dye uptake need to be regularly monitored to ensure that sufficient dyestuff is adsorbed.

Optimum dyeing conditions for the Sanodal dyestuffs are given as:

Sanodal dye	*Concentration*	*pH value*
Yellow 3GL	3 g/l	5.5±0.5
Gold 4N	30 g/l	5.0±0.5
Red B3LW	5 g/l	5.5±0.5
Blue G	5 g/l	5.5±0.5
Turquoise PLW	12 g/l	5.0±0.5
Deep Black MLW	8 g/l	4.5±0.5

All dyeings should be for 20-30 minutes at 60±5°C, with the exception of the Gold 4N (ferrioxalate) dye which is used at 40-55°C for 20 seconds to 5 minutes according to shade.

Combination of Sanodal dyes and light bronze electrolytically coloured finishes, to give muted shades of red, blue, gold and brown, have also been used architecturally in recent times, and are known under the name of 'Sandalor' finishes (Fig. 10-4). These have been described in more detail in Chapter 8. Jankowski and Matthée[42] have described the wider use and performance of these combination colours in Germany.

Sheasby and Carter[43] have compared the performance of a range of black dyeings (with conditions deliberately varied to give a range of lightfastness values) in accelerated U.V. lightfastness tests and outdoor exposure tests at 3 sites in the U.K. They show that 24 hours exposure in the UVIARC test (B.S. 6161: Part 8: 1981)produces fading equivalent to an average period of 8 years exposure at these sites. In this. period the best of the dyeings had only faded to Grade *3* on the Grey Scale, whereas the worst had lost much of their colour.

Heat resistance

Resistance to heat is not a notable characteristic of the organic dyestuffs used for colouring anodized aluminium, since most of them are destroyed by heating to about 400°C, and this is very often a quick test for an organic dye. For certain applications, such as kitchen utensils, reflectors and guard-grilles used over heaters, it is important to select colours which are more resistant to heat. **A** colour applied to films of normal thickness is considered as good in this respect if it withstands a temperature of 250°C for 1 hour without change of shade, but the stability depends on both the temperature and time of exposure. There are scarcely any organic colours that will not fade rapidly at 300°C, and not many that can

survive about 10 hours at 250°C without considerable fading, the safe maximum being 150°C for most colours and not much above 100°C for some. The heat resistance of some Sandoz dyestuffs has been shown in Table 10-5.

On the other hand, inorganic pigments such as ferric ammonium oxalate have a very high degree of heat resistance and will often remain unchanged at over the melting point of aluminium.

Control of dye baths

The quality of the dyed finish depends on the temperature, time, pH and concentration of the dye baths, as well as on anodizing and sealing conditions, and all these should be strictly controlled. The pH is best measured with a glass electrode or by titration against N NaOH or N H_2SO_4.

The concentration of the dye is usually difficult to determine by chemical analysis and is therefore estimated by comparison either in a Lovibond Tintometer, in Nessler glasses or by spectrophotometer against four standards containing ¼, ½, ¾, and full dye concentration respectively. If necessary, the dye solution may have to be diluted.

In a typical test,[44] a 5-10 ml sample, depending on the dye, of the solution is diluted to 500 ml. This solution is filtered and a 25 ml portion is compared with a freshly-prepared dye solution of known concentration in a 50 ml comparison tube. Viewing against a white background, the standard solution is diluted until both solutions appear to be equal in depth of colour. The strength of the dye bath is then calculated.

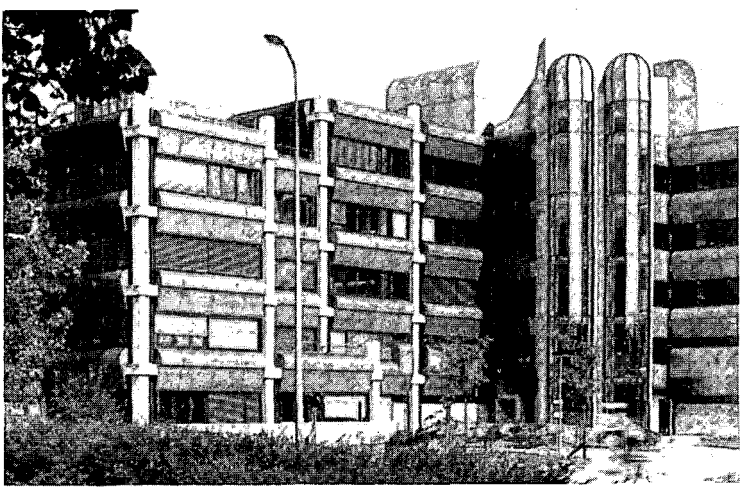


Fig. 10-4. Sandalor yellow finishes used on administration building, Zoetermeer, Holland [Courtesy of Sandoz Ltd.]

Colourimetric determinations by means of light transmission methods are not very reliable when dealing with mixtures of dyestuffs. They are also suspect with older dyebaths because a proportion of the dye becomes combined with metallic ion impurities transferred from the anodizing electrolyte and is no longer available for dyeing. The use of a spectrophotometer for dye bath control has been described in detail by Hoban.[45]

A good practical method is to keep a fresh sample of a new dyebath in a closed container in a dark place. When the production bath needs checking some dyeing tests tire carried out on sample pieces simultaneously in the old and unused baths, and additions are made to the former until it dyes to the same shade in the same time as the original bath. The addition to be made to the production bath may then be calculated from this.

Volumetric methods of analysis have been developed for some dye baths. Class and Class[46] have described a method for the quantitative determination of the amount of dyestuff taken up by the oxide film: the dye is dissolved from the sheet with phosphoric acid of pH 1.2, and, after reduction, the dye concentration is determined by extinction methods using ultra-violet light. In a second direct method, dyed and natural anodized films were dissolved and the solutions compared using a spectrophotometer. Sandoz use this method with their Sanodal system to ensure that an adequate amount of dye has been adsorbed, and they strip the dyed coating in a sodium hydroxide-EDTA solution. The extinction values of the production and control dyeings, produced at the same nominal dye concciitratioii, are measured at a wavelength appropriate to each dyestuff in a spectrophotometer. The results indicate the additions required to obtain normal dye activity, and, if the bath contains too high an amount of nonactive dyestuff, that the bath should be renewed.

Glayman[47] has investigated methods for testing the concentration of dye and the performance of dye solutions under various conditions of operation, and stressed the advantages of the spectroabsorptiometer for the measurement of colour and comparisons between dyebaths.

Kuroda and Uji[48] have examined the relationship between the zeta-potential and the affinity of the anodic oxide coating for dyestuff. The sealed coating had a potential of about +30 mV, and the unsealed coating was variable but approached the value for the sealed coating on prolonged washing; at the same time, the adsorption power was decreased due to hydration of the oxide. The adsorption power was maintained for a long time by storage in a desiccator. The zeta-potential was shifted towards negative when dyeing in acid dye baths owing to adsorption of the anion of the dyestuff. With basic dye baths the potential was kept positive because the dyestuff was not adsorbed by the coating. Using tannic acid treatment the coating could be dyed with basic dyestuff because the zeta-potential of the coating was more negative.

Solvent dyeing

In general, dyestuffs which do not contain water-soluble groups have better fastness to light and heat than those that do, and a number of such dyes have been used in solution in benzene, toluene, acetone, ethanol, chlorinated benzenes or substituted naphthalenes.[49,50] Application is by dipping, spraying or roller coating. It is claimed that solvent colour absorption is instantaneous and that the full colour is developed in 2-10 minutes. There are, of course, other advantages of using solvents; e.g., pH control is unnecessary and no salts are formed in the coating. The light-fastness and heat resistance of some solvent dyes is noted in Table 10-11.

TABLE 10-11

Light and heat stability of solvent-dyed anodized aluminium[50]

(Dyestuff used 1-2 g/l in trichlorobenzene. Exposure tests: 2 years in industrial atmosphere facing south at 45°. Heat stability: 300°C for 1 hour plus 400°C for 2 hour; total time including heating and cooling 6 hours)

		Light fastness		*Heat stability*	
Dye	*Chemical type*	*% Fade*	*Rating*	*Colour change*	*Rating*
Yellow QB	Quinaldine	None	Excellent	None	Excellent
Golden Orange DP	Anthraquinone	Darker	Fair	Redder and brighter	Very good
Red Brown AA	Anthraquinone	None	Excellent	Darker	Good
Brown MX	Anthraquinone	Trace	Excellent	Darker	Good
Crimson DHY	Anthraquinone	None	Excellent	Slightly bluer	Very good
Rubine YX	Anthraquinone	None	Excellent	Slightly bluer	Very good
Rubine RR	Anthraquinone	None	Excellent	Slightly yellow, duller	Good
Red Violet PH	Anthraquinone	None	Excellent	Slightly bluer	Very good
Green MX	Anthraquinone	None	Excellent	Slightly bluer	Very good
Red Blue DNC	Anthraquinone	None	Excellent	Slight	Excellent
Violet 5RB	Anthraquinone	None	Excellent	Greener and darker	Fair
Blue RB	Anthraquinone	None	Excellent	Slight	Excellent
Navy Blue R	Anthraquinone	None	Excellent	Slightly redder	Excellent
Blue PBY	Anthraquinone	None	Excellent	Darker	Good
Green Blue RL	Anthraquinone	None	Excellent	Slight	Excellent
Violet Black AH	Anthraquinone	None	Excellent	Slightly weaker	Excellent
Black MG	Anthraquinone	None	Excellent	Slight	Excellent

A range of solvent dyestuffs has been marketed by Sandoz Ltd. under the registered trade name of Savinyl dyestuffs, and these included some of the former solvent dyes sold by Durand and Huguenin as Origal dyes. The dyes are listed in Table 10-12 where the results obtained refer to coatings of approximately 12 μm thickness formed in 230 g/l sulphuric acid at 19°C, and dyeing was carried out for 2 minutes at 20-25°C.[51] The high speed action of these dyes means that they are suitable for application by brush or hand swabbing, and they can be used to rectify some dyeing faults even when dyeing has been carried out in aqueous solutions. Bosdorf[52] has described the use of such dyes for artistic decoration on anodized aluminium to which he gives the name of 'Aluchromy'.

TABLE 10-12

Properties of the Savinyl dyestufs[51]

Name	Shade	Methanol			Ethanol			Acetone			Methyl ethyl ketone			Trichloro-ethylene			Ethyl glycol		
		g/l	Depth of shade	Light-fastness	g/l	Depth of shade	Light-fastness	g/l	Depth of shade	Light-fastness	g/l	Depth of shade	Light-fastness	g/l	Depth of shade	Light-fastness	g/l	Depth of shade	Light-fastness
Savinyl Yellow 3GS	greenish yellow										100	2	1						
Savinyl Yellow GRL	greenish yellow	**20**	2	6	50	**3**	6	250	4	2	200	4	**4**				200	**4**	**5-6**
Savinyl Yellow RLS	yellow	**40**	3	3	30	3	5	20	4	6-7	20	3	**3**	10	3	7	100	**2**	**4-5**
Savinyl Yellow RLSN	yellow							20	3	6	20	3	3	**5**	**4**	**5-6**	200	3	**4-5**
Savinyl Yellow 2RLS	reddish yellow	**30**	**4**	6	100	4	6	80	**4**	**7**	**150**	**3**	**5**				*100*	3	5
Savinyl Orange RLS	orange	**50**	3	5-6	30	**2**	5-6	100	3	6-7	30	**3**	**4**				200	3	**5-6**
Savinyl Scarlet RLS	scarlet	20	3	4-5				150	3	6	60	2	**4-5**				200	3	**5-6**
Savinyl Fire Red 3GLS	red	**7**	**4**	**5**				250	4	8	200	2	7	**50**	3	7	**2**00	3	7
Savinyl Fire Red GLS	bluish red	7	3	6-7	100	**4**	6-7	**25**0	4	8	200	3	7	**4**	3	7-8	200	3	7-8
Savinyl Red BL	red							10	**4**	6-7	10	3	**5-6**				40	2	2
Savinyl Red 3BLS	ruby red	20	**4**	**4**	20	**4**	3 4	**150**	**4**	**1**	**30**	**3**	**4-5**				90	3	2
Savinyl Blue B	bluish violet				*1*	4	6-1	**5**	**4**	**8**	**10**	3	7-8						
Savinyl Blue RS	reddish blue							**5**	**3**	**5-6**	10	2	7-8	**50**	3	7			
Savinyl Blue GLS	blue	50	4	6	**50**	**4**	6	25	4	7	200	3	7-8	**3**	2	6	200	**2**	7-8
Savinyl Blue 3GLS	blue	100	**4**	8	100	**4**	8	*5*	**2**	**7**	*10*	**2**	8				200	2	7-8
Savinyl Green B	dull blue-green							5	1	6				**50**	3	7			
Savinyl Green 2GLS	green										200	2	7	10	3	7-8	200	2	6-7
Savinyl Brown GLS	brown				30	**3**	3 4	*25*	**4**	**3**	10	3	3						
Savinyl Black BN	blue-black							**10**	3	6-7	10	2	5-6						

Notes.

1. Depth of shade: **1** = pale; 2 = medium; 3 = heavy dyeing; **4** = very heavy dyeing.
2. At the indicated concentrations for application the deepest dyeings are obtained.
3. Where no rating is given the solvent **is** not in general suitable.

Great care is needed in the handling of the organic solvents used for dyes of this type because they are frequently highly inflammable with the risk of explosion if used in a confined space, and the fumes can be toxic or narcotic, and in practice solvent based dyes are very little used.

Colours have been produced by heating anodized aluminium in a solvent which boils at 175-250°C in contact with phthalocyanine-forming reactants such as phthalic anhydride, phthalonitrile or phthalamide.[53]

Dale has suggested a process in which the solvent used for the organic dyes is removed by means of a second solvent, preferably a chlorinated benzene, which does not dissolve the dye.[54]

2. COLOURING WITH INORGANIC MATERIALS

These are, in practice, less important than organic dyes as the colour ranges obtainable are more restricted. The colours are more heat-resistant though not generally as bright. Thus, while organic dyes frequently change colour at just over 100°C (see Table 10-5), many inorganic colours will not change up to the melting point of the metal.

There are five methods which can be considered for the application of inorganic colours:

(A) The coating is treated consecutively with two compounds which react to form a pigment, e.g.:

Red brown: The work is immersed in copper sulphate solution, then in potassium hexacyanoferrate II solution:

$$2CuSO_4 + [Fe(CN)_6]K_4 \rightarrow [Fe(CN)_6]Cu_2 + 2K_2SO_4$$

Brown: Silver nitrate and potassium dichromate or chromate:

$$2AgNO_3 + K_2Cr_2O_7 \rightarrow Ag_2Cr_2O_7 + 2KNO_3$$

Dark brown: Lead acetate and ammonium sulphide:

$$PbAc_2 + (NH_4)_2S \rightarrow PbS + 2NH_4Ac$$

or cobalt nitrate and hydrogen peroxide in ammoniacal solution:

$$2Co(NO_3)_2 + H_2O_2 + 4NH_4OH = 2Co(OH)_3 + 4NH_4NO_3$$

Yellow: Lead acetate and potassium dichromate or chromate:

$$PbAc_2 + K_2CrO_4 = PbCrO_4 + 2KAc$$

or cadmium acetate and ammonium sulphide:

$$CdAc_2 + (NH_4)_2S = CdS + 2NH_4Ac$$

White: Lead acetate and sodium sulphate:

$$PbAc_2 + Na_2SO_4 = PbSO_4 + 2NaAc$$

Blue: Potassium hexacyanoferrate II and ferric sulphate or chloride:

$$2Fe_2(SO_4)_3 + 3[Fe(CN)_6]K_4 = [Fe(CN)_6]_3Fe_4 + 6K_2SO_4$$

Black: Cobalt acetate and sodium sulphide:

$$CoAc_2 + Na_2S = CoS + 2NaAc$$

By far the most common use of a double dipping treatment of this type was the production of bronze finishes in cobalt acetate and potassium permanganate solutions. These bronze finishes were widely used in architectural applications in the past, but because of their complexity and the difficulties of colour control, they have now largely been replaced by electrolytically coloured bronze finishes. The conditions used have been described in Chapter 8 (page 732 ff).

An inorganic black coating can also be obtained[55] by immersion of the anodized coating in 1-2% iron alcoholate solution at 43-52°C for up to 10 minutes. The coating is then rinsed and immersed in either hydrogen sulphide solution or 3.5% ammonium sulphide solution for up to 5 minutes. Finally, the work is immersed for 10-20 minutes in 1-4% potassium dichromate solution at 93-100°C in order to oxidize traces of sulphur, after which it is sealed in the normal way.

In yet another method, the anodized work is immersed in ferric ammonium double salt solution followed by sulphide solution."

A light-fast green finish can be obtained by immersion in a copper salt solution followed by a ,solution of an inorganic sulphide and hydrogen sulphide or an organic sulphur compound,[57] or by immersion in a metal salt solution with an anthraquinone dye.[58] The use of a sulphide solution first, e.g. $Na_2S_2O_3.5H_2O$ followed by precipitation from salts of Co, Ni, Fe, Cu, Mo, Bi or Cd has also been the subject of a patent.[59]

Green is also obtainable from the reaction between copper sulphate and sodium arsenite and orange from antimony potassium tartrate and hydrogen sulphide.

Kape and Mills[60] have discussed the production of inorganic colours by double decomposition processes in some detail and Table 10-13lists a number of the possibilities which they examined as having some possible practical significance.

TABLE 10-13

Production of inorganic colours by double decomposition[60]

First reagent	*Second* ***reagent***	***Possible*** *chemical compound produced*	***Colour range***
$FeSO_4(NH_4)_2\ SO_4.7H_2O$	NH_4VO_3 (1% wt/vol)	Basic ferrous vanadate	Light greenish yellow
Tannic acid	NH_4VO_3 (1% wt/vol)		Green-black
Tannic acid	$Na_2Cr_2\ O_7.2H_2O$		Yellow-orange
Tannic acid	$FeSO_4(NH_4)_2SO_4.7H_2O$		Violet
Tannic acid	$Fe(NO_3)_3.6H_2O$		Violet
Gallic acid	Na_4VO_3 (% wt/vol)		Yellow
Gallic acid	$Na_2WO_4.2H_2O$		Very pale yellow-green
Gallic acid	$Na_2MoO_4.2H_2O$		Yellow-orange
Gallic acid	$Na_2Cr_2O_7.2H_2O$		Orange
Gallic acid	$FeSO_4(NH_4)_2SO_4.7H_2O$		Violet
Gallic acid	$Fe(NO_3)_3.6H_2O$		Violet
$Pb(CH_3COO)_2.3H_2O$	K_2CrO_4	$PbCrO_4$	Yellow
$K_4Fe(CN)_6$ (i)	$Fe(NO_3)_3.6H_2O$ (ii)	Ferric ferrocyanide	
$Pb(CH_2COO)_2.3H_2O$ (iii)	K_2CrO_4 (iv)	and lead chromate	Green
Bismuth citrate complex	$K_2Cr_2O_7$	Bismuth dichromate	Yellow
Tl_2SO_4	$K_2Cr_2O_7$	Thallium dichromate	Yellow
$ZnSO_4.7H_2O$	K_2CrO_4	Zinc chromate	Yellow
$BaCl_2.2H_2O$	K_2CrO_4	Barium chromate	Pale yellow
	K_2CrO_4	Silver chromate	Brick red
$Pb(CH_3COO)_2.3H_2O$	K_2SO_4	Lead sulphate	White
Tl_2SO_4	Sodium cobaltinitrite	Thallous cobaltinitrite	Yellow
Ammonium ferrioxalate		Ferric oxide	Yellow-brown

Frequently it does not matter in this process which of the compounds is adsorbed first. 1% solutions are generally suitable and the temperature is normally kept low. If one treatment does not produce sufficient colour intensity, the process may be repeated.

Heating the film to 150-200°Cimproves the porosity and hence the absorption. Alternatively, higher current densities or temperatures in the anodizing process may achieve the same result. Frequently non-aqueous solvents such as ethyl alcohol may replace water with lead acetate, ferric chloride, cobalt nitrate, zinc chloride and copper salicylate. Similarly methyl alcohol is used as a solvent for

barium bromide, and carbon disulphide for antimony chloride in order *to* increase pigment absorption.

With the exception of the cobalt acetate potassium permanganate double-dip bronze, none of the double decomposition processes have acquired any commercial importance.

(B) The coating may be dipped into a solution of a heavy metal salt which is hydrolysed within the coating to give the pigment. This method may be used to obtain an old brass colour by immersion in 2% ferric ammonium oxalate solution or 5-10% ferric oxalate with 2-5% ammonium oxalate. Other solutions that may be used include also an acetic acid solution of ferric chloride, a mixture **of** ferrous sulphate and potassium ferrocyanide, and potassium permanganate solution. The ferric hydroxide precipitate may be toned with gallic or pyrogallic acid to a deeper colour,[61] and one process provides for the precipitation and toning in a single solution with a suitable stabilizer.[62]

As has already been described in Chapter 8, the main use of the ferric ammonium oxalate gold has been in architecture, and many anodizers still have a gold dyeing tank today. The Sanodal 4N dye in the Sandoz range is also of this type.

(C) Sulphuric acid coatings produced with alternating current contain significant amounts of sulphur and this fact may be utilised for producing colours by dipping the coating into a dilute metal salt solution and 'developing' the colour in boiling water during sealing. Colours obtained in this way are shown in Table 10-14 and may be intensified by dipping in ammonia solution before the colouring treatment.

Kape[63] has studied the colouring of a.c. sulphuric acid anodized films in some detail and his work has been described in Chapter 7 (page 485).

(D) The anodic coating may be electrolytically coloured by immersing it in a metal salt solution and passing alternating current between the work and a suitable counter electrode. This is now by far the most common form of inorganic colouring and, as its main application is in architecture, it has been discussed at length in Chapter 8.

(E) Direct current has also been used *to* produce colour effects by both electrodeposition and electrophoresis, but less frequently.

Shenoi and Indira[64] anodized aluminium in a 20% phosphoric acid/12% sulphuric acid mixture (volume) for 5-10 minutes at 12-15 volts and investigated a procedure for obtaining black non-metallic coatings by electrodeposition from a solution containing:

nickel sulphate	I20 g/l
sodiurn acetate	20 g/l
ammonium molybdate	30-40 g/l

used for 10-40 minutes at 30-40°C and from 2-5 amp/sq ft (0.21-0.54 A/dm^2).

TABLE 10-14

Colours obtained on a.c. sulphuric acid coatings

Salt solution	*Concentration (% w/v)*	*Colour developed on hot water sealing*
silver nitrate	1	olive brown
lead acetate	2.5	mahogany
cadmium acetate	1	yellow
cobalt acetate	1	black
copper sulphate	2.5	green
tartar emetic	1	orange
ferric ammonium oxalate	2	black
ferrous ammonium sulphate	1	olive green
selenium dioxide	1	canary yellow
bismuth ammonium nitrate	1	brown
stannous sulphate	1	brown-yellow
potassium permanganate	1	pale yellow

Schmidt[65] has used electrophoresis at low currents and high voltages to impregnate the porous structure of as-formed coatings with alumina from aqueous suspensions in order to improve the stability and performance of coatings when used in the high vacuum conditions encountered in space vehicles, where unsealed coatings are preferred. He has also deposited colloidal carbon from aqueous and alcoholic suspensions to give black coatings for assisting temperature control, and other materials may be deposited. The main requirement is that the particle size of the material in suspension should be less than 13 millimicrons.

Alameda[66] in Madrid has studied the impregnation of anodic coatings with various metals and by various methods including electrolytic, electroless catalytic plating, chemical reduction and thermal decomposition, and he also made a study of the properties of ferromagnetic materials inside the matrix of the oxide coating. The coatings impregnated with iron, nickel or cobalt are not ferromagnetic either before or after annealing at 500°C, and the coatings on 99.5% aluminium do not lose their highly insulating character when impregnated with metals. The electroless methods were able to deposit metal inside the matrix and to build adherent coatings over the film. The high temperatures required for pyrolytic decomposition caused crazing of the films, and in the case of materials such as cobalt acetyl acetonate which volatilises at 130-170°C but does not decompose until 300-400°C it was necessary to use thermal shock tactics with a torch flame or by immersion in molten tin. Cobalt impregnation resembled stainless steel. Apart from the appearance the low density films of gold, rhodium, platinum, palladium, silver, etc., obtained by these methods in the form of an array of metal islands

disseminated in a highly insulating matrix have applications in electronic devices or light amplifiers.

Work in Japan has examined the magnetic properties of metal deposits in anodic coatings and Pilot Pen Co. have applied this in the production of magnetic recording disks.[67,68,69] Fe, Co, Ni, Co-Ni, Fe-Ni and Fe-Co were electrolytically deposited into various porous anodic coatings and particularly good recording and memory properties were obtained with the Co-Ni and Fe-Ni deposits. Electroluminescence in anodic films is another property extensively investigated by the Japanese and reviewed by Tajima and others.[70,71] These methods have been described in more detail in Chapter 7.

More recently workers in Japan have described methods of colouring based on deposition of fine pigments within the pores of the anodic film. In one method[72] an aqueous dispersion of an organic pigment or carbon black, which is finely divided to give a particle size in the range of 3 to I50 nm, is deposited within the pores by electrophoresis. A film having larger diameter pores than normal is needed, and this is produced by high voltage anodizing, for example in oxalic or phosphoric acid. Voltage:; of the order of 150 V are used, and a 10 micron film is produced. Additional pore enlargement can also be achieved by immersion after anodizing in 5% phosphoric acid solution. The 10%carbon black dispersion was deposited by electrophoretic treatment, with the aluminium as anode, at 60 V d.c. for 1 min at 25°C. **A** carbon electrode was used as the cathode. The aqueous carbon black dispersion was produced by milling 100 g of carbon black and 5 g of sodium polyacrylate as a dispersant per litre of solution for 5 hours.

In another process[73] a pigment, **a** dispersant **and a** water-soluble organic solvent are used in combination with a water-soluble amine.

3. SPECIAL PROCESSES

Multi-coloured effects

Nameplate processes

The production of nameplates and other articles in two or more colours is now very common, but the procedures are apt to be confusing because the end result can be achieved by various routes, which represent permutations of the techniques available. The object is selective application of a colour to the surface, or selective bleaching, or selective application of a lacquer or resist that assists the achievement of this objective. The techniques depend on the availability of suitable resists, or of coloured inks of the correct properties and consistency.

The resist materials, or Reserves, are non-colouring pastes, specially formulated for easy application, rapid drying, accurate reproduction of patterns, and many

other requirements. Commercial products are Reserve White SG (suitable for silk-screen printing), Reserve Black 1000, Reserve Orange 6000 (for pre-blackened sheet), and Vifa-Coat 2000 (an easily removable ink giving sharp outlines). The inks or colour pastes are linseed oil-based formulations containing solvent-type dyes of low molecular weight which can readily migrate from the paste into the anodic film. Speiser[74] has listed the many requirements which both the inks and resists must fulfil before they can be considered satisfactory. The inks may also act as resists, since when they are applied and dried, the surface can be coloured in an aqueous solution of a second colour in those areas which are not protected by an ink.

Occasionally the reserve pastes are applied by hand on small articles such as badges, etc., but more generally the method of application is by means of a silk screen or by offset printing. The 'silk' screen is a fine mesh made of nylon or terylene with selected areas blanked off by means of patterns made in a special adhesive-backed paper, or prepared photographically by the bichromate-gelatine procedure. Offset printing machines are of the flat bed or rotary type where the ink or resist is conveyed to the sheet by means of a master plate or negative, which is a specially prepared roller or lithographic plate. The printing pastes are not usually very suitable for offset printing because they do not act rapidly enough, but they are very suitable for silk-screen work.

A typical example of a sequence used to produce a multicoloured pattern by means of the offset lithographic process would be the following:[75]

1. Anodize, rinse thoroughly and dry.
2. Using the offset process, print those areas that are to remain uncoloured with resist ink.
3. Dye with the first colour, rinse rapidly and dry.
4. Parts required in the first colour are offset printed with the resist ink again.
5. Bleach the unprotected areas in 10% nitric acid.
6. Dye again in second dye; rinse and dry.
7. Repeat stages 2 to 6 for as many colours as required.
8. Remove the resist with a suitable solvent.
9. Seal in boiling water.

There are variations on the above theme and in Fig. 10-5 are summarised a number of procedures for obtaining sheets with areas in one colour, or two-coloured effects, but the procedures can be adapted for several colours and other routes are implied. For instance, black on gold may be prepared by aqueous dyeing of the lighter colour, resist printing of the gold areas and overdyeing the gold with black.[74,76]

The reserve pastes are fairly resistant, but will not withstand etching or re-anodizing. In this case it is the practice to sprinkle finely powdered asphalt onto the resist and heat it to 130°C to melt it, thereby producing a coherent film which

will allow deep etching to produce patterns with depth or contrast, and if necessary to follow with a second anodizing treatment.

Less regular patterns can be applied by having an appropriate resist material dispersed in or on the surface of an aqueous solution. Thus Yoshida Kogyo[77] have suggested dipping an article into a coating bath containing streaks of an acrylic lacquer on its surface, in order to produce a 'wood-grain' effect after anodizing. These 'wood-grain' finishes have been widely used in Japan for architectural applications, and other, more direct, ways of producing them have already been mentioned in Chapter 8 (page 618). The use of a floating oil film as a resist to give differential electrolytic colouring effect has been described by Tateyama Aluminium.[78] Ugine Kuhlmann, on the other hand, have used a.c. treatment in a nitric acid electrolyte containing a fluorinated anionic surface active agent, to produce aluminium with a 'lizard-skin' appearance.[79]

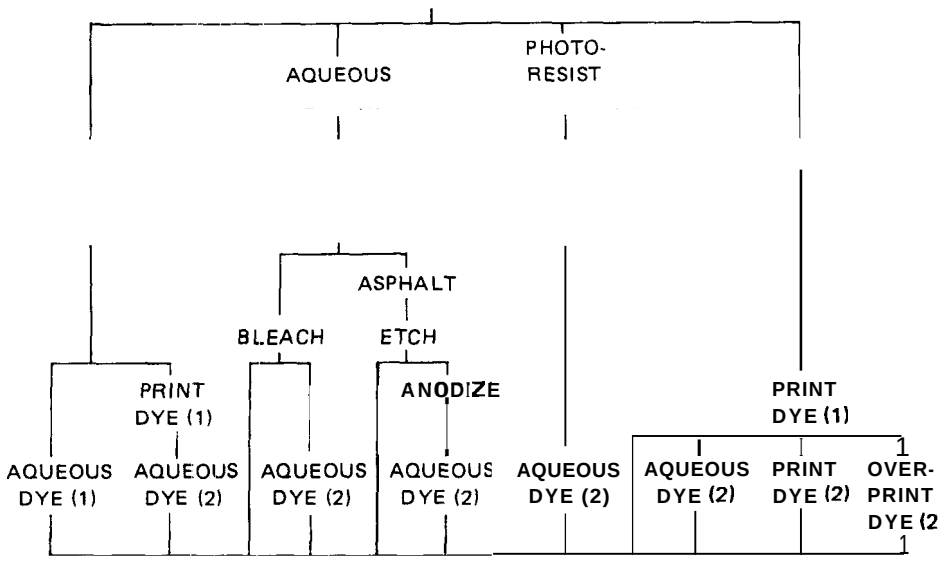


Fig. 10-5. Some procedures for obtaining sheets with areas in one or two colours

Reynolds Metals, suggest the use of two anodizing treatments having a different appearance to produce patterned effects.[80] This process has particularly been used to produce gold and bronze patterns of varying shades using integral colour

anodizing processes. The panel is first anodized in an integral colour process to a relatively light shade and is partially sealed. A vinyl silk screen resist is then locally applied and the anodic film etched away in the non-protected areas. A second anodizing treatment to give a darker shade of bronze is then carried out and the process repeated using accurately registered silk screens for as many different bronze tones as are required. Finally the panel is completely sealed and the resist removed in a suitable solvent.

More recently a laser-based process, which is said to depend on the unique interaction of the CO, laser with anodized aluminium, has been suggested for producing a variety of dyed colour images.[81]

Solvent-soluble dyestuffs

The introduction of printing pastes based on solvent-soluble dyestuffs has represented a notable advance in the simple production of multi-coloured effects on anodized aluminium. Some of the printing pastes developed in the graphic industries will provide strongly-adherent films which are capable of resisting subsequent alkaline etching or even sulphuric acid anodizing; such materials constitute effective resists but are generally less able to transfer the colour to the underlying film, and they can also be very difficult to remove, easy removal being of course an important requirement for the colouring of anodized aluminium. Also, they contain a high concentration of dyestuff and can be expensive. A range of inks of this type (e.g. Sinvaluminum) have been marketed specially for serving the dual purpose of colouring and resisting.[82]

If however the demand for a resisting effect is limited to the protection of the underlying surface from a subsequent aqueous dyeing operation, it is possible to incorporate into the ink a hydrophobic substance which will penetrate the oxide layer to produce a hydrophobic barrier. Such substances are paraffins and chlorinated paraffins, paraffin oil and soluble resins such as colophony (rosin), terpenes, terpene alcohols and long chain alcohols. Preparations of this kind possess a relatively high dyestuff yield and are easy to remove. Printing pastes of this type are covered by patents and marketed as Aluprint pastes,[74] and their use has been described by Sandoz.[83] The Aluprint 2N pastes are intended for simple applications such as single and multicolour signs and have no reserve properties, and the Aluprint 3R pastes are used for more complicated signs involving relief patterning or multiple anodizing or dyeing treatments. The plates are dried after each printing operation and this is preferably carried out in warm air (70°C maximum). During drying the dyestuff contained in the printed paste diffuses into the oxide film, leaving the resin and thickening agents on the surface, and this is removed after final sealing.

Printing pastes based on solvents are generally less light fast than colours based on aqueous dyes. Substances which penetrate into the oxide with the dye may impair the performance to a degree which is unpredictable for any individual dye. Speiser[74] has referred to a yellow azoic dye which showed hardly any change

in light fastness when used with Abitol (a hydro-abietylitic alcohol), while a navy-blue, known as very fast, had almost completely bleached out after 500 hours in the Fade-0-meter when printed in the same way.

Inks have been developed where the dyestuffs are incorporated in a carrier in which they are quite insoluble, and after application to the anodized surface they are subjected to a solvent for both the carrier and the dye, which causes the latter to penetrate the coating.[84]

It has also been proposed to use a water paste composition consisting of water soluble gums and starches, dye solvent tniscible with water, and different colour dyes. After application of the uncoloured coating the article is immersed in water at 54-88°C to allow dye penetration, sealed in nickel acetate and the protective coating removed mechanically.[85]

These solvent based dyestuffs are the basis of the system for direct painting on aluminium, which is generally referred to as 'Aluchromy'. This process has been described by Bosdorf[52] and Victor[86] and is really used to produce individual works of art, rather than functional labels or nameplates.

Photographic resists

One of the methods indicated in Fig. 10-5 is a photographic resist process. In this method the oxide film is coated with a layer of a photo-sensitive resist ink containing bichromate and a carrier such as gelatine, albumen, polyvinyl alcohol, etc. The photosensitive layer is dried in the dark and exposed through a negative. The parts exposed to light are hardened and the rest of the layer can then be easily washed off. The parts of the film not covered by the hardened resist ink can now be dyed normally with aqueous dyestuffs. Processes of this kind have been in use for many years for producing chemically engraved patterns as well as for the selective colouring of anodized aluminium, and improvements have been protected by patents.[87,88,89] Very fine detail can be reproduced by such processes, which are frequently used for optical or electronic instruments. More recent examples also use U.V. light-sensitive, photocurable polymers,[90] and irradiation of diazo compounds which are capable of forming a dye."

Péchiney have disclosed a multiple colouring method which is particularly suitable for use with electrolytic colouring processes,[92] and the technique has been described by Patrie.[93] The anodized material is coated with a bichromated colloid and exposed to light through a positive photographic pattern. The print obtained is developed and the material electrolytically coloured in a conventional nickel, cobalt, copper or silver based electrolyte. The remaining colloid is then removed and the film sealed in boiling water. The interesting aspect of this technique is that areas of the colloid which receive insufficient light are not rendered completely soluble, so represent a partial barrier to penetration of the metal ions in the electrolytic colouring bath. By this means, therefore, with an image with tone gradation, the tones are reproduced by varying depths of bronze or maroon shades after electrolytic colouring.

Contact processes

There are also simpler methods of producing multi-coloured effects in which an intermediate carrier is employed to convey the dyestuff to the anodized surface. In one process[94,95] a paste of linseed oil and dyestuff is printed on a sheet of thin paper, and after drying is transferred from the paper to the anodized surface by means of heat and pressure. This process is also referred to as sublimation dyeing or transfer printing, and it has been described by Dixon.[96] A wide range of dyestuffs suitable for transfer printing are available but the limitation of the process is the availability of suitably printed papers. Clearly **a** very large quantity of a particular item has to be required, before the production of the appropriately printed paper can be considered. Nevertheless several patents relating to this colouring technique have appeared in recent times.[97,98,99,100] Another technique[101] uses a foil of polyvinyl acetate resins on which solvent-soluble dyestuffs are printed. The foil is then placed in contact with the anodized surface and heated to approximately 100°C. It can be removed later in boiling water.

The change of colour which some dyes undergo with pH has been utilised in one process[""] to produce a colouring medium with thymol-sulphonic phthalein which may be red, violet, brown or yellow according to the pH value. The ink is applied to the anodized surface and then locally exposed to the influence of a base or an acid to produce various colours in the surface.

The techniques already described are mostly only applicable to flat or nearly flat surfaces, but a novel method of multicolouring shaped articles has been developed in Japan.[103] In this process a thin starch or polymer based film, which can be printed with a pattern, is floated on the surface of a suitable liquid. **An** object immersed in this bath picks up the film, which can either represent a resist pattern for immersion dyeing or act as a printing medium itself by transfer dyeing. After colouring the unwanted film is removed.

Plant

Automatic plant has been used for multicolour dyeing and a detailed process sequence for a plant of this type, capable of treating 4,000-5,000 sq ft per day, has been described by Millett[104] (see Fig. 10-6). The resist is applied by inking rollers to the printing plates and from this via a rubber-coated cylinder to the anodized plate. The latter is then dyed with the minimum of delay and the printing process repeated after each dyeing, using the printing places for each colour in sequence from the lightest to the darkest colour. Parts of the first colour which are not masked are bleached with a dilute sodium hypochlorite solution. When the sequence is complete, the resist is removed in an o-dichlorobenzene-type stripper, the plate is rinsed and sealed, and finally buffed with a soft calico mop.

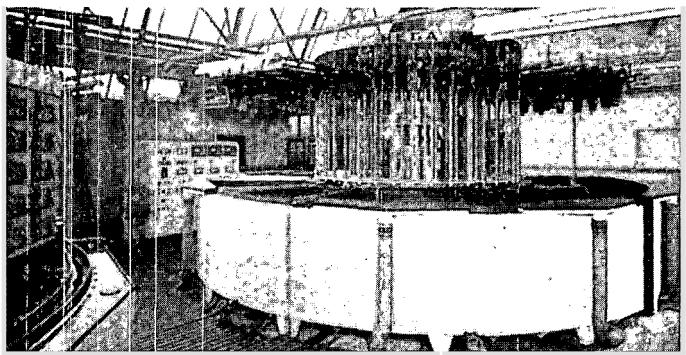


Fig. 10-6. 'Carousel' design machine lor the automatic anodizing and dyeing of aluminium name plates

Photographic processes

Similarly to inorganic dyeing processes, light-sensitive salts may be adsorbed into the pores of the coating, as in the Seo photographic process.[105,106,107] Both sulphuric acid coatings. and chromic acid coatings[108] may be employed for this process, and the work may be either immersed in a solution of the photosensitive material or, where these are insoluble (e.g., silver halides), they may be produced within the film. In the first class are solutions containing 1% iron chloride and *3%* tartaric acid, iron-silver mixtures, etc., which are developed with gallic/oxalic acid mixtures, and diazo salts. Alternatively, the work is immersed first in a solution of the ammonium halide and subsequently in silver nitrate solution, or it may be prepared by centrifuging the work with a highly concentrated solution of ammonium chloride and sodium bromide, drying and immersing for 10 minutes in 10% silver nitrate solution at 30°C, with subsequent rinsing and drying. This is developed with acid developers such as potassium oxalate, ferric sulphate or citric acid.

In a Russian process,"" which is the same as the Seo photo process, anodic oxide coatings of 10-15 μm (0.4-0.6 mil) thickness are obtained in 10% sulphuric acid at 30°C, 1.5 A/dm^2 (15 amp/sq ft) in 45-60 minutes. Subsequently silver bromide is precipitated by immersion in 10% potassium bromide followed by immersion in 10% silver nitrate solution, the cycle being repeated many times as it was found that even after 39 immersions only a third of the pore volume was filled with silver bromide. The highest speed in developing is obtained with an amidol developer, though hydroquinone can also be used. Higher potassium bromide concentrations are necessary than in normal developing to prevent fogging.

The exposure is carried out with a carbon arc behind a negative of glass, film or stencil, with an average exposure time of 1 minute at a distance of *22.5* cm (9 in) from a 2 kW lamp. Fixing is carried out in the ordinary way with 'hypo' solution, after which the film is sealed in a nickel or cobalt solution.

Colour photography may be carried out by the three-colour process, i.e., exposure to three negatives in turn, producing the red, yellow and blue primary colours respectively. By an alternative method,'"" the work is treated for 15 minutes at 20°C in a 1% glue solution, then at 85°C for 1 hour in a solution containing 0.25 parts by weight of an ester of a leuco dye,[111] 0.12 parts by weight of 80% acetic acid, 0.015 parts of cellulose spent liquor, 0.01 parts by weight of a formaldehyde-bisulphite addition product and 100 parts of water. A final treatment is given in 0.2% 66" Be sulphuric acid and 0.1% sodium nitrite at 70°C.

Blue prints can be prepared by impregnating the surface with 300 g/l ferric ammonium citrate + 200 g/l potassium ferricyanide, which after exposure are developed in 0.1% hydrochloric acid.'"

Sepia toned prints can be produced by impregnating the surface with a solution prepared by adding 260 g ferric ammonium citrate + 92 g citric acid in 1 litre of water (or 320 g ferric ammonium oxalate + 64 g oxalic acid) to 100 g/l silver nitrate with sufficient citric acid to take up any precipitate formed. After exposure a pale yellow colour is obtained which may be deepened by using one of the usual gold-toning baths. The developed photograph is fixed in 3% sodium thiosulphate.[112]

A process has been patented for impregnating the anodic coating with light-sensitive diazo-compounds together with a dyestuff developer,'" and another uses **naphthoquinone-diazide-sulphoacid.""** A further process uses potassium permanganate + lactic acid + potassium formate as the light-sensitive medium: after exposure the film is locally dyed with hydrochloride of aniline (for bluish violet), paratoluidine (for red) or naphthylamine (for bluish-grey to black).[115]

Jogarao *et al.* have reviewed in detail the procedures for producing photographic images in the anodic film,[116] and elsewhere they have discussed stencil, lithographic, photo-offset, photographic and silk-screen printing of aluminium nameplates.[75] Thomi[117] has also discussed the methods for producing photographic prints, and Speiser[76] and Patrie[93] have reviewed again the various procedures for multicolouring of anodized aluminium.

Absorption of other compounds

Lastly one would mention the possibilities of the anodic coating for absorbing a whole range of substances which remain invisible but whose presence may be made known by other means, and one feels that the potentialities implicit here have not been explored as yet. Fluorescence tests are known of course for demonstrating the presence of certain materials which have been adsorbed by the anodic film.

One unusual application which makes good use of the otherwise unfortunate propensity of the anodic coating to absorb phosphate very readily has been to prepare small grains of aluminium which are labelled with ratio-active phosphorus by anodizing wire and absorbing phosphate ions in the presence of trivalent chromium which helps the stronger fixing of ^{32}P. The wire is then cut into 5 mm lengths and used in interstitial 8-therapy for the treatment of malignancies.[118]

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CHAPTER 11

Sealing Anodic Oxide Coatings

1. GENERAL NOTES

One of the earliest observations regarding the anodized surface of aluminium was its similarity to other porous media in its susceptibility to fingermarking, or its tendency to become coloured or stained in contact with dyestuffs or other materials. By analogy the first ameliorative action was to apply an oil or wax or some other organic top coating, and if resistance to staining were the only criterion of an acceptable surface then such treatment would have been quite adequate. A number of wax formulations were in fact devised and some of these still find application. At the same time the ability to absorb inorganic salts from aqueous solution was noted, and attention turned naturally to materials like chromates, dichromates and silicates because of their well known beneficial effect in enhancing the corrosion resistance of aluminium. Thus when the first comprehensive account of anodizing was published by Jenny in 1938, less than half a page was devoted to sealing in hot water and only the above methods were accorded any importance.[1]

Modern notions on sealing started from the observation that the propensity of the anodized layer for absorbing dyes is one that decreases spontaneously with time, and this was attributed to a reaction between the aluminium oxide and the water vapour in the air. From the earliest times it has been believed that in sealing, the anhydrous oxide is hydrated, expands and fills out the pore spaces, the boehmite-type $Al_2O_3.H_2O$ crystal form being produced with resulting increase in elasticity and decrease in hardness and wear resistance. That anodic oxide coatings lose their absorptive power when in contact with steam was first recorded by Setoh and Mitaya.[2] It was found that the hydration resulting from steam treatment was

not only more effective than any wax or oil in sealing the surface, but the reaction was irreversible, the resulting work being more resistant to leaching or fading and the corrosion resistance enormously enhanced. It is doubtful whether anodizing would have achieved its present importance without the complementary property of responding to sealing in this manner. Although the importance of the operation was understood from the start, a good thirty years were to elapse before one could discuss the mechanism with any great degree of confidence, and it continues to be a controversial subject.

The word 'seal' itself calls for some comment. It is frequently used in connection with other porous surfaces such as wood or plaster where the term is similarly applied, or more often still to closing an opening, but the Oxford dictionary scarcely mentions this usage, while devoting about three pages to concepts associated with religion and royalty. The French 'colmatage' is etymologically more precise since it specifically describes a process of filling up holes as in a filter or sieve, and is more appropriate than the Italian 'fissagio' (fixing) or the German 'Nachverdichtung'. Nevertheless, the English term has brevity to commend it and seems to be acquiring an international status: one might turn up the Oxford dictionary and find this definition of seal: 'to decide irrevocably the fate of a person or thing; to complete and place beyond dispute or reversal', and where anodic films are concerned this would be prophetically apposite since, for many applications, the performance depends on the quality of the sealing operation. The term has more recently aroused considerable international discussion in connection with the low temperature processes that have developed widely. In this case the agreed term has become 'cold impregnation'. This is because sealing, for example in the new European Standard EN 12373-Part 1:2001, is defined as 'treatment of anodic oxidation coatings on aluminium to reduce porosity and the absorptive capacity of the coating by hydrothermal processes carried out after anodizing'. The key word here is 'hydrothermal' and it was argued that the low temperature processes produced a different sealing mechanism, which did not involve the same hydrothermal process, and could therefore not be called 'sealing'. Nevertheless the term 'cold sealing' is often used.

2. SEALING IN HOT WATER, STEAM AND VAPOUR

Sealing in deionised or distilled water at or near to its boiling point is the simplest technique and the most universally useful; it is also regarded by many as the most effective method. At first glance both the mechanism and practice of sealing are quite simple. The conversion of aluminium oxide to one of its hydrates, probably boehmite, is accompanied by an increase in volume which bridges over and closes up the porous structure to give a coating which is both impervious to liquids and more resistant than the unsealed coating to most chemical environments by virtue of its inherent stability and greater resistance to chemical attack. While

such an explanation is given and accepted for general purposes it is quite well realised that the facts and figures point to a considerably more complex situation.

Effect on anodic oxide coating

In hot water sealing of industrial anodic oxide coatings, the aluininium oxide, both barrier layer and the porous coating, is at first hydrated. After a short time, however, the circulation of water through the pores is impeded, and only the surface layer of the coating continues to be hydrated until the upper portions of the pore channels are plugged.'

Hoar and Wood[4] studied the sealing mechanism by measuring the electrical impedance of sulphuric acid and anodic oxide films on 99.99% aluminium sealed in a variety of media arid came to the conclusion that the pores become filled by inward movement from their sides at the same time as they are plugged at the surface (see Fig. 11-l) until the pore volume is about 99% filled.

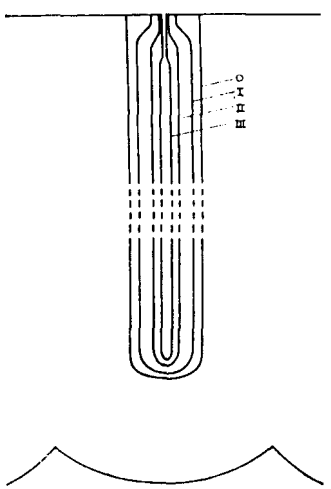


Fig. I I-I. Schematic diagram of the progress of sealing. **O** is the wall of the unsealed pore while I, II and III are successive stages of sealing[3]

Thus, the structure of the anodic oxide coating does not appear to be significantly changed by hot water sealing, although Ginsberg and Wefers[5] have observed, under the electron microscope, the formation of needle-shaped crystallites both in the interior of the oxide coating and between them. These crystallites appear to grow norinal to the fibres and appear to consist of γ-AlOOH. After a time the

crystals form a coherent layer which grows inwards from the surface. According to these authors, the formation of boehmite in hot water sealing:

$$Al_2O_3 + H_2O \rightarrow 2AlO(OH),$$

involves transport of hydroxyl ions through the lattice under a high field. The latter is due to hydrogen ions which diffuse thermally through the film.

A simple illustration might put the problems of sealing into perspective. If a fragment of anodic film anodized in sulphuric acid and measuring 2 mm square ($^1/_{12}$ inch square) were magnified to cover the 147 square miles of the Isle of Wight, then the pore population' would equal the population of the world, and each would be represented by a 15 cm (6 inches) diameter pipe standing 45 cm (18 inches) from its neighbours. For a good 30 micron coating each of these pipes would stand as high as the Eiffel Tower, resting on a 20 cm (8 inches) barrier layer. Such dimensions are not easily visualised and discussions on sealing should be considered against such a background.

Spooner[7] calculated that if the hydration is a uniform effect all over the surface then in normal sealing, pores of 120 Å diameter would be reduced by only 14 Å and that a lot more sealing would not affect the situation much. He deduced that most of the effect begins at the film surface where the pore is physically closed, or nearly so, and that it progresses only very slowly with increasing time into the depth of the pores. It has been long debated how far down the pores the coating would seal, but studies at UMIST[8] by infra-red spectroscopy have shown that sealing will ultimately continue down to the barrier layer if prolonged for about 24 hours.

Spooner[7] has given the figures in Table 11-1 for the composition of the sealed and unsealed coating, and they are very similar to the compositions determined earlier by Mason.'

TABLE 11-1

Composition of sulphuric acid coatings (Spooner[7])

Constituent	*Unsealed Coating*	*Water-sealed Coating*
Al_2O_3	78.9%	61.7%
$Al_2O_3.H_2O$	0.5	17.6
$Al_2(SO_4)_3$	20.2	17.9
H_2O	0.4	*2.8*

Scott determined the composition of sealed sulphuric acid films in 1945[10] and found Al_2O_3 72%; H,O 15%; SO, 13%. These measurements were made on very thick porous coatings obtained by anodizing foils to completion. Twenty years

later" he used a different analytical technique to analyse normal coatings detached from the metal surface and then sealed, and obtained results which were practically identical with the previous ones. Recalculating Spooner's values into the simple form used by Scott we get:

	unsealed	*sealed*	
		Spooner	Scott
Al_2O_3	*85.3*	82.0	72%
H_2O	*0.5*	5.4	15
SO;	14.2	12.6	13

This suggests that the films used by Spooner were partially hydrated and to a lesser degree than those of Scott, but both investigators agree that not all of the alumina becomes hydrated and that not all of the water present is in the combined form.

Investigiations *of* sealing mechanism

The mechanisms of sealing have proved an intriguing study and in recent years a wealth of inventive genius has been poured into the subject of anodic film examination using the following techniques:

(a) Infra-red absorption studies where identification of the types of alumina bond gives an indication of the type of oxide present.[8,12,13]
(b) Exchange reactions between hydrogen in the film and its isotope deuterium, indicating which OH groups are at the surface and available for exchange.[8,13]
(c) Impedance and capacitance measurements to calculate the extent of pore closure.[4,14,15,16]
(d) Electron microscopy to examine pore structure and formation of crystalline growths.[8,17,18,19,20,21,22]
(e) Weight changes on sealing.[7,23]
(f) X-ray diffraction and electron diffraction studies."
(g) X-ray emission spectroscopy."
(h) Differential thermal analysis.
(i) Radioactive tracer studies.[26]
(j) Electron probe micro-analysis on cross sections of films.[14]
(k) ESCA. spectrometry.[27]
(l) Electrochemical Impedance Spectroscopy.[28,29]

As a result of all this work a reasonably accurate account of hot water sealing is now possible.

By means of X-ray spectroscopy Spooner and Forsyth[25] established that sealing of the oxide coating begins at the surface and slowly proceeds towards the interior. The as-formed anodic film, which is amorphous Al_2O_3, produces no patterns on X-ray diffraction, but as sealing proceeds the characteristic Debye-Schemer patterns indicative of a crystalline form of oxide are seen to originate at the surface and move inwards as they become more pronounced. It has been rather assumed that the rhombic crystalline form is that of the monohydrate, boehmite ($Al_2O_3.H_2O$), but the material in the coating is not quite identical with this product.

Hoar and Wood[4] had also detected long term changes in the anodic film structure by means of impedance measurements of the coating when immersed in a neutral electrolyte employing a.c. bridge techniques. They found that while an unsealed 15 micron coating produced in sulphuric acid showed a pore resistance of 20-25 ohm/cm^2 at 19°C, the resistance was increased to 4000 ohm/cm^2 after 30 minutes sealing, and to over 100,000ohm/cm^2 after sealing for 24 hours in nickel acetate at 95°C. This suggests that commercial sealing might be improved by extending the treatment beyond the customary 30 minutes, but Spooner[30] has in fact reported that when sealing was extended from 30 to 60 minutes he found a reduction in the corrosion resistance of panels exposed in an industrial atmosphere. There is great doubt, therefore, whether the continual increase in impedance, which is noticed on prolonged sealing, is accompanied by any commensurate enhancement of the corrosion resistance of the work so treated; this is a point of some importance since the fashion is growing of monitoring and testing the degree of sealing by means of such impedance measurements.

Hoar and Wood[4] have also found evidence that allowing the coating to dry between anodizing and sealing may slow down the sealing action considerably. This observation is allied to an earlier patent in which anodized parts are rinsed and then dried at 88-100°C for 10 minutes before sealing in boiling water in order to obtain particularly hard coatings.[31]

Infra-red spectroscopy should provide a useful tool for detecting the various forms of aluminium oxide because each form of oxide will have its characteristic absorption bands, and investigations along these lines have been pursued by Frederickson[32] and Dorsey.[33] These bands are numerous, however, and some are weak, and it is easy to misinterpret the data. In a very detailed study of the aluminium-water reaction, Vedder and Vermilyea[13] have presented, amongst other things, a full description and analysis of the absorption bands in the infra-red spectra. There are spurious bands associated with the stretching vibrations caused by molecular water in the ambient film which have been incorrectly identified.

O'Sullivan, Hockey and Wood[8] have examined the infra-red spectra of anodic films in the as-formed condition and after evacuation to eliminate effects of absorbed water. Then they placed the samples in contact with heavy water, deuterium oxide, to permit an exchange reaction between deuterium and the hydrogen in the hydroxyl groups in the anodic film. This would only occur in the regions which were accessible to the heavy water, that is, throughout the thickness in the as-formed film, and only at the surface when completely sealed. These changes could readily be seen

by changes in the absorption bands. They demonstrated (Fig. 11-2) that in the unsealed film a certain amount of water could be removed by evacuation, and that a free exchange with deuterium was possible. As sealing proceeded the water became locked in the film and less exchange with deuterium took place. For a thick sulphuric film the sealing at 10 minutes is limited in extent, but it is much more effective after 30 minutes as shown by the overlapping curves (a) and (b) in the third graph, while sealing is complete after 24 hours, when neither evacuation nor deuteration produce any change. These authors were very cautious about proceeding any further with the interpretation, and concluded that 'no unequivocal identification of individual alumina hydrates can be made from a consideration of this region of the spectrum, as has been attempted previously *by other* **workers.'**

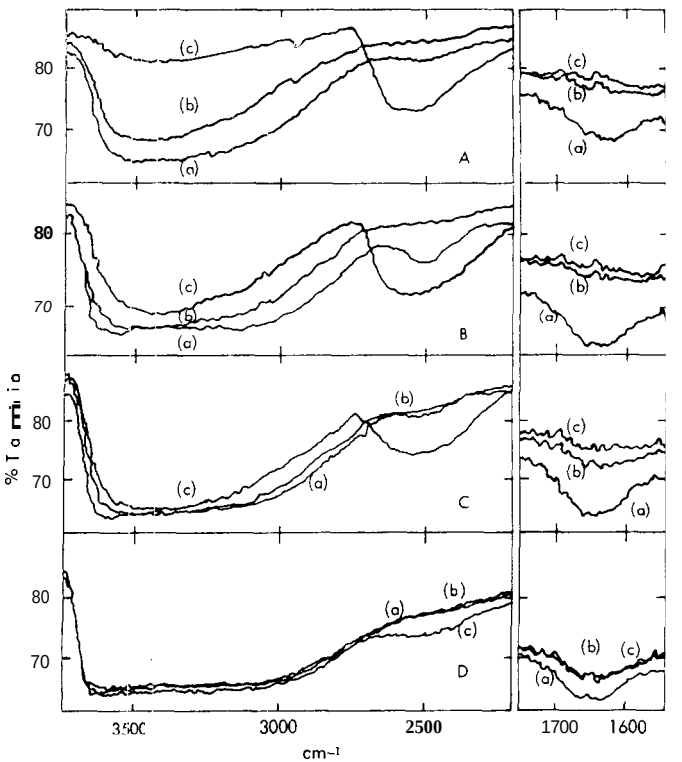


Fig. 11-2. Infra-red spectra of an unsealed oxide film[8]

A. Unsealed
B. Sealed for 10 minutes
C. Sealed for 30 minutes
D. Sealed for 24 hours

(a) under ambient conditions
(b) after evacuation
(c) after deuteration

In considering the reaction products Vedder and Vermilyea" concluded that the main product in the hydration reaction is a 'pseudoboehmite' of extremely small crystal size, with the majority of its hydroxyl ions spatially arranged in much the same manner as in boehmite, but with an excess of hydroxyl ions that have not found a boehmite-like environment. Its composition is $Al_2O_3.nH_2O$ where n is between 1.5 and 2.5.

Wefers,[18] in one of the most complete studies of sealing mechanism, describes the chemical reactions that occur in the hydration of an aluminium oxide film. Owing to the very small size of the particles making up the anodic film structure these will dissolve when exposed to water at elevated temperatures. This dissolution mobilizes the incorporated acid anions (e.g. sulphate) which decrease the pH near the oxide/liquid interface. When the aluminium concentration exceeds the solubility product, hydrated aluminium oxide is re-precipitated on the pore wall surfaces and at the outer film surface. Within the pores the rate at which this reaction occurs is controlled by diffusion and is influenced by the pH of the sealing solution and its chemical composition. At the film surface convection essentially eliminates concentration gradients, and the dissolved aluminium is rapidly precipitated, forming a voluminous layer of hydroxide gel. Increasing pH facilitates the formation of crystalline boehmite and the highest pH is reached at the solid/liquid interface where acid anions are leached out of the gel and rapidly dispersed. Crystalline boehmite, therefore, first forms on the external surface of the film, and the relative abundance of solution there facilitates crystal growth at the expense of gel formation.

Later workers at UMIST[28] have used electrochemical impedance spectroscopy for studying the sealing process, both at boiling point and at room temperature. This study, by interrupting the sealing process, revealed the importance of pore hydration resistance after the plugging or bridging over of the pore mouths. The importance of gel-like material development within the pore volume at the sealing temperature was established, and the work showed the compaction of the gel-like material in the form of more crystalline hydrated aluminas as a consequence of the reduction to room temperature, the so-called 'ageing' effect. Modifications to the equivalent circuit of sealed anodic films were made to allow simulation of impedance response, and this allows consideration of this method as an on-line monitoring technique for sealing. This will be discussed again later in the Chapter.

Study by the same technique of several sealing methods was made by Mansfeld *et al.*[29] The methods included boiling water and nickel acetate, as well as the use of cerium acetate and yttrium acetate solutions. Of the latter, cerium acetate in particular gave results equivalent to nickel acetate sealing.

Workers in Greece[34] examined coatings sealed for up to 4.5 hours and noted the amount of water retained, and its ratio to the pore void volume. They confirmed the rapid plugging of the pore mouths and the complete blocking of the neck of the pore, and this significantly retarded the hydration process taking place behind it. For an average pore, the plug was found to form for up to half the total pore length present. They suggested that the formation of a gas phase, which occupied a part

of the unfilled pore volume, was in part responsible for the hydration retardation.

The sealing process can therefore be summarised as an initial dissolution reaction at the film arid pore wall surfaces with release of the anion, reprecipitation of this material on the pore walls to give a pseudoboehmite gel, and preferential conversion of the gel to crystalline boehmite at the film surface. This effect is shown diagrammatically in Fig. 11-3.

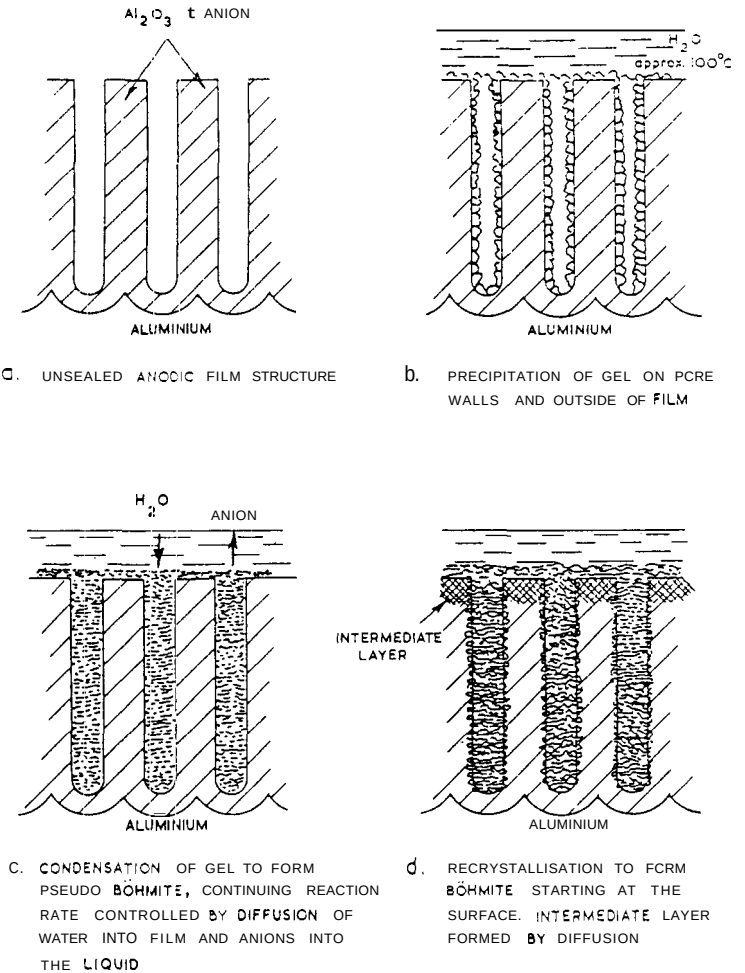


Fig. 11-3. General mechanism of water sealing of anodic oxide coatings[18]

A feature indicated in Fig. 11-3, but not previously mentioned, is the presence of a so-called 'intermediate layer' near the outer surface of the anodic coating.

This is a feature noted particularly in work at UMIST, but first described by Wefers.[18] Studies by Thompson ***et al.***[19] using very long sealing times (up to 72 hours) to seal phosphoric acid anodized films gave direct evidence of the presence of the intermediate layer, as did the work by Furneaux and Wood.[20] The latter authors found that the protection value of the intermediate layer depends primarily on its thickness, which increases with sealing time at a rate that increases with solution temperature and decreasing solution acidity. The surface structure of a film sealed for 24 hours is shown in Fig. 11-4.

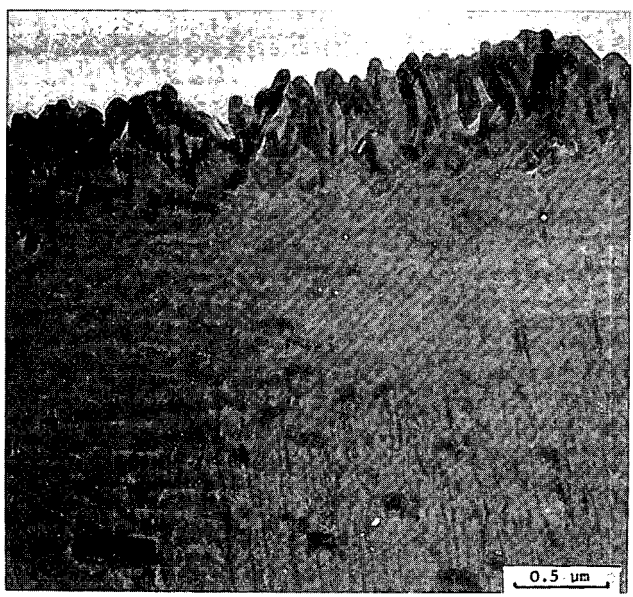


Fig. 11-4. Replica electron micrograph of super purity aluminium sample anodized to a thickness of 25 µm in a 1.5 mol/l sulphuric acid electrolyte and sealed for 24 hrs in distilled water at 100°C[20]

In this surface region the original pore structure is completely lost and there is a clear demarcation line between the intermediate layer and the remaining pore structure. The intermediate layer continues to grow for many hours in the sealing solution and may become several microns in thickness, but within normal practical sealing times it is usually less than a micron in thickness. Its importance, however, may be very great, as more recent work[21] is indicating that some of the short term weathering effects seen on coloured anodic coatings, such as iridescence, may be due to the presence of the intermediate layer.

Thompson and Wood" describe the reactions taking place during sealing as follows:

(a) Hot water is able to penetrate the pores very rapidly, and, at its relatively high pH, tends to precipitate hydrated alumina there as it meets outwardly diffusing acidic solution containing aluminium ions in the pores. The hydrated alumina developed is probably an extremely poorly developed crystalline form of pseudoboehmite. Dissolution of the pore walls and barrier layer adjacent to the pore renders the cell material surrounding the pore irregular, and the pores become largely blocked by the solid product deposited via this dissolution/precipitation process.

(b) Dissolution on the macroscopic film surface occurs and in this situation precipitation of pseucloboehmite, or in certain cases a more clearly defined crystallographic, diffraction-sensitive form of boehmite takes place, obliterating the outer pore structure and often possessing a platelike or needlelike form. to a thickness of about one micron.

(c) An intermediate layer of featureless morphology develops beneath the surface crystallites and grows progressively in depth, until it is up **to** several microns thick under typical conditions.

(d) Over periods of many hours more subtle changes sometimes take place within the cell walls and the precipitated material in the pores. Agglomeration apparently occurs, with larger particles tending to grow at the expense of smaller ones by dissolution-precipitation processes. Such processes redistribute the porosity but with no significant change in the macroscopic Film volume.

(e) The hydrothermal treatment limits the removal and access of molecular water from the pores and intercrystallite regions and apparently increases progressively the hydroxyl content of the film. This probably occurs on the microcrystallite surfaces, and by the formation of the poorly hydrated aluminas.

(f) The processes described occur at different rates for films formed in different acids with the acid anion playing a distinct role in the process. The inhibitive effect of phosphate on sealing is well known and films formed in phosphoric acid may only be sealed after prolonged hydrothermal treatments. It is considered that phosphate suppresses hydrolysis sites which are considered to be the initiators of the reaction; other acid anions may play a role in this initiation process and/or have an effect on the development of colloidal alumina, its polymerization and eventual precipitation in the pores. Other workers consider that hydroxyl ion:; exchange with acid anions in the film and also predict the loss of anions from the film as a whole during hydrothermal treatment.

The sealing process

The most convincing demonstrations of the process of sealing have come of course from electron-micrographs of replicas of the film surface, of the metal/film interface after removing the underlying metal, and also of fracture sections obtained by bending anodized specimens to a V-shape. Notable contributions have been made again by workers at UMIST[17 19 20 22] and by Wefers.[5 18]

Surface replicas of the unsealed coating (Fig. 11-5) show a clear pattern of the pore openings, and these are still clear after 1 minute sealing, and are still visible but less clear after 10 minutes in boiling water. But after 30 minutes sealing the porous structure is completely obliterated to be replaced by a crystal-like arrangement.

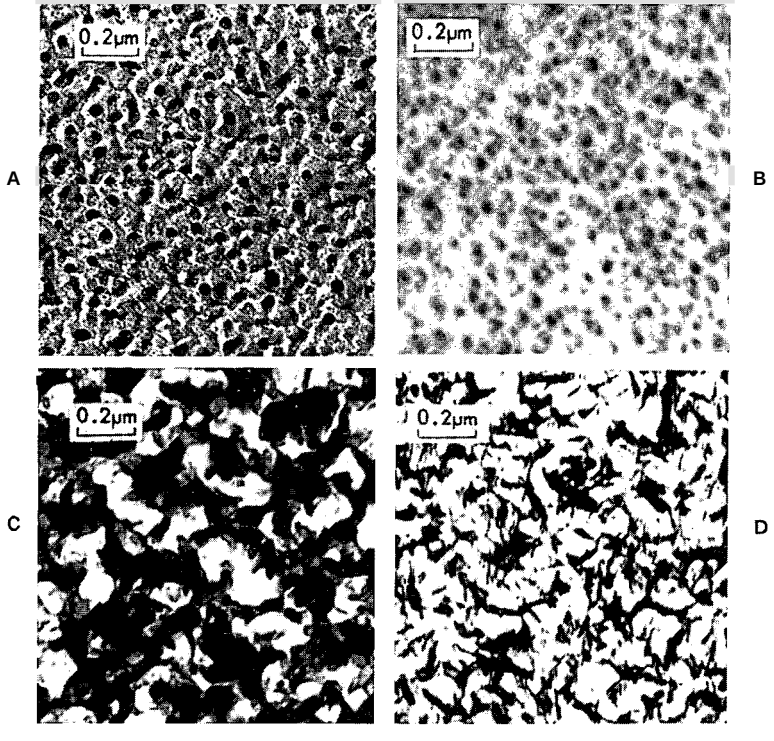


Fig. 11-5. Electron micrographs of surfaces of films sealed for various times in boiling water"

(A)	1 minute	(B)	10 minutes
(C)	30 minutes	(D)	24 hours

After 24 hours a needle-like structure is observed above this. An important practical aspect of this observation is that the crystalline material seen on the surface of the film, which is of course boehmite, is in fact the sealing smut or sealing bloom which always occurs as a result of conventional sealing. The surface of a film sealed in the presence of smut-preventing agents (described later) has been observed by Davidson,[16] and the domed areas covering the original pores can be clearly seen in Fig. 11-6.

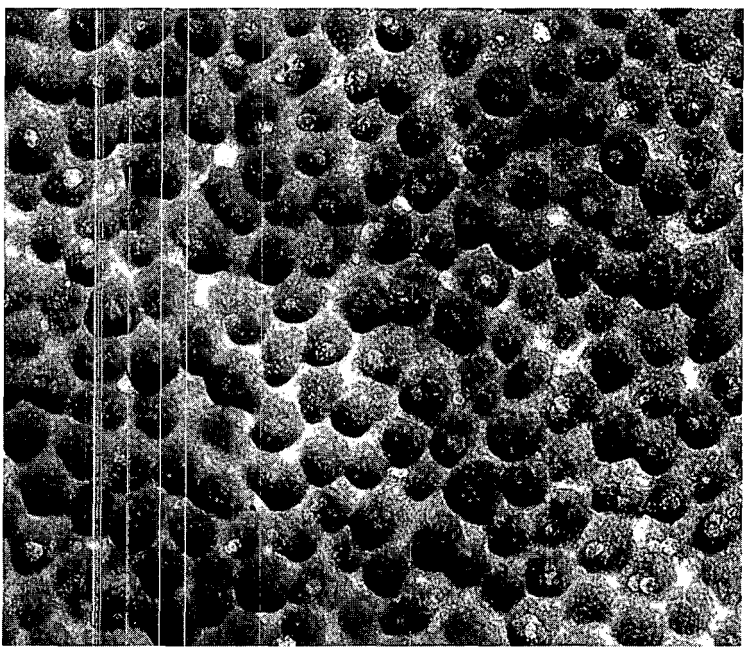


Fig. 11-6. Surface of sealed anodic coating produced in 165 g/l H_2SO_4 electrolyte at 20°C and sealed in water in the presence of an anti-smutting agent[35] (× 300,000)

The platinum/carbon replicas of fracture sections enable the film to be studied at locations close to the oxide/air and metal/oxide interfaces. Fig. 11-7 shows replicas of films produced in 2% w/v oxalic acid for 1 hour at 25 mA/cm^2 and 25°C;[17] similar studies have been published of films produced in 1.5M sulphuric acid at 25°C,[6] in 0.5M phosphoric acid at 20°C,[19] and in a Duranodic integral colour anodizing electrolyte at varying temperatures.[18] Working again with specimens anodized in 2% oxalic acid, which gives perhaps a clearer pore structure than the sulphuric acid electrolyte, Wood and O'Sullivan[17] have given this description of the progress of sealing.

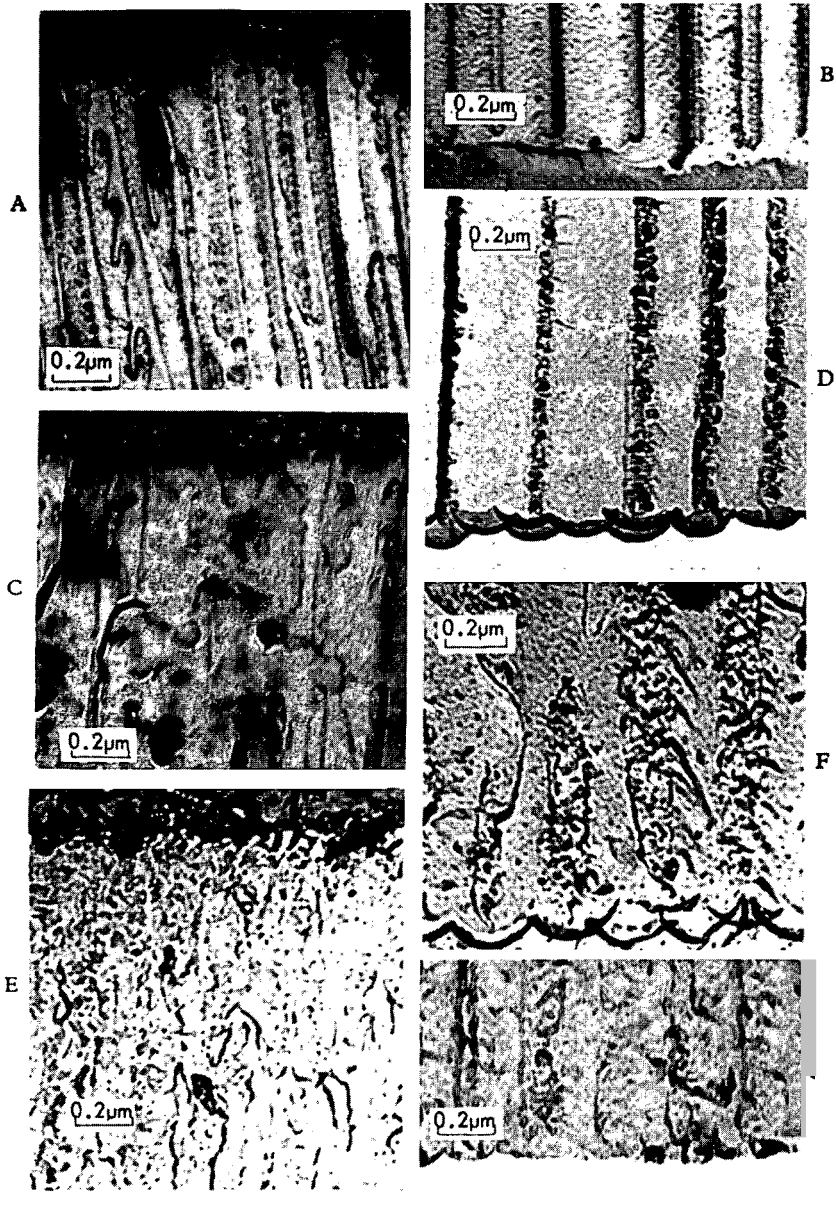


Fig. 11-7. Electron micrographs of sections of films sealed for various times in boiling water"

(a) and (b) 5 minutes. (c) and (d) 10 minutes. (e) and (f) 30 minutes. (g) 24 hours. Micrographs on the left depict the outer interface and on the right the region near the barrier layer

'After 1 minute little effect could be seen in any region of the film. After 5 minutes, some slight effect could be detected close to the outer interface (Fig. 11-7a), while close to the barrier layer there was no significant change (Fig. 11-7b). Treatment for 10 minutes gave a more pronounced result, the porous structure being difficult to detect in the outer region of the film (Fig. 11-7c), although the pores were still visible on the corresponding outer surface.

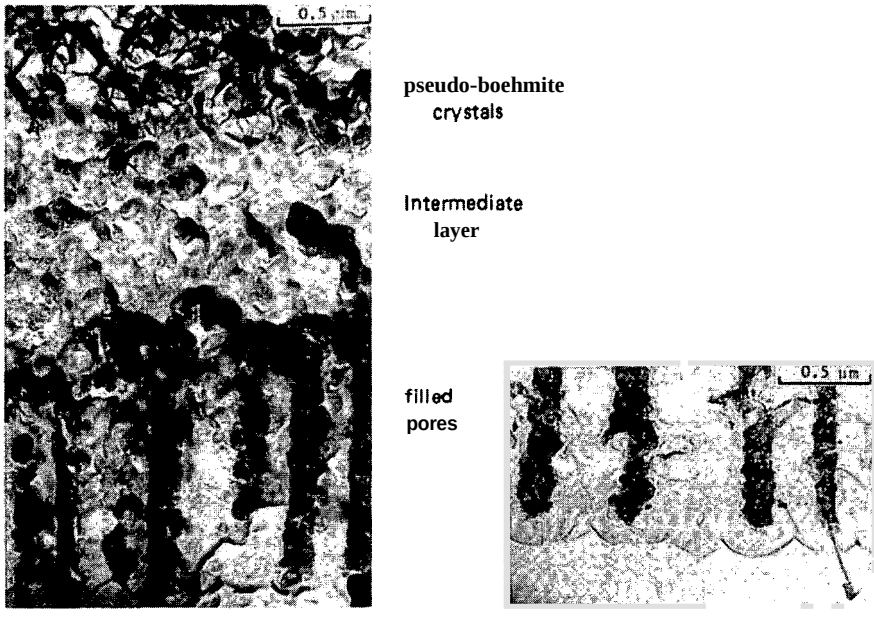
'Close to the barrier however (Fig. 11-7d), although the porous morphology was still clearly visible, the pores were now partly filled with apparently solid particles, *ca.* 100-400Å in size. Comparison of Fig. 11-7c and d indicates that the sealing reaction had affected both the pores and the cell walls near to the outer interface, while close to the barrier layer the cell walls remained apparently unaffected. Little further morphological change occurred in the film structure close to the outer interface on more prolonged sealing, except that the porous structure became virtually undetectable (Fig. 11-7e).

'Nevertheles!,, changes were still occurring close to the metal; the regions corresponding to the pores in the unsealed film could still be detected there clearly for sealing tirnes up to 30 minutes-1 hour (Fig. 11-70, although these were possibly more difficult to define after treatment for 24 hours (Fig. 11-7g). These "filled pore!;" had a rougher more open structure than the apparently unreacted parts of the cell walls, which seemed to consist of a more compact oxide, even after treatment for 24 hours. The longer the sealing time, at least up to 30 minutes-1 hour, the more the fibrous regions extended laterally into the more compact cell walls, producing an effective increase in the "filled pore" diameter.

'Any Corresponding decrease in thickness of the unreacted part of the barrier layer was not readily detected due to the tendency of the film to break away from the metal through the barrier layer rather than at the film/metal interface. However such a reaction would probably occur, and there is some evidence for it with the 24 hour specimen (Fig. 11-7g).

'Examination of micrographs from entire sections showed the extent of sealing to decrease gradually as the metal was approached, rather than there being a distinct 'plug' near the outer interface.'

From the work of Thompson *et al.*[19] on phosphoric acid anodized films, a replica electron micrograph of a fractured anodic film sealed for 72 hours in boiling water is shown in Fig. 11-8. The outer boehmite crystals, the intermediate layer, the pore filling and the texture changes in the original cell material are all evident.



(a) section near the film/solution interface (b) section near the metal/film interface

Fig. 11-8. Transmission electron micrographs of carbon replicas of fracture sections of porous anodic films formed on aluminium at 150 V in 0.4M phosphoric acid at 20°C for 70 minutes and subsequently sealed for 72 hours in boiling water"

Sealing in practice

It has of course been known for a long time that sealing is a slow process. This can readily be established by direct measurements and Fig. 11-9 indicates the rate of uptake of water over a six hour period, as measured by Spooner.[36] It can be seen that, whilst there is not a big difference in weight gain on sealing with sulphuric acid, oxalic acid and sulphophthalic acid anodized samples, chromic acid films show a very rapid initial weight gain. On the other hand those produced by phosphoric acid anodizing show an initial inhibition of water uptake, followed by a rapid weight gain. Although the pores in this film are larger, the presence of phosphates is known to retard hydration.[3,37]

Spooner saw little difference between films sealed in boiling water, steam at atmospheric pressure and steam under higher pressure, in terms of sealing weight gain, nor between films sealed in water and nickel acetate solutions. On the other hand sealing is claimed to be accelerated by neutral alkali salt,[38] by capillary active substances,[39] or by boehmite accelerators such as ethanol-amines.[40,41]

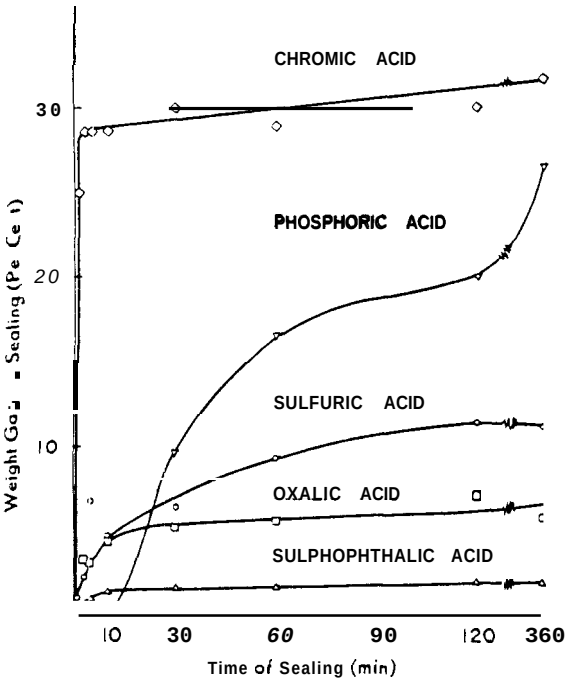


Fig. 11-9. Weight gain (%) on water sealing for porous anodic films[36]

Table 11-2 shows the relationship between thickness of the anodic film and water content after sealing.

TABLE 11-2

Relation between thickness and water content on sealing[42]

(a) in distilled water at 100°C, 30 minutes.
(b) in distilled water at 100°C, 240 minutes.
(c) in 2% nickel ammonium sulphate at 95°C, 15 minutes

Anodizing time (min) d.c. H_2SO_4, 18°C 20 *amp/sq ft*	*Film* thickness *(mil)*	Water content (g/ft^2) after sealing *(a)*	*(b)*	*(c)*
5	0.1	0.07	0.10	0.09
15	0.3	0.08	0.20	0.19
30	0.5	0.31	0.36	0.21
60	1.0	0.65	0.66	0.57
120	1.7	2.85	3.13	2.47
240	1.8	2.90	2.43	0.37

1 mil = 25.4 μm 0.93 g/ft^2 = 0.1 g/dm^2

Effect of temperature

The effect of temperature on sealing in hot water is very pronounced. It should normally be carried out at between 98 and 100°C, a temperature of 95°C being perceptibly slower while at temperatures below 90°C the rate of sealing is substantially reduced. Hunter, Turner and Robinson[3] measured the time required to completely convert the barrier portion of a porous type film into the hydrate and, although this is a different situation from sealing a normal coating, the results shown in Fig. 11-10, where the temperature is plotted against the reciprocal of the time, indicate quite well how time is implicated in normal sealing also.

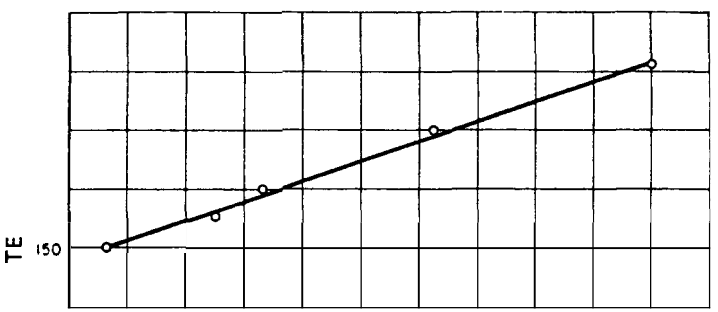


Fig. 11-10. Effect of water temperature on time required for complete hydration of barrier portion of a porous-type film[3]

By taking the weight loss in an acidified sodium sulphite medium to be an index of sealing, Sheasby, Guminski and Castle[43] have published data on the effect of temperature on sealing for 30 minutes in deionised water, from which the data in Table 11-3 are taken.

In this test sealing is considered to be adequate if the weight loss is less than 0.20 mg/cm^2. By means of the same test the effect of time of sealing at 100°C is also demonstrated (Table 11-4).

Effect of pH

The pH value of the sealing water is very important and a range of 5.5-7 can be recommended. Anything sealed at a pH below 5 can be expected to show deterioration in long term exposure and there is little evidence that time tends to rectify this misdemeanour as it does in the case of some others. Variation of the pH value can be anticipated from carry-over of sulphuric acid from the anodizing bath and this must

be counteracted by additions of ammonia or caustic soda, but there is a limit to the amount of dissolved electrolyte that can be allowed to build up in the bath. For this reason it is advantageous to buffer the seal bath against changes in pH and a 1 g/l solution of ammonium acetate is effective in doing this[44] (see also p. 897).

TABLE 11-3

Effect of sealing temperature using Kape test[43]

Sealing temperature °C	Weight loss - 20 min sulphite mg/cm^2
100	0.10
97	0.14
94	0.22
90	0.67
85	1.78

TABLE 11-4

Effect of sealing time using Kape test[43]

Time at 100°C minutes	Weight loss - 20 min sulphite mg/cm^2
5	2.41
10	1.25
20	0.18
30	0.10

TABLE 11-5

Influence of pH on bleeding of dyestuff during sealing

(1.5 g/l Aluminium Golden Orange RLW, 15 minutes 60°C, sealed at 100°C in distilled water for 30 minutes)

pH	*Shade*	*Bleeding*
2	White	Very strong
3	Weak orange	Strong
4	Dark orange	No bleeding
5	Dark orange	No bleeding
6	Dark orange	No bleeding
7	Dark orange	No bleeding
8	Dark orange	No bleeding
9	Medium orange	Strong
10	Weak orange	Very strong

The pH of the sealing solution also influences the rate of bleeding of a dyestuff in the sealing bath, and this effect is seen in Table 11-5.

Effect of water characteristics

Apart from the temperature and time, the type of water used for sealing is important. Thus Fig. 11-11 shows the effect of temperature and pH on the sealing efficiency obtained with three samples of water. With nearly neutral tap-water, the sealing efficiency, even at optimum temperature, does not reach 100%, probably due to precipitation of lime in the pores; more acid tap water is rather more efficient. With distilled water, however, complete sealing can be obtained even at 80°C.

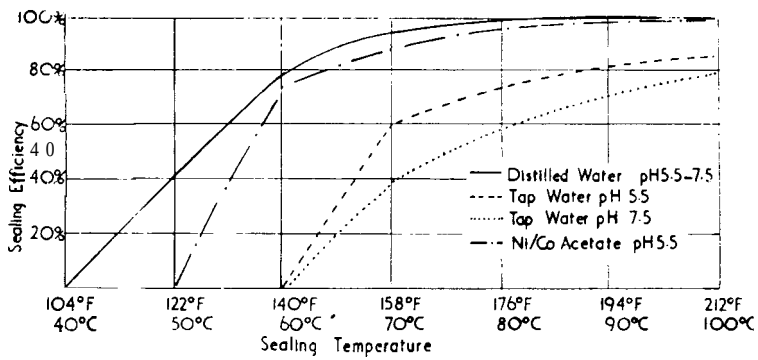


Fig. 11-11. Effect of temperature and pH in various sealing processes (sealing time 30 minutes. The sealing efficiency was determined by overdyeing with 3.5 g/l Aluminium Blue LLW for 15 minutes at 60°C)

Impurities in the sealing water vary in their effect on the chemical resistance of the work, and there is a certain amount of conflicting evidence on what contaminants can or cannot be tolerated in the supply water. This is due in part to the use of different criteria and different methods of testing. Richaud[45] found that constituents such as aluminium, sodium, sulphate and hypochlorite had virtually no effect, and there was unanimous agreement that phosphate or silicates constituted the most powerful inhibitors of the sealing process;?[46,47] recommended maxima being 5 mg/l PO, and 10 mg/l SiO_3. Spooner[46] also set quite rigorous limits for fluoride (5 mg/l) and chloride (100 mg/l) but Scott[47] found fluoride as NaF to be harmless at 50 mg/l and chloride at 400 mg/l to be without effect as either calcium, sodium or potassium chloride. Both Kape[48] and Richaud[45] found Cu^{2+} and Fe^{3+} to be detrimental to sealing, leading to staining and blooming during service, but were

not in agreement on Ca and Mg which Richaud found to be beneficial up to a point, 100 and 150 mg/l of magnesium improving the chemical resistance of the sealed film to nitric acid (see Fig. 11-12). Scott[47] considered Ca^{2+} to be generally harmless but found that a sealing solution deteriorated badly when refluxed with calcium carbonate for 5 hours (one hour having little effect), and calcium bicarbonate saturated with carbon dioxide also produced very bad sealing. Kape and Richaud employed weight loss tests in sulphite solution and dilute nitric acid respectively, while Scott used as a criterion the depth of colour in a spot test following attack with sulphuric acid/sodium fluoride mixture,[48] which is the basis of a commonly used test. Owen and Cole[49] confirm the harmful effects of small amounts of silicate, phosphate, fluoride, copper and iron in both water and chromate containing seals.

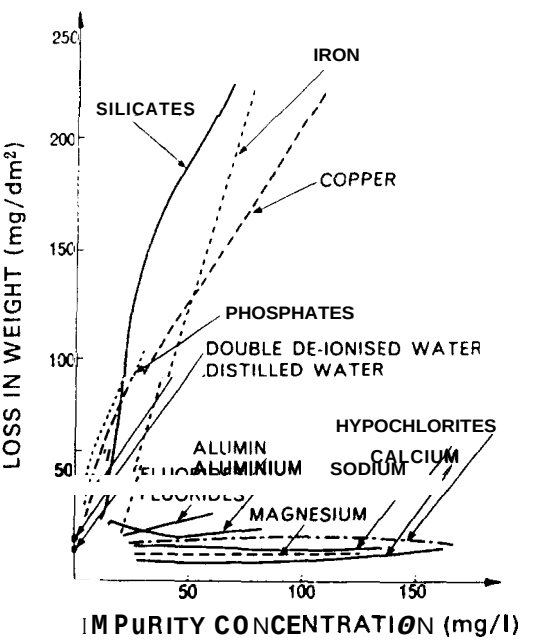


Fig. 11-12. Loss in weight of a 0.5 mil (13 μm) anodic oxide coating sealed in water containing various impurities, in nitric acid solution of pH 1[45]

More recently Kliment[50] used dye spot (ISO 2143), admittance (ISO 2931) and weight loss (ISO 3210) tests to evaluate the effect of a range of impurities in hot water sealing processes. His results are shown in Tables 11-6 and 11-7.

TABLE 11-6

Cations as sealing bath impurities

Cation	*Critical limit concentration*	*Maximum concentration tested*	*Source of cation impurity*
Na^{+}	>1000 pprn	1000 ppm	untreated water
K^{+}	>1000 ppm	1000 ppm	untreated water
Ca^{2+}	>1000 ppm	1000 ppm	water hardness up to 5000 ppm
Mg^{2+}	>1000 pprn	1000 ppm	water hardness up to 100 ppm, anodic **oxide** film
Fe^{2+}	>60 ppm precipitate	60 ppm precipitate	colour bath, gold dye bath, untreated water
Sn^{2+}	>400 ppm precipitate	400 ppm precipitate	colour bath
Al^{3+}	>100 ppm precipitate	100 ppm precipitate	anodic oxide film, anodizing bath, colour bath, etching bath, rinse water

TABLE 11-7

Anions as sealing bath impurities

Anion	*Critical limit concentration*	*Maximum concentration tested*	*Source of anion impurity*
SO^{2}_{4}	450 ppm	500 ppm	anodizing bath, chemical polishing bath, colour bath, anodic oxide film, untreated water up to 250 ppm
Cl^{-}	1000 ppm	1000 ppm	untreated water up to 200 ppm, etching bath
NO_3^{-}	>1000 ppm	1000 ppm	desmutting bath, chemical polishing bath, untreated water up to 100 pprn
F^{-}	14 ppm	15 ppm	cold sealing bath, etching bath, untreated water up to 2 ppm
PO^{3-}_{4}	7 ppm	40 ppm	chemical polishing bath, untreated water up to 7 ppm
SiO_2	17 ppm	100 ppm	untreated water up to 50 ppm, anodizing bath, etching bath
Oxalic acid	>1000 ppm	1000 ppm	anodizing bath, gold dye bath

He found that cations were generally harmless, with many precipitating before they reached a problem level, so control was not necessary. However he recommended removal of calcium and magnesium from hard waters using cation exchange. On the other hand several anions were confirmed as harmful, notably phosphate, silicate and fluoride, and he established upper limits of 7, 17, and 14 pprn respectively. He also recommended maximum levels of 450 ppm of sulphate and 1000 ppm of chloride. Interestingly he found that the effect of the critical

anions, phosphate, silicate and fluoride, was best detected by the weight loss test (ISO 3210). It must be remembered, however, that these are laboratory experiments under good sealing conditions, and practical limits in production are often somewhat lower than the figures quoted.

Effect of silica in water

The silica tolerance in sealing water is so low that it constitutes a special problem. Deionised water from a two column plant is a reliable and quite cheap source for sealing water. It is monitored with a conductivity meter but this does not take account of the silica content which also needs to be kept under surveillance. The first batch of water to come through a regenerated plant is very low in silica, but when silica breakthrough occurs the content can be considerably higher than the supply water for a period, and this fact is not registered. Eventually it falls to the level of the supply water, and on average the silica content of the deionised product is the same as the supply level. If this is satisfactory then there is no problem except to see that the temporary rise is diluted with the silica-free fraction, but in cases of high silica it means that the output from the plant is quite appreciably restricted. Fig. 11-13 contains data relating to a small laboratory plant used to supply approximately 363 litres of water per regeneration, and a running record is given of conductivity, pH and silica content.[51]

Sheasby[52] has shown that the effect of silica in seal water is pH dependent, with the greatest effect occurring at lower pH. This is shown in Table 11-8.

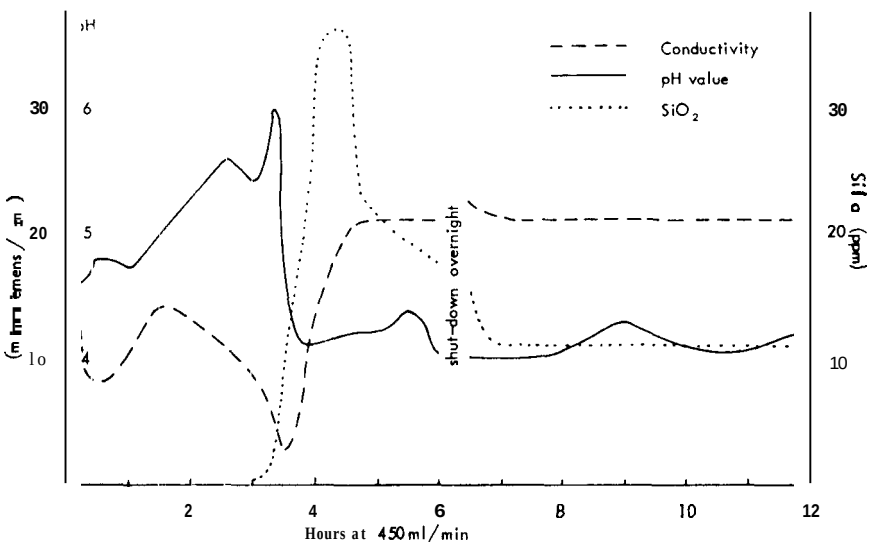


Fig. 11-13. Quality of water from two-column deioniser[51]

In this test (acidified sodium sulphite) a weight loss of less than 0.20 mg/cm^2 is normally required for acceptable sealing quality. A pH of 6.0 or above is therefore preferable to minimise the effect of silica on seal quality.

It is also important to realise that seal tests are not all equally sensitive to the presence of silica, and measurement of admittance, in particular, will not normally indicate poor seal quality caused by either silica or phosphate contamination.[53,54]

The silica content of water can be determined quite readily by a colorimetric method employing a standard Lovibond Disc 3/13 in a comparator. Marquardt[55] and Pake[56] have also referred to this hazard associated with the use of deionised water, and Cochran[57] has recorded the effects of silica but noted that it is of less importance with a nickel acetate seal.

TABLE 11-8

Effect of pH and silica content of seal water on weight loss (mg/cm^2) in acidified sulphite solution (ISO 2932: 1981) (Al-Mg-Si alloy anodized to 25 micron)[52]

SiO_2 (ppm)	pH 5.0	pH 6.0	pH 7.0
0	0.22	0.07	0.05
2.5	0.80	–	0.02
5	1.09	–	0.04
10	1.22	0.13	0.04
20	1.22	0.19	0.09

Practical considerations

Maintaining a large tank of water in the requisite state of purity and at the correct temperature can be both expensive and difficult. The first counsel is therefore to prolong the useful life of the water by avoiding carry-over of any soluble material from the preceding treatment stages. This means designing the jigs or racks so that drag-out is cut-down to the minimum, and that hollows, pockets or recesses are avoided. This may mean arranging to tip or even invert the load, and in the case of long hollow or complex extruded sections there should be provision for tilting these so that they can drain more readily. Having arranged this the rinsing operations must be carried out with agitation, and there is no better long term economy than to employ at least two rinsing stages in clean water with an adequate soak time before sealing. For the same reason some plants continuously deionise the last rinse before sealing.

Large flat sheets are also difficult to rinse and these are best handled by passing them through a line of fan-tail water sprays. A relatively slow withdrawal of work from the anodizing or rinse tanks will be found to be more effective than draining. In fact it is technically the most efficient to use two thirds of the time available for withdrawing the work and one third in draining after removal.'' Particular attention must be paid of course to any solutions containing phosphates, phosphoric acid or silicates since these must be kept out of the sealing water at all costs in view of the stringent limits fixed for them.

Maintaining the temperature of a large open tank can be difficult because evaporation and heat losses are high. Insulation of the tank sides with foamed polystyrene or fibre glass, when feasible, helps to conserve heat, but the use of polypropylene spheres to cover the surface will reduce both the heat and water requirements to a very significant degree. Frequently such measures enable an adequate sealing temperature to be reached in situations where it was previously not possible. In one plant evaporation losses were reduced from 30 to 8 gallons per hour with a consequent reduction in heat losses.[59] Many plants also use seal tanks with lids.

Steam sealing

The use of steam for sealing is a logical extension of the hydrothermal process and practical interest has been rnaintained in it ever since Setoh and Mitaya put the idea forward in 1929.[2] There is no question that when properly managed a steam scaling plant is every bit as effective as one using boiling water and **the** results probably superior. It has been used in Japan and other parts of the Far East and in Germany,[60,61] but to a very limited extent elsewhere.

Steam has the following advantages over water:

- It is quicker in action.
- The quality of the seal does not depend on the purity of the supply water nor on its pH value.
- There is no problem with maintenance or control and consistent results can be assured.
- There is less tendency to bleeding of dyed work.

The disadvantages of steam (which can be overcome by suitable design) are:

- The plant is more expensive to manufacture and more difficult to operate.
- The work must be totally enclosed to ensure a positive pressure of steam.
- It is not always easy to ensure displacement of air.
- There is condensation in the plant from the considerable quantities of steam which must be discharged.

Controversy centre:; around the temperature and pressure which should be employed for steam sealing. In Japan it has been the practice to autoclave the work under pressure at about 160°C while temperatures of 100-110°C have been more

common elsewhere. Neunzig and Rohrig concluded that steam at 95-110°C is superior to any other method.[61]

Using the loss of weight in 50% nitric acid as the criterion of sealing, results from tests by Thomas[62] are given in Table 11-9, where the values are related to sealing in distilled water as 100%.

TABLE 11-9

Weight loss of specimens sealed for 30 minutes (30 minutes in 50% nitric acid at 20°C)

Sealing medium		*Weight loss (dist. water = 100%)*
tap water	100°C	135%
distilled water	100°C	100
deionised water	100°C	100
steam	100°C	63
	110	42
	115	63
	120	48
	125	53

The table indicates that steam is very effective and a substantial improvement on distilled water, but there is nothing particularly significant in the variations in the range 100-125°C, which seem to represent a normal scatter. In a further series of tests using sulphuric acid/potassium fluoride as the attacking medium the weight loss ratio of steam to water sealing was reduced to 90% but with the advantage still to steam. In similar tests using the loss of weight in sulphuric acid as a criterion Spooner[7,30] found that by operating at 15 p.s.i. (about 110°C) the weight loss was only a half of that obtained when using steam in an open vessel. Harris[51] found in qualitative tests that dry steam at 150°C was not as good as distilled water at 100°C for sealing. Survila and Andrews,[63] in an extensive comparative examination of steam and water sealing, concluded that water sealing was less effective than steam sealing, but they were essentially using steam at about atmospheric pressure at around 100°C.

These experiments have a pronounced unreliability factor because it is not normally possible to operate at a high temperature without climbing through the lower temperatures in order to get to it. Thus, even in tests at 125°C there is considerable activity and a fair degree of sealing in the 100-110°C range before reaching 125°C.

Steam probably operates best when it is damp and condensing on to the surface, when sealing can be extremely rapid. A positive pressure giving a temperature of about 110°C ensures intimate contact between the steam and the

work and helps to eliminate air. A flow of steam is probably better than an air/steam mixture in a hermetically sealed space. High temperatures are not necessary, the sealing probably taking place while reaching them.

Although the advantages nearly all seem to lie with steam sealing on the basis of accelerated tests, it is only fair to point out that when it comes to outdoor exposure these advantages do not appear to count for much since there is no reduction in the frequency of pitting of the thinner films. This is a fairly common feature of accelerated corrosion tests when they try to sort out degrees of perfection. The fact is that sealing in steam and pure water are both extremely good; there is nothing to choose between the end products and a decision between the methods must be based on grounds of cost, convenience or confidence. In recent times energy cost considerations have pushed developments in the opposite direction towards reduced temperature sealing processes.

A steam sealing plant may be operated by boiling a reservoir of water in the sealing tank itself with a suitably tight fitting lid to contain the steam, and ideally condensing coils to prevent excessive losses when the tank is opened. The steam may be generated in a separate boiler and introduced into the tank, which is preferable since efficient boilers operating from gas or oil can be used. But undoubtedly the method of construction which is best suited to the properties of the material, notably the fact that it is much lighter than air, is to use an insulated and inverted chamber with an open base into which the steam is introduced. It rises to fill the chamber, completely displacing the air, and if the steam supply is controlled by means of a thermostat at the bottom of the chamber it remains full of steam with **surprisingly** little wastage. The chamber can be mobile or remain stationary while the work is introduced into it from underneath by means of an elevator. A steam sealing apparatus has been covered in a patent.'' Some plants, particularly in the Far East, remove work from the jigs before steam sealing and put it on suitable stillages which are placed in the empty steam sealing chamber. When the chamber is full it is closed and steam under pressure is fed into it. In this way a whole shift's production can be sealed in one operation without having to open the chamber, but work must be handled carefully in the unsealed condition to avoid staining.

In the case of dyestuffs, which show a marked tendency to bleed in hot water, steam sealing is the ideal treatment, owing probably to the very high rate of heat transfer that can be achieved, and it is also very suitable following cold dyeing operations.[65] Very thorough rinsing is necessary before steam sealing because any trapped acid which leaches out and runs over the surface can be disastrous, whereas in water it would be diluted in the large volume employed.

Vapour sealing

Although a high temperature has generally been considered essential for effective sealing it has been claimed in Germany that the vapour from a mixture of water and a chlorinated hydrocarbon can be used for sealing at a considerably

lower temperature than the boiling point of water.[66] This was done in a vapour degreasing-type plant where compressed air was forced through the boiling mixture to maintain a state of turbulence, the mixture containing half water and half either trichloroethylene or perchloroethylene.

3. SEALING SMUT OR BLOOM

The phenomenon of sealing smut or sealing bloom formation is a normal side effect of the sealing reaction, and, as already indicated, it represents the formation of boehmite crystals at the film surface. In practice it is a considerable nuisance as it appears as a thin powdery layer which on clear work is usually invisible until the surface is dried and rubbed with the finger, when a white mark appears, like a chalk mark. On coloured work, particularly the darker colours, it appears as a heavy velvety smut layer which is irregular in appearance. It is often referred to in N. America as 'chalking', though that term is more correctly applied to the powdering effects occurring when soft anodic coatings weather. In Germany it is called 'belag' and in France 'farinage'. It should not be confused with weathering bloom, which is a whitish etching effect occurring on poorly sealed work exposed to the weather. All these terms have been defined in several languages in an ISO glossary of terms (ISO 7583: 1984).

Smut formation

It is the boehmite crystals at the surface of the sealed anodic coating that represent the visible smut layer. This layer does not constitute more than 1 or 2% of the film weight; it is a cohesive film in its own right which is transparent, of interference thickness and only made visible when broken up by rubbing; it can be dissolved in acid, when it is seen to separate from the surface as a thin friable layer. The fact that the surface smut differs from the underlying film in hardness and solubility confirms that it is a different form of hydrated oxide. The best thing that can be said in favour of sealing smut is that it never appears unless sealing has been well performed and constitutes therefore an indication of good sealing. Indeed there are some that consider that sealing is inadequate unless taken to the point where smut appears.

Smut removal

It is however an embarrassment which the industry could well do without, and costs much money to deal with. Traditionally the method for dealing with it has been either to apply a wax or wax emulsion to the surface, which tends to make it invisible (only to reappear later), or to remove it manually by wiping or polishing with a very fine abrasive. Sometimes it has been dealt with by immersing the

sealed work in 30% nitric acid at 20-30°C for about ten minutes. This is an effective method for removing it but is only safe when the work has been thoroughly sealed. or the film proper becomes subject to attack. This method has generally been used in conjunction with steam sealing which is rather less subject to departures from perfect sealing than any other method. It has also been used for eliminating smut from architectural work produced by integral colour anodizing. Baker,[67] in an extensive investigation, has shown that the smut formed in a normal boiling water seal does not always dissolve very readily in nitric acid, but that produced by nickel acetate does. Alcoa therefore developed a system of sealing first in 5 g/l nickel acetate solution and then dipping for 3 minutes in 40% by volume nitric acid to remove the smut.[68] This method gives good appearance and satisfactory quality, provided that the initial anodic film quality and seal quality are good.

Smut prevention

Another method of dealing with smut has been to try and prevent its formation. This has been done by trying to terminate the sealing action just before smut forms, but when sealing has already been quite effective, or at least effective enough to pass a standard test, and this is achieved either by curtailing the time, reducing the temperature, or lowering the pH or a combination of all three. However this is a dangerous practice, as the sealing smut represents the completion of the sealing reaction at the anodic film surface; it can be appreciated that suppression of sealing; smut can mean that the sealing reaction itself is being suppressed, with serious consequences in terms of performance.

Another move in this direction has been to suppress sealing smut by the addition of phosphate: which is known to be a more potent inhibitor of sealing than any other material. However in the suggestion of Amore and Murphy[69] the addition is carefully controlled to between 3 and 10 parts per million, and steps are taken to maintain this concentration steady because, during sealing they calculate that 1 dm^2 of a 7.5 μm coating will remove 1.72 mg of phosphate from the bath.

However, the most common practice today is the addition of organic additives to prevent smut formation, and very many additives of this type have been developed; they are described in a later section of this Chapter. Most must be used with care as, particularly when high levels of additive are present, they can inhibit the sealing reaction within the pores as well as at the film surface. When they are used, frequent checks of seal quality, preferably using an acid dissolution test, are essential.

The interesting feature of recent approaches to the problem of smut prevention has been the frank recognition that it is not an unmitigated nuisance to be stopped at all costs, but that it is concomitant with good sealing and that the steps to deal with it must be finely calculated to remove it without prejudice to the sealing operation.

4. SEALING BATH ADDITIVES

We have so far considered only the use of relatively pure water, or water containing unavoidable contaminants for the hydrothermal sealing of oxide coatings. We will next consider the use of water containing deliberate additions in larger amounts. There are very many compounds which inhibit the hydration mechanism and very few which accelerate it. Sealing baths of this type may de dependent on a different or auxilliary mechanism of sealing. Nickel salts, ammonium acetate and triethanolamine are added most commonly, and dichromate solutions, which are dealt with in a later section of the Chapter, are used in most aerospace and defence work. In practice the most common additives now used are those which prevent smut or bloom formation during sealing and these are covered in the section on anti-smutting additives.

Nickel salt sealing

A great deal of aluminium is sealed in solutions containing nickel and cobalt salts. The salts are absorbed into the coating where they are hydrolysed and precipitated as the hydroxides. As nickel and cobalt hydroxides are almost colourless in small amounts, this method is very suitable for sealing dyed coatings. Whitby found that it was more effective than hot water sealing, though rather less so than dichromate sealing. There is little or no difference between the nickel and cobalt salts, which are frequently used together,[70,71] e.g.:

nickel acetate	5-5.8 g/l	15-20 min
cobalt acetate	1 g/l	70-90°C
boric acid	8-8.4 g/l	pH 5-6 (optimum)

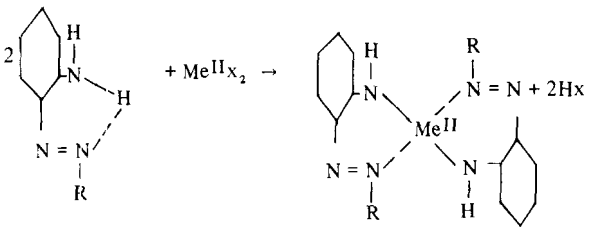
Nickel sulphate or nitrate has been used instead of the acetate while the double sulphate with ammonia has also been employed. After sealing, the work is frequently additionally immersed in hot water.

According to Speiser,[71] three different reactions play a part in nickel/cobalt acetate sealing:

(i) closing of the pores by hydration, as in hot water sealing.
(ii) hydroxide precipitation in the pores due to hydrolysis, which will prevent bleeding of the dyestuff.
(iii) chemical reaction between the nickel and cobalt and the dye molecule to form a new metal complex.

Reaction (iii) explains why some dyestuffs (e.g. Bordeaux RL, Bronze G, Brown RL, Yellow Brown *ZG*, Olive Brown RW, Black LLW and Black LL) are more light- and weather-fast after sealing in nickel/cobalt acetate, though it is usually accompanied by a slight change of shade. On the other hand some colours,

e.g. Golden Orange RLW, Orange GL, Red GLW and Red RLW, are less light-fast after nickel/cobalt acetate sealing than after hot water sealing, while others which do not react with the nickel or cobalt may be unaffected. **A** typical reaction between an *o*-aminoazo dyestuff and nickel and/or cobalt (Me") is:



The effect of sealing temperature on the efficiency of nickel/cobalt acetate solutions at pH 5.5 was shown in Fig. 11-11, while the effect of time is shown in Fig. 11-14.[71]

The advantages of nickel acetate sealing are that a lower temperature may be used and that the quality of the supply water is of less importance; tap water may often be employed. For dyed work nickel acetate sealing is sometimes essential where the dyed work must not be taken up to boiling temperature.

The corrosion resistance of nickel acetate sealed work is probably inferior to that produced in pure boiling water unless the former has also been carried out at boiling point, which loses one of its advantages. Kaden[72] has shown that in long term exposure tests nickel or cobalt acetate sealing is inferior to steam sealing both in industrial atmospheres and in neutral rural atmospheres, and CIDA international tests point to the development of a heavy bloom on samples sealed in nickel salts when exposed in London.[73] There is also a tendency to form a troublesome nickel hydroxide deposit on the surface, and sometimes a permanent whitish discolouration which cannot be removed; the addition of a wetting agent is of help in avoiding this, but the higher the temperature the more trouble there is likely to be. Frequently a double treatment may be used where a nickel acetate seal is used at 80°C for a short time as a preliminary fix, since most of the benefit is conferred in the first two or three minutes, followed by the normal treatment in boiling water.[46]

Incorporation of nickel into the film has been demonstrated by Spooner and Forsyth[25] using X-ray emission spectroscopy on progressively dissolved coatings, and by Wood and Marron[14] using an electron probe microanalyser on cross sections of thicker films to demonstrate the distribution of nickel through the coating (see Fig. 11-15).

One great advantage of nickel acetate sealing is its ability to tolerate silica in the supply water, without apparent detriment, at levels where water sealing would be quite seriously affected. Cochran[57] has reported good sealing with 100 ppm SiO_3 in a nickel acetate seal, while 50 ppm of SiO_3 in pure water caused failure of work in sealing tests.

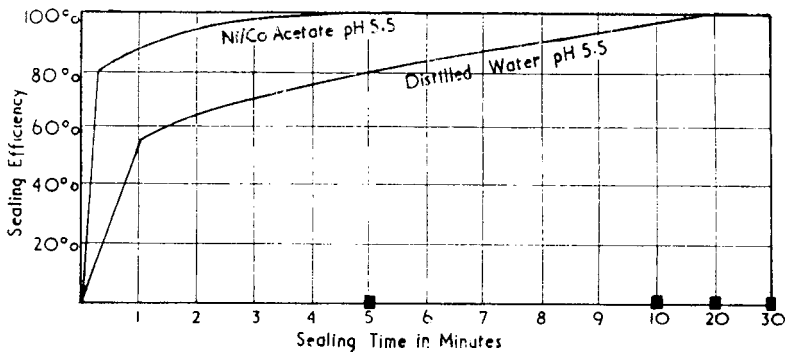


Fig. 11-14. Influence of time on sealing efficiency (sealed at 100°C. Sealing efficiency determined by over-dyeing with 3.5 g/l Aluminium Blue LLW for 15 minutes at 60°C)

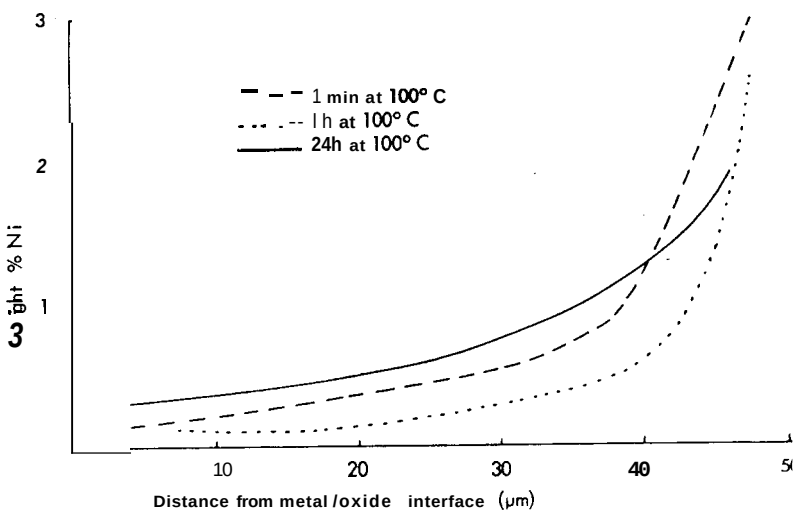


Fig. 11-15. Distribution of nickel in anodic oxide coatings sealed in concentrated nickel acetate solution[14]

Sealing in 15 g/l nickel sulphate solution has also been described and, under some conditions and in some sealing tests, has been claimed to give results superior to distilled water or nickel acetate sealing.[74] Another report rates it as equivalent to nickel acetate, easier to control and also to give good results in the

presence of silica," but the sulphate radical can give trouble with bleeding of organic dyes. Nickel sulphate and nickel formate have been used, particularly in Italy, and Sacchi *et al.*[76] have compared nickel sulphate and nickel acetate sealing. They concluded that a 15 g/l nickel sulphate solution gave better seal quality, as measured by acid dissolution and corrosion tests, than nickel acetate, and in most cases was also superior to water sealing.

Ammonium acetate

The addition of ammonium acetate to a hot water sealing solution is to be regarded as complementary to hot water sealing since it effects an improvement in performance by guarding against the rapid changes of pH value caused by carry over of sulphuric acid into the sealing bath. Sheasby and Bancroft[44] examined the advantages of using a seal which is buffered with ammonium acetate in a short paper which deserves serious attention, because of the immense savings which such an easily applied remedy can entail. They recommended an addition of 0.1% ammonium acetate as being effective, and in one test of a 50 gallon (225 litre) bath in regular use they were able to get a life of 75 days with only two pH adjustments with ammonia, and consistently good sealing as indicated by the weight loss tests in acidified sodium sulphite. In a controlled test with unbuffered deionised water undergoing similar use no fewer than 11 pH adjustments were required in 22 days and at the end of this period the work no longer passed the acidified sulphite test. Use of ammonium acetate has since become common practice in many plants.

In a large commercial plant the pH adjustments have to be made several times a day and it is not easy to do this correctly because of variations throughout the bath. The authors. consider that this is one of the main problems under production conditicins, and there is no doubt that the local situation in the immediate vicinity of the anodic film is also subject to pH fluctuations which are connected with some of the 'unexplained' phenomena of sealing. They have also taken the precaution to carry out accelerated weathering tests on the method of sealing to demonstrate that it had no detrimental effects, and outdoor exposure tests under a variety of conditions have shown that, if anything, films sealed in ammonium acetate have a slightly superior performance to those sealed in deionised water. Sheasby has stated that the buffered water is slightly more tolerant of phosphate and silicate, and this method is now commonly used in the U.K. and elsewhere.

Triethanolamine sealing

Olin Mathieson[40] first described the use of triethanolamine solutions for sealing anodized aluminium and claimed satisfactory seal quality after only 5 minutes treatrnent in such a solution. A 0.003N to 0.02N solution of triethanolamine was recommended at a temperature of 96-100°C.

With the need for smut-free sealed surfaces triethanolamine has also been used in other ways. Alcoa workers[77] used a 3-10 ml/l solution of triethanolamine at about 98°C for 1-20 minutes for sealing, and then desmutted the work by immersion in a mineral acid solution at room temperature. Nitric acid was preferred for this stage, but hydrochloric acid, sulphuric acid and phosphoric acid could also be used.

Alcan, on the other hand, used a dip in an alkaline solution (pH 7-11) before sealing to produce the acceleration of sealing,[41] and then sealed in a conventional sealing bath containing an anti-smutting additive. Triethanolamine was a convenient way of doing this and many Alcan plants used this method in practice. Concentrations of *0.5-5* ml/l of triethanolamine were used at temperatures from 20-60°C and with immersion times of 1-10 minutes at pH 8-10. Sealing in a conventional sealing bath at 98-100°C with a selected anti-smutting additive present then took place in 10-15 minutes, compared to the 30-60 minutes normally required. Under these conditions less sealing capacity is required and, when producing architectural finishes, one triethanolamine bath and one sealing bath can cope with the output of two, or even three, anodizing baths.

High speed sealing with freedom from sealing smut is also claimed by Albright and Wilson.[78] They again use a seal bath at a pH above 7, based on about 2 ml/l of triethanolamine with 20-40 ppm of ethylene-diamine-tetra(methylene phosphonic) acid present. Experience in the use of such a process has been described by Crowther and Renton.[79] Satisfactory seal quality was claimed with sealing times of 1 min/micron. The bath was operated at a pH of 8.2, and both the accelerated sealing additive and an anti-smutting additive were used.

Anti-smutting additives

With the increasing cost of labour, the labour intensive step of cleaning anodized work at the end of the anodizing line is becoming impractical in many areas. Attention has therefore focussed on other ways of eliminating sealing smut or bloom, and chemical additives have been developed which prevent smut formation. As these additives are required to prevent boehmite formation (smut) at the surface of the film without adversely affecting the sealing mechanism within the pores, it can be appreciated that very precise chemical control is required. Many of the compounds suggested are surface active agents and many are capable of complexing metal ions.

Their use has been described by Göhausen[80] who suggests that they are absorbed on the growth faces of the boehmite crystallization nuclei and so inhibit their growth. For this reason relatively low levels of additive can be effective. Speiser[81] lists other characteristics of an effective anti-smutting agent as follows:

Must not adversely affect seal performance.
Must give high product efficiency.

Must not affect seal quality even with an inadvertent overdose.
Must not pive any yellowing or discoloration of the film during weathering.
Must not discolour the anodic film during sealing.
Must not leave any residue on the surface after drying (as most salts do).
Must be thermally stable.
Must not rnake the seal bath sensitive to metal ions (such as AI, Ca, Sn, Ni, Co ion:;).
Must be readily soluble in water.

The requirement for high levels of the additive not to adversely affect seal quality is particularly important, as there is always a temptation to add more chemical than is actually required, in order to ensure that smut formation is completely inhibited. Further additions are made during the life of the seal bath, often on the basis of throughput, and since it is rarely possible to quantitatively analyse the additive level, the final additive concentration is often not known.

Another irnportant factor in the use of sealing additives is that the response of sealing tests to the presence of additives can be very variable. Admittance or impedance tests, for example, are sensitive mainly to the pore filling part of the sealing mechanism rather than to the surface boehmite formation, so they will only indicate poor results with substances that poison the sealing reaction as a whole. Dye spot and weight loss tests, on the other hand, are most sensitive to the chemical resistance of the film and this is controlled by the surface sealing reactions as well as the pore filling. Dye spot tests, in particular, will often indicate adverse seal quality in the presence of additives owing to reaction between the dye and the additive on the film surface. Some of these effects have been described by Friedemann.[82] Evaluation of seal quality must therefore be made with care: when anti-smutting additives are used, and it is often necessary to carry out more than one type of seal test for production control.

Additives which have been claimed to give anti-smutting properties include lignosulphonates,[83] polyacrylic acids,[84] dextrin,[85] amines,[86] hydroxycarboxylic acids,[87, 81] phosphonates,[88] cyclo aliphatic or aromatic polycarboxylic acids,[89] naphthalene sulphonic acids,[90,91] formaldehyde, urea and a sulphonated phenol,[92] agar and gelatine,[93] arid phosphonocarboxylic acids.[94,95] It is difficult to know which of these are most effective or even which are present in most proprietary formulations, but hydroxycarboxylic acids and phosphonates seem to be the most widely used today.[80,81] Information on the use of some of the earlier additives was provided by Friedemann.[96,97] Additive levels are generally about 1-2 ml/l or g/l, and seal temperature, pH and time are the same as for normal sealing.

It is not, of course, normally possible to use the additives with steam sealing, but the acrylic acid type of additive has been used in a hot water rinse prior to steam sealing. Whilst this produces some reduction in smut level, it is usually less effective than additions to the hot water seal itself.

5. DICHROMATE SEALING

This process was first patented by Dunham in Britain[y8] and by Edwards in the U.S.A.[99] for sealing sulphuric acid anodic coatings and chemical oxide coatings produced by the Alrok process. Dichromate sealing is frequently used for non-decorative purposes. It gives the coating a yellow colour and is, therefore, often unsuitable for decorative applications unless used only for a short time at low concentration.

The corrosion-inhibiting properties of the chromate incorporated in the coating were at first believed to be the prime factor in the sealing process. Thus, Edwards in his patent states that dichromate is to be preferred to chromate as the coating will absorb twice as much hexavalent chromium from solutions of the former. Later evidence has shown, however, that the chromate absorbed is only one of the factors involved. Thus, Schenk[39] goes so far as to say that as the dichromate, which he assumes is converted in the coating to a basic aluminium chromate, is absorbed only loosely and as the pores are not completely closed. it is leached out when in contact with water, with the result that for work subjected to moist exposure conditions, dichromate sealing is actually inferior to hot water.

Much, however, depends upon the composition of the dichromate solution employed. Dichromate sealing is really a combination of two processes, viz. (1) the absorption of chromate, which is provided by low pH solutions, and (2) the closing of the pores by the normal hot-water sealing, which also locks the Cr^{6+} in the pores and which takes place best at higher pH values (above pH 6). The corrosion resistance is a function of the closing of the pores and the resistance of the absorbed chromate to leaching (see Table 11-10). The importance of the latter will, however, depend on the type of exposure; in dry conditions, pH of the sealing solution is less important.

TABLE 11-10

Resistance to leaching of anodic oxide coatings sealed in dichromate solution

pH of sealing bath	3.72	6.32	8.5
	Chromium desorbed in		
Time in NaCl solution	*3% NaCl solution (mg/sqft)*		
5 minutes	1.65	1.09	0.34
1 hour	5.18	2.07	0.63
48 hours	18.19	5.40	1.09
240 hours	20.56	5.96	1.39
Cr remaining in film	5.0	8.7	7.1

The inhibitive effect of the chromate is particularly useful as a protection against stress corrosion in the Duralumin-type and other high-strength alloys, especially where there is danger of traces of sulphuric acid remaining after anodizing. The older sealing method, now, however, largely replaced by the method given 'below, used to be immersion for 30 minutes in a 5% potassium dichromate solution., free from chloride and sulphate. In the case of decorative anodizing, the dichromate-sealed coating is sometimes rinsed in hot water.

Tomashov and Tyukina's accelerated method

An important contribution to the knowledge of the mechanism of dichromate sealing was made by Tomashov and Tyukina,[100] who developed an accelerated method which found large-scale application in the U.S.S.R. and which was adopted as a standard process in this country.")' These authors worked on the Alclad Duralumin-type alloy and investigated dichromate and chromate mixtures ranging from pH 3.7-8.5, the solution being 0.68M with respect to chromium, i.e., equivalent to 10% potassium dichromate. The increase in weight due to hydration was determined (Table 11-11) and also the extent of chromate desorption by leaching in 3% sodium chloride for periods up to 4 hours.

Mechanism

The increase in weight of the coating during sealing was very rapid in the first few minutes in solutions of pH between 6.64 and 6.32, corresponding to the following ratios:

$$\text{pH 6.64, ratio } \frac{\text{chromium as } Cr_2O_7^{2-}}{\text{chromium as } CrO_4^{2-}} = {}^1/_3$$

$$\text{pH 6.32, ratio } \frac{\text{chromium as } Cr_2O_7^{2-}}{\text{chromium as } CrO_4^{2-}} = 1$$

and complete sealing was obtained in 5-10 minutes. These authors assumed that, because of the rapid rate of sealing, complete pore closure was achieved in the first 5-10 minutes as a result of the expanding $Al_2O_3 \rightarrow Al_2O_3.H_2O$, the rate of the diffusion process being markedly reduced with a reduction of the cross-section of the pores and hence the true surface area of the film.

This increase in sealing rate was even more rapid at higher pH values, e.g. at pH 9.0 (sodium carbonate added), but a maximum was reached at 2 minutes, after which there was a reduction in weight due to dissolution of the film in the alkali solution. The latter occurred also with pure chromate solution (pH 8.5). At the higher pH values, hydration was greater and a denser film was obtained:

$$Al_2O_3 \text{ (d. 3.42)} \rightarrow Al_2O_3.H_2O \text{ (d. 3.014)}$$
$$\rightarrow \text{33\% increase in volume of oxide.}$$

TABLE 11-11

Effect of sealing treatments[100]

Sealing solution	Increase in wt due to hydration (mg/sq ft)	Al_2O_3 combinedas chromate (mg/sq ft)	%	Al_2O_3 hydrated (mg/sq ft)	%	No. of atomic layers of Al combined as chromate	No. of atomic layers of Al (in oxide) hydrated
$K_2Cr_2O_7$ (0.68M)	69.7	53.4	4.46	395	32.9	22.8	169
$K_2Cr_2O_7$ (0.68M)	(65)	(26.7)	(2.23)	(369)	(30.7)	(11.4)	(157)
$K_2Cr_2O_7$ (0.34M) + K_2CrO_4 (0.34M)	97	31.6	2.63	550	45.8	13.5	235
K_2CrO_4 (0.68M)	121.3	19.1	1.6	688	57.3	8.1	293
Hot water	103			584	48.6		37
Hot water	139			787	65.6	-	250

Values in brackets assume formation of the oxychromate, others of oxydichromate.

9.3 mg/sq ft = 1 mg/dm^2.

From the pH change during sealing, which rises with increasing surface area of anodized work treated, the authors deduced that absorption was not molecular, but was an anion exchange which resulted in liberation of one equivalent of alkali from the chromate, forming aluminium oxychromate:

$$OAl.OH + KHCrO_4 \rightleftharpoons OAl.HCrO_4 + KOH$$

accompanied by reaction leading to the dioxychromate:

$$\begin{matrix} OAl - OH \\ \\ OAl - OH \end{matrix} + KHCrO_4 \rightleftharpoons \begin{matrix} OAl \\ \diagdown \\ \\ \diagup \\ OAl \end{matrix} CrO_4 + KOH + H_2O$$

This theory was confirmed by determination of the ratio of liberated alkali to absorbed chromate (approximately 27.2 mg Cr per sq ft of sealed apparent surface area of film) which was approximately 1:1. The oxychromate is assumed to be formed in more acid solutions, and the dioxychromate in the higher pH ranges.

Both of the reactions are reversible, and with increase of hydrogen ion concentration (lower pH) the equilibrium is shifted towards the right. Leaching takes place when the oxychromate is hydrolysed, i.e., a shift towards the left of the equation. In neutral solution this is slower as chromate is less easily hydrolysed than dichromate, added to the impeding effect of the more rapidly and completely closed pore space by hydration in solutions of higher pH.

Operating conditions

The best corrosion resistance is obtained at pH 6.7 and, as can be seen from Table 11-10, which is compiled from Tomashov and Tyukina's results, the corrosion resistance as determined by loss in weight on immersion in a peroxide-containing salt solution is not primarily related to the amount of chromate absorbed, which falls off with decreasing pH, but to a combination of the degree of hydration together with that proportion of chromate which is locked in the pores (Fig. 11-16) and hence is resistant to leaching, the latter being a function of the former as well as of the amount of chromate initially absorbed. In the low pH solutions, the major factor influencing corrosion resistance is the degree of hydration, which to some extent is prevented by chromate absorption. It must not, however, be forgotten that corrosion results apply to exposure to aqueous solutions only.

In practice, these authors recommend the following two solutions:

(1) For the highest corrosion resistance:

$K_2Cr_2O_7$	100 g	
Na_2CO_3	18 g	2-4 minutes
or NaOH	13 g	or up to 10 minutes
H_2O	1 litre	
pH	6-7	
Temp.	90-95°C	

(2) For a reduced chromate consumption:

$K_2Cr_2O_7$	15 g	
Na_2CO_3	4 g	2-4 minutes
or NaOH	3 g	or up to 10 minutes
H_2O	1 litre	
pH	6.5-7.5	
Temp.	90-95°C	

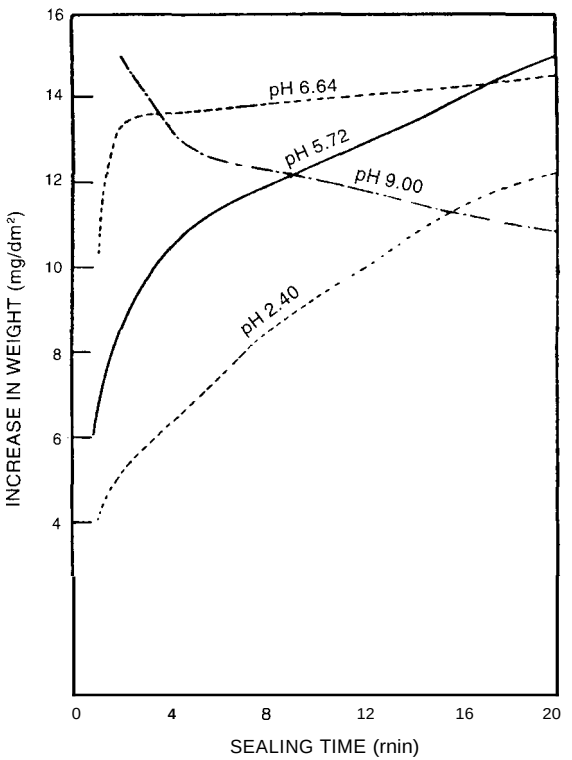


Fig. 11-16. Effect of sealing time on weight increase of sulphuric acid coatings sealed in chromate-dichromate solution at different pH values

If sodium carbonate is used, the solution should be boiled to drive off the carbon dioxide. With each addition of 100 g $K_2Cr_2O_7$, 18 g Na_2CO_3 should be added to solution (1) and 27 g Na_2CO_3 to solution (2) to keep up the pH.

The suitability of the method has been confirmed in production of coatings on Al-Mn, Al-Mg, AI-Si and Al-Cu-Mg-Mn alloys as well as on clad alloys. The results were confirmed by corrosion resistance tests carried out by Whitby[102] (see Table 11-12).

Specification DEF STAN 03-25/2[101] recommends solution (1) used at pH 6.7 and a temperature above 96°C for a time not less than the anodizing time. The alternative is a 40-60 g/l potassium or sodium dichromate solution used at pH 5.6-6.0. A related international aerospace standard (ISO 8087: 1984) uses an even more dilute solution (30-50 g/l) at a pH of 5-6 for a time of 20-30 minutes. Owen and Cole[49] have investigated the effect of contaminants in these dilute solutions and concluded that the harmful effect of silicate, phosphate, fluoride, iron and copper, already described on **p.** 885, apply to chromate solutions also.

The pH in the concentrated solution (1) may be determined by using bromothymol blue, and in the more dilute solution by using bromocresol purple as indicator, or by the electrometric method. (Note: The pH values given by the (colorimetric method are 0.3-0.4 units higher than those obtained with the glass electrode.)

TABLE 11-12

Effect of sealing treatments on corrosion resistance and mechanical properties of anodized 2014 (HS 15)[102]

Anodizing process	*Sealing*	*Exposure to salt solution fog (days)*	*Ultimate tensile strength (mean of 3)*	*Elongation % on 2 inch (mean of 3)*	*Loss in wt mg/sq ft/day (mean of 3)*
None	–	–	31.0	9.3	–
	–	57	21.03	0.2	157.8
CrO_3	–	509	21.0	0.75	26.2
	–	57	25.17	1.8	55.4
H_2SO_4	Boiling H_2O (30 min)	509	19.2	1.2	15.0
	Normal $K_2Cr_2O_7$ (30 min)	509	30.5	8.0	Trace
	Rapid method (1)	509	30.1	6.8	Trace
	Rapid method (2)	509	30.3	7.8	None
	$K_2Cr_2O_7$ then $ZnCrO_4$ (30 min)	509	30.4	7.8	Trace
	$ZnCrO_4$ then $K_2Cr_2O_7$ (30 min)	509	30.0	8.2	Trace
	Cobalt acetate (30 min)	509	30.3	10.0	4.2
	Nickel acetate (30 min)	509	29.9	9.2	4.0
	Na metasilicate:	57	19.9	0.6	140.1
	Na, O : SiO_2 = 1 : (30 min)				
	Soclium silicate:				
	Na_2O : SiO_2 = 1 : 2.05 (30 min)	509	11.4	0.3	49.2
	Na_2O : SiO_2 = 1 : 2.65 (30 min)	509	30.4	9.8	4.7
	Na_2O : SiO_2 = 1 : 2.91 (30 min)	509	26.8	4.3	4.2
	Na_2O : SiO_2 = 1 : 3.0 (30 min)	509	29.4	6.3	5.7
	Na_2O : SiO_2 = 1 : 3.3 (30 min)	509	30.4	8.7	4.1
	Na_2O : SiO_2 = 1 : 3.4 (30 min)	509	30.5	7.0	6.1
	Na_2O : SiO_2 = 1 : 3.4 (cold; then HAc)	509	5.0	0.3	82.1

Double sealing treatments

Double sealing treatments involving dichromate solutions have been investigated in the U.S.A.[103] with the specific purpose of improving the corrosion resistance of anodized aluminium in contact with copper. Panels which had been anodized in 15% (wt) sulphuric acid for 30 minutes at 21°C and 12 amp/ sq ft (1.3 A/dm^2) were sealed in 50 g/l sodium dichromate solution for 10 minutes and this was preceded or followed by sealing in other solutions for 10 minutes, before testing under salt spray in contact with copper. The highest corrosion resistance was obtained by presealing in 5 ml/l alkyl polyethylene glycol followed by dichromate sealing. Good results were also obtained by 5 g/l nickel acetate sealing followed by dichromate sealing.

Nickel acetate treatment followed by dichromate sealing in the automotive trim industry has been described by Holden *et al.*[104] Combinations of a nickel acetate pre-seal followed by normal hot water sealing, and nickel acetate sealing, are also described, the main benefit of the pre-seal being reduced sensitivity to phosphate and silicate contamination.

Other Russian work on sealing

As mentioned above the dichromate method of sealing has been widely used in the Soviet Union, apparently to the exclusion of other methods since the monograph by Fedot'ev and Grilikhes did not mention sealing in boiling water.[105]

Studies on sealing have been consistently pursued by Belov and Bogoyavlenski but they have not been generally available in the English language. They have concerned themselves with dichromate-chromate solutions and used the radioactive ^{51}Cr isotope to determine the absorption of the chromate ion.[106 107] In the pH interval corresponding to the minimum dissolution of the oxide layer the absorption of chromate ion diminished with increasing pH value but the weight of oxide increased. Desorption took place more readily from films impregnated at lower pH values, but there is practically no desorption of sulphate ions.

They have also made a comparative study on the absorption of sulphate, chromate and phosphate ions[108 37,109] and showed that it increased with rising temperature and diminished when the pH value increased. The affinity of the film for the ions was in the order $H_2PO_4^-$, SO_4^{2-}, CrO_4^{2-}, and the high phosphate affinity was accompanied by weak hydration, explaining the comparative ineffectiveness of phosphates as sealants. In studying the penetration of various anions and their subsequent protective power, they have found it impossible to advance one single mechanism as an explanation for the sealing mechanism.[110]

They have also examined the interaction between water and the oxide film[111] and noted three effects, chemical, physical-chemical and mechanical. The state of the water attached to the film and the structure and properties of the film itself depend sharply on temperature. The protective properties of the film were increased to the greatest extent by treatment in water at 90-95°C for 30-60 minutes.

6. SODIUM SILICATE SEALING

This method of sealing, which has already been described as the sealing process used for M.B.V. chemical oxide coating, was also first patented by Dunham in Britain[98] and by Edwards in the U.S.A.[70] While some progress has been made since then[112,113] the method is, however, less important than water, nickel/cobalt acetate or dichromate sealing for anodic oxide films and is used infrequently.. Edwards states that an $Na_2O:SiO_2$ ratio of 1:3 or higher is preferable, or, in the case of potassium silicate, $K_2O:SiO_2 = 1:4$. Anodized coatings sealed in this way lost 5.3% of their elongation value after exposure to 20% salt spray for 52 days, as agairist 4.5% when dichromate sealed, or 16% when left unsealed. Further comparisons are seen in Table 11-12.

According to Schenk,[42] the sodium silicate used has a $Na_2O:SiO_2$ ratio around 1:3.86 and the silicate acts as an inhibitor to weak alkali solutions. **A** modification of this treatment, in which the work was first sealed in water-glass and then immersed .in dilute acetic acid, was at one time used on die-castings but is not now recommended.

In the corrosion tests carried out by Whitby[102] in 3% salt solution fog, the optimum sotla-silicate; ratio corresponds to roughly $Na_2O:SiO_2 = 1:3.3$, and this author believes that aluminium silicate is formed by the action of the precipitated silicic acid on the aluminium hydrate or by double decomposition of sodium silicate with aluminium sulphate in the sulphuric-acid anodic coating.

Above a $Na_2O:SiO_2$ ratio of 1:2.9 the solution is neutral, and below this range it is alkaline; e.g., the metasilicate with a ratio of 1:1 is not suitable nor are silicates of ratio below 1:2.9. The sealing solution is normally used with a sodium silicate content of approximately 5% at 90-100°C for 30 minutes.

Coating with an alkali metal or organic silicate followed by a coating of a **polyorganohalogenopolysiloxane** has been suggested for protecting anodized aluminium iigainst icing by lowering the adhesion of ice to the surface.[114] The use of organopolysiloxane for sealing has also been the subject of another patent.[115]

Silicates in solution are potent inhibitors of the hydration process and the sealing mechanism in this case is obviously the physical plugging action of the growth within the pore of an aluminium silicate. The suppression of hydration is a very questionable procedure. There is a danger that silicate sealing can be made to perform remarkably well in accelerated tests, especially where an alkaline attacking medium is used, while such advantages do not show up in exposure to naturally occurring corrosive environments. Also silicate sealing has a very pronounced tendency to cause a permanent white bloom or discolouration in the coating which is particularly noticeable on bright anodized work.

Silicates have also featured in procedures employing two baths in sequence, where the intention was presumably to induce a more effective pore plugging action.

Dual sealing processes

Pédat[116] has suggested overcoming the problem of sealing smut, and also the tendency for silicates to discolour the coating, by using two consecutive processes, one containing nickel acetate or copper sulphate and ammonia at a high pH value, followed by 30 minutes at 99°C in:

sodium sulphate	30 g/l
sodium silicate	25 g/l

Cohn[117,118] proposed a similar idea in his 'Hi-Barrier Dual Seal' using the following two treatments in sequence:

1. Nickel acetate 5 g/l at 82°C for 20 minutes.
2. Sodium silicate 20 ml/l at 95°C for 15 minutes.

TABLE 11-13

Comparison of a silicate type dual seal with boiling water

Type of test	*Time*	$\frac{Wt.\,loss\ with\ water\ seal}{Wt.\,loss\ with\ silicate\ seal}$
2% caustic soda	10 min	17
0.2% caustic soda	75 min	5
2% sodium carbonate	90 min	1.5
10% hydrochloric acid	180 min	3
10% sulphuric acid	600 min	3
10% phosphoric acid	200 min	4
$2^1/_2\%\ H_2SO_4$ + 1% KF	5 min	2.5
CASS Test	18 hour	less pitting with silicate seal
Marine exposure	1 year	permanent white bloom with silicate seal. Water good.
Industrial exposure	1 year	5 micron films severely pitted in both cases. Thicker films good.

Sealing of this type was investigated by Thomas,[62] and Table 11-13 summarises the apparent improvement produced in the chemical resistance to various media, while on outdoor exposure the bloom formation was worse on the dual sealed panels, and pitting frequency high at an industrial site but no worse than with water sealing.

7. COLD IMPREGNATION (COLD SEALING)

Early work

The increasing cost of energy has made many companies seek ways of reducing the cost of the sealing operation. Triethanolamine acceleration of sealing has already been described, but another approach is to try to use much lower seal temperatures.

An earlier method! from Japan[119] was said to enable acceptable sealing in 5 minutes and perfect sealing in 10 minutes at room temperature by using an aqueous solution containing 0.5-3% ferricyanide, 0.1-1% phosphate and 0.1-0.5% calcium chloride at a pH which is controlled to about 4.5 with an organic acid. The inventors compared it favourably with other systems, including those based on nickel or cobalt acetates.

Alcoa'"' described sealing at a minimum of 60°C in a solution containing 2-6 g/l of a hydrolysable metallic salt, such as nickel acetate or nickel sulphate, 5-20 ml/l of an ethanolamine and 50-2000 ml/l of a soluble sulphate. Sealing smut was produced in this solution and was later removed by dipping the sealed work into a mineral acid solution. Later patents by Alcoa used much lower temperatures for sealing in ammonia vapours.[121] In this method the work was placed in a sealed container over the vapours produced by a 20-40% (wt) solution of ammonium hydroxide. The vapour temperature was in the range of 16-58°C and the sealing time at least 5 minutes. In practice at least 30 minutes sealing at the higher seal temperatures was required in order to pass the acid dissolution tests. Samples sealed in this way are said to be smut-free, and both sulphuric acid anodized and integral colour anodized work was successfully sealed.

However, in the 1980's a great deal of work in Italy led to the development of very practical cold seal systems.[122,123,124,125,126,127,128] These seal systems are used at about 30°C and are based on solutions which contain fluoride or silica compounds in the presence of nickel salts, originally in a water-alcohol mixture.'?' The water-alcohol solvent apparently lowered the solubility of the salts and facilitated precipitation within the pores of the anodic film. It is clear from these conditions that conventional hydrothermal sealing is not involved in these processes and that pore plugging by nickel salts, fluorides or silicates is more the mechanism of sealing. For this reason there has been a great deal of discussion about whether the process should be called 'cold sealing'. In particular, within the European Standards group, CEN/TC132/WG15, and within the Qualanod organisation, it was eventually agreed that the general term for this process should be 'cold impregnation' to distinguish it from conventional hydrothermal sealing. Thus the European Standard on anodizing, EN12373:Part 1:2001, defines cold impregnation as 'a treatment of anodic oxidation coatings on aluminium to plug the pores and reduce the absorption capacity of the coating by chemical processes carried out at low temperature after anodizing'. As the process has developed it has become simplified, and in general now only uses a solution of nickel fluoride.

The first use of fluorides for low temperature sealing seems to have arisen in Japan, where Yoshimura and Kagaya[130] described the use of a range of fluoride solutions at room temperature and 50°C for sealing. Best results were obtained with nickel fluoride and chromium fluoride solutions. Later Okuno Chemical Industry[131] described the use of a 0.5% nickel fluoride solution containing iso-amyl alcohol for 5 minutes at 30°C for sealing anodized aluminium.

The early Italian work was also based on a nickel fluoride/alcohol mixture,[122] and quoted typical examples of 6.5 g/l of a nickel compound, 2 g/l of a fluorine compound and 50 g/l of 2-butanol. The use of silicon compounds, fluoroborates or fluorosilicates was also mentioned. Sealing for 10-15 minutes at about 30°C was recommended. Work sealed in this way has been shown by Strazzi to have good corrosion resistance and good seal quality,[''] and was considered equivalent in performance to that produced by conventional sealing.

The first Italtecno work[124] was based on the use of salts such as nickel acetate or nickel fluoride (6-7 g/l) in the presence of ethyl silicate (1 g/l), a suitable silane such as aminopropyl triethoxysilane (0.3 g/l) and an alcohol such as iso-butyl alcohol (15 g/l). These solutions were used for about 10 minutes at 30°C and a pH of 5.5-6.5. Experience in Italy and America with products sealed in this way was apparently good.[125] Grace[126] used a similar combination of a nickel salt and a surfactant for cold sealing, the preferred surfactants being fluorocarbon esters, fluorinated ethers or polysiloxanes. Again a temperature of 20-30°C was used at a pH of about 6 for a time of up to 30 minutes and good corrosion resistance was obtained from the finishes sealed in this way.[127,128] TEC A Systems also claim a fluoride containing, low temperature, seal solution.[''] Amchem describe a nickel fluoride bath also containing ammonium and acetate ions.[''']

Current practices

Since its development much work in Italy and other areas has simplified the process, and it has become much more standardised. Processes generally use a solution of about 5 g/l nickel fluoride ($NiF_2.4H_2O$) at a pH of 5.5-6.5 and a temperature of 25-30°C, with a treatment time of about 1 min/micron. This is typified in the detailed regulations that the Qualanod Specifications[134] lay down for the use of cold impregnation processes. In these they indicate that excess fluoride ions can attack the anodic coating, so the molar ratio between nickel and fluoride should not exceed 1:2. In practice this means that the concentration of nickel must be greater than 1.55 times the free fluoride content. They recommend that nickel ion and free fluoride contents should be maintained within 1.2-2.0 g/l nickel ion content and 0.5-0.8 g/l free fluoride ion content. One problem that can be experienced is the work looking slightly greenish after impregnation, and this has been countered by replacing a small amount of the nickel salt by an equivalent cobalt salt. Qualanod allows 5-10% to be substituted in this way. They also point out that fluoride is consumed at a higher rate than nickel, and additions of ammonium fluoride are required to maintain the correct balance.

They also indicate some temperature sensitivity, too high a temperature, particularly when the free fluoride content is at a high level, causing the anodic film to be attacked, leaving a powdery surface. Contamination of the bath can cause problems and the suggested limits for contaminants are shown below:

sodium or potassium ions	less than	300 ppm
amonium ions	less than	1500 ppm
sulphate ions	less than	4000 ppm
phosphate ions	less than	5 ppm
aluminium ions	less than	250 ppm

A major problem with cold impregnation systems was that, as will be discussed later, the use of low temperatures meant that the mechanism of sealing was different. Thus it war. difficult to predict the outdoor exposure performance of films treated in this way, and for many years they were used to only a limited extent in external architectural applications. The problem was increased by the fact that some of the conventional sealing tests did not indicate satisfactory results with cold impregnated work. In particular admittance values, measured on freshly treated work, were well outside the accepted limits, so one of the normal production control methods could not be used. With time admittance and other seal test values improved, and it was clear that a continuing sealing or 'ageing' effect was taking place. However, as a result of these problems, Qualanod insisted on having the results of at least 5 years outdoor exposure tests before approving the system for exterior architectural use. This approval came in 1991 with the successful completion of the exposure tests,[135] and the subsequent inclusion in the Qualanod Specifications of a recommended operating practice for cold impregnation systems based on nickel fluoride.[134] Cold impregnation is now widely accepted for architectural work in the USA and the Far East, but is still used to a more limited extent in Europe.

However there was some limitation to the Qualanod specification, as it required that a double sealing treatment was used. The first stage was the conventional nickel fluoride impregnation process, but this was to be followed by ageing by hot water treatment. This second stage was to be carried out using a conventional hydrothermal sealing treatment at a minimum of 96°C for between 0.8 and 1.2 min/micron, or in a 5-10 g/l nickel sulphate solution at a minimum temperature of 60°C for the same time. Many workers had found that this second stage treatment overcame the admittance problems and allowed the work to be tested conventionally, as well as giving improved performance, but much of this work had been carried out at temperatures below 96°C. Workers in Spain[136] examined the effects of ageing in wet conditions at room temperature and 50°. They used conventional seal quality tests as well as electrochemical impedance spectroscopy to study the ageing process, and concluded that ageing at 50°C led to virtually instantaneous fulfilment of the quality standards in the dye-drop and acid dissolution tests, and that of the admittance test within 4-5 hours. They further concluded that

the rapid ageing of cold impregnated films made two-step cold impregnation unnecessary, and they pointed out the usefulness of electrochemical impedance spectroscopy in following post-seal transformations.

On the other hand workers at Loughborough University of Technology[137,138] concluded that post treatment for 1-1.5 min/micron at 60°C in deionised water would not allow the cold impregnation process to satisfy the admittance test, and they found that sealing quality improved the higher the temperature and the longer the time of the post-impregnation process (Figs. 11-17 and 11-18).[139] They believed the optimum process to be post-treatment for 10min in boiling deionised water. The satisfactory use of nickel sulphate solutions at 60°C as a second stage treatment has been described by Pozzoli and Boi,[140] who also claimed benefits for spray sealing.[141]

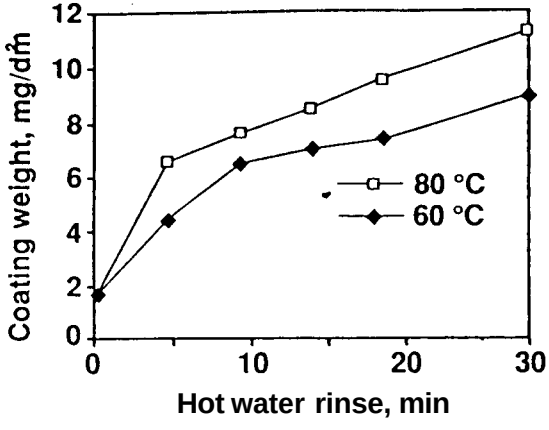


Fig. 11-17. Weight gain of cold-sealed films with hot-water rinse post-treatment vs. time

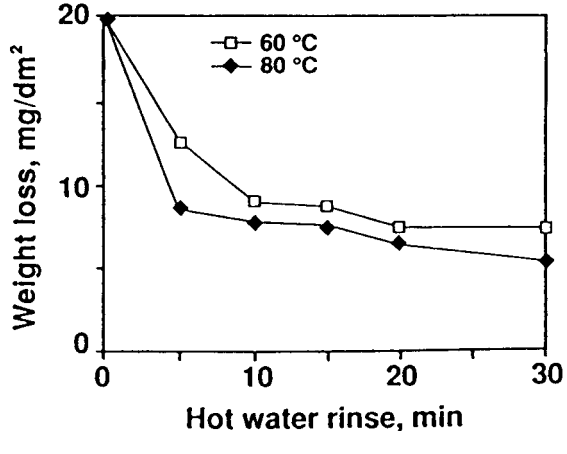


Fig. 11-18. Effect of hot-water rinse post-treatment on seal quality, determined by phosphoric/chromic acid dissolution test

Another problern that was solved by the double treatment was that of crazing of cold impregnated anodic films during outdoor exposure.[142] This was thought to result from the greater hardness of cold impregnated work, as less of the anodic film is hydrated, and was a serious problem with this type of work exposed in hot, dry climates such as the Middle East. Work in Italy[143] demonstrated that a double sealing treatment solved the problem, the temperature of the hot water sealing bath needing to be increased from 70°C to at least *85°C* as the anodic film thickness increased.

Ellard and Morita[144] studied a range of commercial cold impregnation systems and confirmed the problems of admittance testing, but showed considerable variation in test results from one system to another. They added acetic acid salt spray resistance to the range of tests included, and showed that the performance of all the cold impregnation systems was inferior to that of conventionally sealed samples, but again there was considerable variation from one system to another. Because of concern over acid resistance, they suggested the use of a new test, immersion in 50% nitric acid solution for 24 hours at room temperature, as a method of evaluation, and measured the anodic film thickness loss in this test. Again there was considerable variation, as shown in Table 11-14, with conventionally sealed work (sample 1) only losing 4 microns of coating, but many of the cold impregnated specimens (samples 2-9) showing total removal of the 25 micron coating. However all the impregnation systems in this work were single stage processes and did not include any post-impregnation treatment.

TABLE 11-14

Thickness loss (pm) of 25µm finishes in the nitric acid immersion test

Seal identification number	*Thickness loss (µm)/time aged*			
	Clear anodized		*ANOLOK 547*	
	24 h	*14 days*	*24 h*	*14 days*
1	4	4	4	4
2	25	25	25	17
3	25	25	25	25
4	25	5	25	5
5	25	25	8	15
6	25	5	15	5
7	25	6	25	7
8		6 (6 days)		6 (6 days)
9	23	8	21	8

Ellard and Short[145] took this process further, trying to find a practical test method that could be used for on-line evaluation of cold impregnation processes. They concluded that quality of impregnation was related to the amount of nickel in the film, and this could be evaluated using a nitric acid dissolution spot test, followed by the use of Merck test papers to evaluate the amount of nickel released. This method gave good agreement with chemical analysis of nickel content after acid dissolution. However extraction of nickel became more difficult as the film aged, and testing within 1 hour of completion of the impregnation step was essential. However, although an interesting suggestion, this method has not been standardised or used in practice.

Over the last 10 years the cold impregnation process has been modified and optimised and many of these changes have been summarised by Mura and Pozzoli.[146] Concentrations have become lower with time, as in the Qualanod Specifications,[134] ratios have been optimised, and new additives have been introduced. Workers at Loughborough[147] have published detailed work on the effect of a range of parameters, and the same authors have indicated the role of surfactants in these baths.[''] They found that the presence of a surfactant in the nickel fluoride solution had no effect on weight loss and dye absorption seal quality test results, but it improved admittance values. Most effective was 25-35 ppm of a nonionic, fluorinated, alkyl ester surfactant (FC 430 from 3M). The problem of the green colour produced by nickel salts, which mainly occurs with films that have been produced under conditions giving excess pore wall attack, has also been tackled by the use of additives.[149] Henkel suggest the addition of an azo or azo-metal dyestuff to the nickel bath, so the colour imparted by the nickel ions and the dye offset one another.[150]

Workers in China[''] have suggested increasing the pH of the cold impregnation bath to 7.0-7.5, and using a lower nickel salt concentration, in order to reduce nickel and fluoride salt consumption. Paolini and Dito[152] have examined the use of alternatives to nickel fluoride, and suggest that nickel lactate and nickel fluoborate have possibilities. However the former had to be used at a temperature of 50°C, and the latter was limited by its instability to hydrolysis. On the other hand German workers[153] suggest the use of much more concentrated solutions in a 2-stage process. The first stage was for 10 min at 30°C in a 6% cobalt fluoride, 30% nickel fluoride solution, followed by 50 min at 70°C in water containing 2 ml/l of a triazine derivative as a smut inhibitor. Italian workers[''] have suggested the use of microwaves for speeding up the hydration stage of cold impregnation processes, and they indicate as little as 0.5 min/micron for the post-impregnation .treatment time. They suggest that this technique may be particularly suitable in the coil anodizing industry, and that it may also be applicable to conventional hydrothermal sealing.

The cost of chemicals is a major factor in cold impregnation processes and this has led Burbidge[155] to develop processes for the recovery of nickel and fluoride ions from the rinse waters.

One surprising aspect of cold impregnation has been the suggestion by a health worker in Sweden[156] that material treated in this way may be a source of dermatitis in workers handling it. She cites a case of an engraver who suddenly developed dermatitis when handling anodized aluminium products. It was shown that he was sensitive to nickel, and that nickel ions were being released from the sheets on which he was working, which had been sealed by cold impregnation.

The mechanism of cold impregnation

It was clear frorn the early development of cold impregnation processes that the mechanism of pore closure differed from that of conventional hydrothermal sealing. Pore closure by a boehmite plug, which normally only occurs at high water temperatures, did not play a part, and plugging was mainly happening as a result of the deposition of nickel salts in the pores. It was this fundamental difference that was leading to different reactions in the conventional seal quality tests.

This mechanism was studied by Short and Morita[157,158] using electron probe microanalysis (EPMA), transmission electron microscopy (TEM), electron spectroscopy for chemical analysis (ESCA), and scanning electron microscopy (SEM). The distribution of Ni, S and F was studied in suitably prepared cross-sections of a 10 micron cold impregnated film. The EPMA and ESCA results are shown in Figs. 11-19 and 11-20. From this work they concluded that cold iinpregnation takes place as a result of precipitation of $Ni(OH)_2$, $Al(OH)_3$ and AlF_3, all in a hydrated form, in the top **3-4** microns of film. Several factors, such as the pH increase observed in the impregnation solution, the dissolution of some of the sulphur in the film, the presence of nickel and fluoride in the impregnated layer, the binding energy data, and the morphology of the impregnated surface, all favoured a dissolution / precipitation reaction as the pore plugging mechanism. They therefore proposed that, initially, the F^-ion in the solution is absorbed by the anodic film to form a complex ion, which subsequently dissolves. The dissolution of the anodic film, and observed loss of sulphate ion, result in a localised pH reduction in the pore. This reduced pH accelerates dissolution, resulting in a pH gradient in the pore. When the aluminium dissolved in the solution in the pore mixes with the higher pH solution at the pore mouth, the aluminium precipitates together with nickel ions to form a mixture of hydroxy-fluoro aluminium, hydroxy-aluminium and hydroxy-nickel, though results also indicate a significant loss of aluminium to the solution. During subsequent ageing, the $Ni(OH)_2$, AIF, and $Al(OH)_3$ react with water in the pores, and further water from the atmosphere, to give further hydration, and this results in expansion of the pore-filling media. This expansion produces a more solid plug and hence an improvement in seal quality.

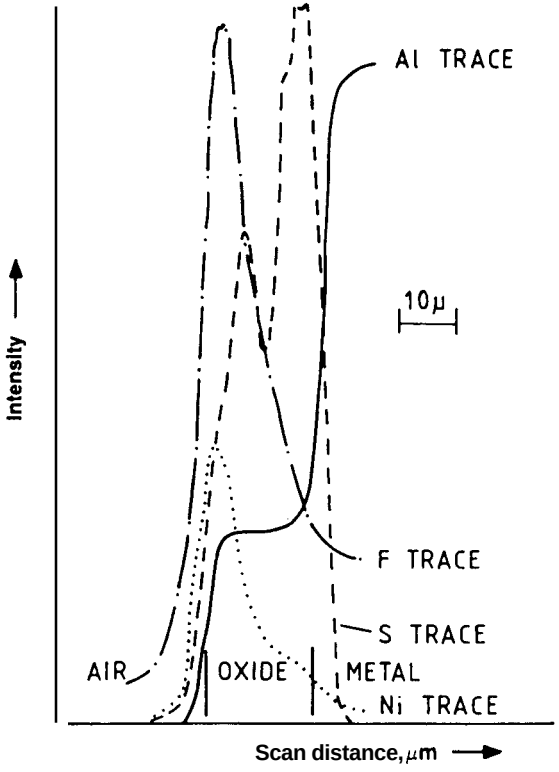


Fig. 11-19. Distribution of Ni, S, F, and Al from EPMA scans of cross section of a cold-impregnated anodic film

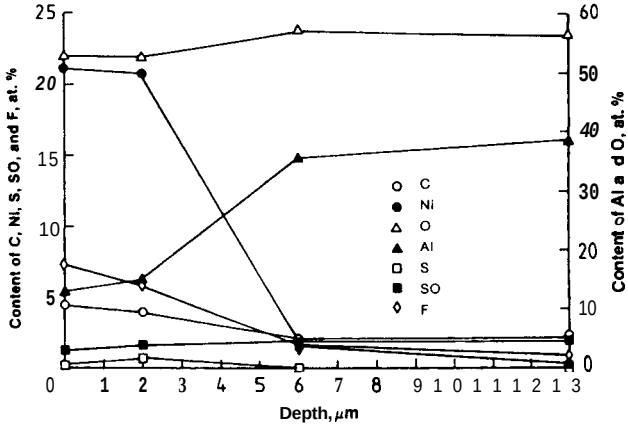


Fig. 11-20. Mole fraction of elements detected in cold-impregnated anodic film by ESCA

A detailed study by workers in China[159,160] used X-ray diffraction, infra-red spectroscopy, thermogravimetry and differential thermal analysis, but essentially came to the same conclusions. They indicate that for thin films (up to 5 microns) the pores are completely filled by precipitation in the cold impregnation process, but for thicker films the outer part of the pores is plugged, but below this the pores are unfilled. This corresponds with the distribution of nickel and fluoride, which they found to be mainly in the outer layers of the film.

This distribution of nickel and fluoride is confirmed by workers in Italy,[161] who used X-ray diffraction, energy dispersive analysis of X-rays (EDAX) and scanning electron microscopy (SEM). They pointed to the aggressive nature of the nickel fluoride solution, and suggested that it increased the reactivity of the outer anodic layer, enhancing the re-precipitation reaction at the pore mouth, a suggestion made by Cavallotti *et al*[162] much earlier. They indicated the good alkali resistance of the impregnated product, but did not examine its acid resistance, a property which other workers found to be inferior.

Researchers at Loughborough University of Technology[163] agreed with the work of Short and Morita,[157,158] but suggest that the increase in pH of the impregnation bath with use is due to hydroxyl ion formation, resulting from ion exchange between fluoride and hydroxyl groups on the aluminium. After impregnation the film ages in two stages, the first involving crystallisation of nickel hydroxide and other metal compounds, and this takes place in the first few hours after impregnation. The second stage involves atmospheric hydration of the film creating further sealing and pore plugging.

8. MISCELLANIEOUS SEALING SOLUTIONS AND METHODS

Lead acetate

Similar to nickel-cobalt acetate sealing, this method[71,164] is useful for improving the light-fastness of some dyes which do not give good results by the former process. Two example!; are Aluminium Red GLW and Bordeaux RL in which the light-fastness, after sealing in lead acetate, can be improved to 6-8 and 7-8 respectively (the higher figures are for darker colours in more concentrated dye baths) as compared to 4-7 after nickel/cobalt or hot water sealing.[71]

The lead acetate sealing bath is normally used at a concentration of 2.5-5.0 g/l[164] at 97-100°C for 30 minutes. The pH should be controlled between 5.5-6.0 by the addition of acetic acid.

Other heavy metal salt solutions

The use of nickel, chromium or cobalt in the form of sulphamates has been covered by a Japanese Patent.[165]

Other heavy metal salt solutions have been used for sealing, again because of the improvement in light fastness of coloured work, and in some cases the sealing additive is specific for the dye used. Thus zinc salts are used for green shades and copper and chromium salts for other colours where the dyestuff is a copper or chromium complex.[71] In this case the salts would be used as acetate, sulphate or chloride solutions in Concentrations from 2.5-5.0 g/l at 97-100°C for 30 minutes and at an optimum pH of 6.7.

Nickel, cobalt and copper salts have also been used in a mixed aqueous solution as metal ammonium complexes of hydrolysable salts (0.3-1.5%) at pH 5.5-6.0, where the copper salt must be not less than 25% of the total weight of salts added.[166]

Rare earth metal salt solutions have been used for sealing materials anodized by the Boeing boric acid / sulphuric acid anodizing process in aerospace applications.[167] Cerium or yttrium salts were used in comparison with chromate solutions, and similar corrosion resistance was claimed.

Alkali metal salts

Sealing in concentrated sodium, potassium or calcium sulphate or chloride solutions[28] (120-200 g/l) at 90-100°C, pH 6.5-8.2 for 15 minutes to 1 hour, is stated to speed up hydration of the anodic oxide as compared with normal water sealing.

According to a German process[168,169] sodium sulphantimonate solution, in concentrations of 20 or 80 g/l is used for obtaining hard films at low temperatures (i.e., 20°C and 40°C respectively) in 15 minutes.

Molybdates and tungstates

Spooner has suggested that a sealing bath containing 20 g/l sodium or ammonium molybdate solution at pH 6.5-7 and 100°C for up to 30 minutes has advantages similar to the dichromates but without the attendant discoloration, and this has been covered by a patent by Aluminium Laboratories Ltd.[30,170] Sodium molybdate has also been used with organic additives such as nicotinamide.[171]

Spooner also investigated double sealing treatments,[172] including sealing in water and then sodium silicate solutions, and water plus molybdate solutions, but the best corrosion results were obtained with water sealing followed by sealing in dichromate.

Lockheed[173] have patented a double sealing process in which, in the first stage, the anodized work is immersed in a 5% sodium tungstate, 1% chromic oxide solution at a pH of 6.5 and a temperature of 95°C for about 10 minutes. It is then immersed in a 1% nickel acetate solution at 95-100°C for a further 10 minutes. This system is claimed to give good and consistent seal quality.

Medium temperature sealing

The development of low temperature sealing processes described in a previous section, and some of the problems experienced with this method, have generated interest in so-called 'medium temperature' sealing. These are a relatively recent development, and although several systems are being marketed, little technical information has been published. One of the benefits seen is that, unlike the cold systems, many do not contain nickel and are therefore considered as 'Eco-friendly'.[174]

Some of these processes are based on lithium or magnesium salts, often as the fluoride or acetate. **A** product from Italtechno (Hardwall MTS) is used at a concentration of 30 g/l, a pH of 6.0-6.5 and a temperature of 80-85°C for a time of 2 min/micron.[175] Sealing test results with the product are claimed to be equivalent to those of conventional hot water sealing. **A** lithium fluoride based product from Henkel[176] (P3-almecoseal C3 and C4) uses a two-step process, with a pre-dip for 0.5-1.0 min/micron in 70-90 ml/l of the C3 additive and 35-45 ml/l of the C4 additive at a pH of 5.5-6.5 and a temperature of 22-26°C. The work is then sealed conventionally in hot water for 0.8-1.2 min/micron. A patent relating to this type of sealing"' describes sealing baths, which optionally contain lithium or magnesium ions, and contain 0.0004 to 0.05 g/l of a preferably non-ionic surfactant and 0.0005 to 0.5 g/l of an organic acid, preferably a poly-phosphino-carboxylic acid. Such a bath is used at a conventional pH, and is claimed to allow sealing for a shorter time (1 min/micron) or a lower temperature (80°C) than usual.

Clariant (formerly Sandoz) have used several different approaches. One of their patents[178] describes the use of an aromatic smut-inhibiting additive, which is particularly effective when used in combination with magnesium or calcium salts, preferably in the form of the acetate. The same type of additive used in combination with lithium salts is described by Novomax.[179]

A later Clariant patent[180] recommends the use of sulphonated aromatic compounds and condensates of aldehydes with other aromatic compounds in the form of alkali metal salts. These formulations are claimed to allow effective smut-free sealing at a temperature of 80-85°C. They are said to maintain their efficiency over long use, and to allow good pH control (normal range 5.5-6.5).

Work on a nickel containing, medium temperature seal in the U.S.A.[181] has shown that this type of bath is more sensitive to silicate contamination than conventional seal baths. The work has indicated that this is a complex phenomenon, with the silicate interacting with the surfactants used to control smut formation.

Other organic additives

A variety of approaches has been taken using organic materials to avoid hydrothermal sealing.

Tannin solution is reported[7'] to have been used in a concentration of approximately 5 g/l at 25-96°C for 15 minutes. Without causing hydration, it was stated to stop-up the pores in cold solution.

Reynolds Metals Co. proposed the use of an organic solution containing nicotinamide, ethyl quinoliniurn iodide, 1-ethyl-2.6-dimethyl quinolinium iodide or 6.8-dichloro-2.4-(1H, 3H)-quinazolinedione at 82°C and a pH of 6-6.5 to increase corrosion resistance.[171]

Klingenmaier has proposed a hot aqueous solution used for not less than 5 minutes at 90-100°C containing 0.01-0.1% of disodium 4-dodecylated oxydibenzene sulphonate with acid to produce a pH of 5-7.[182]

In a proposal designed to raise the temperature at which the anodized work begins to craze, Kaiser added to the sealing bath a modifier which could be 0.02-0.04 g/l y-toluene sulphonamide; 0.1-3 g/l of sodium lignosulphonate could also be present.[183]

Barkman patented a dilute aqueous solution of a basic organic nitrogen compound which did not contain a polar substituent, used for 15 minutes at 70-80°C and pH 5-8. The compound could be a heterocyclic nitrogen compound, for example, substituted pyridine or quinoline, or a carbocyclic nitrogen compound such as tolyurea or aminobenzoate.[184]

Levy claimed an aqueous solution containing more than 0.1% of a poly-oxyalkylene glycol (molecular weight 100-200,000) used at over 70°C[185] and Péchiney have used a boiling solution of 10 g/l sodium polystyrene sulphonate at pH 4.9.[186]

More recently, work in the U.S.A., aimed at the avoidance of dichromate sealing in the aerospace industry, has suggested the suitability of treatment in a water-immiscible isostearic acid oil.[187] The addition of small amounts of a chelating agent, benzotriazole, was found to be beneficial,[188] and good salt spray performance is claimed. Earlier patents by the same workers describe the use of long chain carboxylic acids, such as stearic acid, with low molecular weight alcohols such as isopropyl alcohol.[189,190]

Sealing with lacquers, waxes, etc.

Organic substances such as lacquers, waxes, oils or resins act by imparting a superficial impervious layer on top of the coating and are more often employed as an additional protection rather than for primary sealing. Both air drying and stoving lacquers are used. Turpentine solutions of 33 g/l carnauba wax with 33 g/l stearic acid or 150 g/l carnauba wax with 33 g/l beeswax have been used for special purposes. Waxes, oils and resins have the disadvantage of being easily soluble in organic solvents.

Vaseline has sometimes been applied to anodic coatings by hand or by dipping,[191] and impregnation of the film by organic coatings in the vapour phase has been suggested. In one such vapour phase process,[192] sulphuric acid anodized aluminium is exposed to one of the following mixtures: phenol- or urea-

acetaldehyde; phthalic anhydride-glycerol; styrene-furfuryl alcohol. The process is carried out in a closed container above 93°C when the vapours polymerize to form a monomeric synthetic resin within the coating. Japanese workers[193] have even suggested 'smoke sealing', where samples were suspended in an electric furnace packed at the bottom with heavy oil, woodchips and silicone oil, with which they wanted to impregnate the film. The chemical smoke in the furnace was said to achieve this result.

Lockheed[194] have patented a method of applying a water soluble acrylic polymer or co-polymer to the anodized component, and then curing it at a temperature of about 76-94°C for 30-60 min. This treatment is said to allow normal hydration of the coating, as well as giving a cured acrylic lacquer film on the surface, and it is claimed to give superior corrosion resistance compared with conventional sealing. The coating composition includes a water soluble acrylic polymer or co-polymer, an amine-based water solubilising agent, a nitrogen containing cross-linking agent, such as a melamine, and additives to inhibit hydrolysis of the resin such as hydroquinone. It is normally applied by dipping. A later Lockheed patent")' describes the use of a polyurethane resin coating for giving good fluid and environmental resistance in aerospace applications.[196] The resin has a particle size which permits a portion of it to enter the pores of the anodic film, and is used as a colloidal suspension (approx. 7% solids) in an alkaline solvent / water bath at about 82°C. Bath pH is maintained between 7.5 and 8.2 with dimethyl-ethanolamine. The clear coating is air dried, during which the urethane resin crosslinks and becomes part of the anodic coating.

A very broad patent application by Henkel[197] covers the application of a water-based coating containing 25-5000 ppm of an aryl or alkyl triazole, a partially substituted polyvinylphenol polymer or copolymer, and optionally a polar organic solvent. This coating is said to be applicable to many metal surfaces which are capable of forming a protective oxide or conversion coating, but is particularly suitable for sealing anodic coatings on aluminium and magnesium.

Other organic sealing materials have been used for improving frictional properties. For example, the coefficient of sliding friction of samples sealed in a boiling 5 ml/l tetrafluoroethylene dispersion for 5 minutes was 0.07 compared with 0.72 for a sodium dichromate-sealed specimen.[103] Good results were also obtained with boiling solutions of 1 g/l diglyceryl stearate which gave a coefficient of sliding friction of 0.09, while other values were 0.14 for 5 ml/l polyethylene emulsion (20%) and 0.18 for 7 g/l wax emulsion with 5 g/l sodium alcohol sulphate. A tetrafluoroethylene suspension can also be used at 66°C for two minutes. A Russian proposal for reducing friction and improving resistance to wear uses a mixture of sulphur and paraffin wax in an organic solvent such as benzene or carbon disulphide.[198]

One procedure which is intended to follow a conventional sealing in steam or water for ten minutes consists in immersing the work at 85-150°C in a molten polar saturated aliphatic alcohol, acid or amine (with at least 10 carbon atoms) or in a mixture of these, for example, docosanoic acid (behenic acid), stearic acid,

arachidic acid, lignoceric acid, behenyl or stearyl alcohol or amine. The aliphatic compound may also have mixed with it up to 10% of an anti-oxidant and a chelating agent, e.g. behenic acid containing 0.25% triphenyl phosphate and 0.1% tetraethanol.[199]

A commercial organic sealant which was applied by spray and was available as an aerosol has been described in America as Coricone 1700.[200] It was stated in independent tests to improve the resistance to salt spray solution three times, to be particularly suitable for hard coatings, and also to have increased considerably the corrosion resistance of conversion coatings.

Tsuji[201] investigated the use of special silicone sealing treatments for anodized surfaces, in order to reduce the adhesion of ice to the surfaces in refrigerator applications. He used organo-hydroxysiloxanes for this purpose, and cured them at 110°C for 30 min. before boiling water or steam sealing. He found a significant increase in abrasion resistance with films treated in this way.

In somewhat similar work, Dow Corning[202] have used siloxanes to produce a silicone-silica hybrid coating known as Vestar. This was initially suggested as an alternative to sealing, but has since been used as a clear, 5 micron, coating in its own right. Many potential applications for the finish were considered, including reflectors, holloware, automotive trim and architecture but in practice it has achieved limited use. Later work[203] suggests a sealing process where the electrical impedance of the anodized substrate is measured to determine the degree of surface sealing. This method is particularly related to problems of adhesion of silicone structural glazing systems, and work with suitable electrical characteristics is cleaned with a siloxane cleaner before application of the silicone.

In the same general field the use of organo-functional silanes for sealing has been suggested by Aeromarine Technology.[204] The materials are said to react with water at room temperature to form silantriolic compounds, which in turn react with the oxide coating forming a stable chemical bridge between the silicon and the aluminium. Examples quoted of the use of this system are particularly with cold impregnation systems containing nickel and fluoride ions and a small amount of ethyl silicate.

I.C.I. and Alcan[205] examined the benefits of thin (1 micron) inorganic metal phosphate coatings applied to sealed anodic surfaces. They found that such coatings had very good weathering performance, and could give improved lightfastness with some dyed films, but the coatings were difficult to apply in practice. Iron, chromium or mixed iron/chromium phosphates were the most useful.

Electrophoretic sealing

There were some quite early suggestions for sealing in which the use of an electric potential was featured, and anodized aluminium has been sealed at less

than 30 volts in colloidal solutions produced by ion exchange methods containing oxides of either silicon, titanium, thorium or zirconium.[206]

Electrophoresis was used as an alternative process to hydration to fill up the porous structure of the anodized layer with either colloidal alumina or carbon.[207,208] The surface of the aluminium was first heated rapidly to 300-400°C after which anionic colloidal carbon of average particle size 13 millimicrons could be impregnated at 60 volts from an aqueous suspension also containing 5% by weight of colloidal alumina. These coatings were intended for use in space, but there is little indication that they have found application on earth.

However, the deposition of an acrylic resin onto an unsealed anodic coating by electrophoresis has become the standard method of sealing for many extruded architectural products in Japan. The process is usually used in the type of vertical line described in Chapter 8, page 616, and several hundred thousand tonnes of anodized extrusions are sealed in this way each year. Plants of this type have been described by Patrie.[209] The work is pretreated and anodized conventionally to a thickness of about 8 microns, and is then electrophoretically coated with 8-10 microns of clear acrylic resin and stoved at about 160°C. Much of the work is electrolytically coloured before lacquer sealing. The lacquers used normally produce a high gloss finish, but the need for a more matt finish in monumental architectural applications has led to development of semi-matt finishes also.

The process was initially developed in Japan by Honny Chemical Co. Ltd.[210] under the name of 'Honnylite' and they disclose the use of a thermosetting acrylic acid resin, an acrylate resin or an acrylamide. Alternatively a mechanical mixture of an alkyd resin or a vinyl-modified unsaturated alkyd resin and a water soluble melamine can be used. These resins, when prepared for electrodeposition have a muddy white appearance and are usually in the form of an emulsion or dispersion. A concentration of about 30% by weight of the resin is used, often at a temperature of about 25-30°C and a pH of about 8. The anodized work, after thorough rinsing in mains and deionised water is dipped into the water-based resin mixture and current passed between the work (anodic) and a stainless steel cathode. A voltage of 50-100 V, giving a current density of 0.2-0.6 A/dm^2, is normally used for a time of a few minutes. The work is then drained and transferred to an oven for stoving at 120-160°C for 10-60 min. A very smooth clear, glossy finish is obtained and the resin is claimed to penetratt: the pores of the oxide film as well as giving a surface layer.

Since this time, there has been considerable work carried out in Japan on electrophoretic resin deposition, and numerous patent applications have been made. Few have been covered outside Japan, and it is still mainly in that country that the process is used on a large scale. Honny Chemicals*" claimed a method of electrolytic colouring before electrophoretic deposition of resin, but conventional electrolytic colouring systems are most usually used outside

Japan. General Motors[212] also claimed electrophoretic deposition of clear lacquer coatings for sealing anodized aluminium.

Some indications of the mechanism of electrophoretic deposition of resin on porous anodic coatings have been provided by Ashida and Ueda[213] and by Sato.[214] The former workers[213] separated the porous film from the metal, and used it as a diaphragm for electrophoresis in a water-based acrylic/melamine resin mixture. The anodic film was produced in an oxalic acid electrolyte at about 40 V so had relatively large pores, and when it was placed between the electrodes of the experimental cell, acrylic resin and melamine resin particles migrated towards the anode when voltage was applied. **A** small amount of resin passed through the pores, but most deposited on the pore walls. They therefore suggest that in the normal process, resin particles migrate towards the base of the pores, reacting with hydrogen ions generated at the barrier layer to form acrylic acid, which coagulates and fills the pores. Sato[214] described four reactions occurring during the deposition process, deposition of acrylic resin by anodically dissolved aluminium ions, thickening of the barrier layer of the anodic film, generation of hydrogen ions within the barrier layer and neutralization of the acrylic resin by the released hydrogen. Flaws in the barrier layer of the film play an important part in this mechanism as it is there that the hydrogen is generated, so the presence of additives or impurities in the water-based resin solutions strongly affects the coating process. Work is normally rinsed in deionised water before entering the resin coating bath in order to avoid contamination, but Ito and Shibuya[215,216] have reported that small amounts of chloride ion aid resin deposition. Sato[214] indicates that the particle size of the acrylic resin is about 300 Å in diameter, so that the resin will not enter the pores in a sulphuric acid anodized film and will just coat the surface.

Weathering experience with the lacquer coated work in Japan is apparently good, and Patrie and Colombier[217] report excellent performance after 8 years exposure in France.

9. EFFECTS OF SEALING ON THE PHYSICAL PROPERTIES OF THE ANODIC OXIDE COATING

Corrosion resistance

Spooner[7,74] compared a number of sealing methods, including water sealing at different pH, steam sealing and sealing in nickel acetate and silicone solutions, by cathode current flow rate tests and by measuring the weight gain on sealing as well as the material lost by leaching in cold sulphuric acid, salt spray and on outdoor exposure. His results are shown in Figs. 11-21 and 11-22 and Table 11-15.

TABLE 11-15

Effect of miscellaneous sealants on anodic film properties[7] (Anodized in 15% (wt) sulphuric acid, 30 min, 21°C, 15 amp/sq ft, sealing at 98-100°C)

Sealant	*Unit sealing*	*Sulphuric acid weight loss (mg/dm²)*	*Cathodic current density (mA/dm²)*	*Continuous acidified salt spray ratings (h)*	
				(184)	*(344)*
Potassium dichromate 5%	77	38	2.1	5	5
Potassium dichromate 0.1%	74	15	1.8	5	5
Potassium dichromate + sodium carbonate	72	23			5
Sodium molybdate	84	11	1.4	5	4
Barium nitrate	99	12	3.1	3	1
Silicone	29	376	42	1	1
Silicone +water	51	67	2	3	2
Ferric oxalate + water	62	159	4.6	3	2
Nickel acetate	121	44	1.9	3	2
Boric acid anodizing	11	355	4.6	1	1

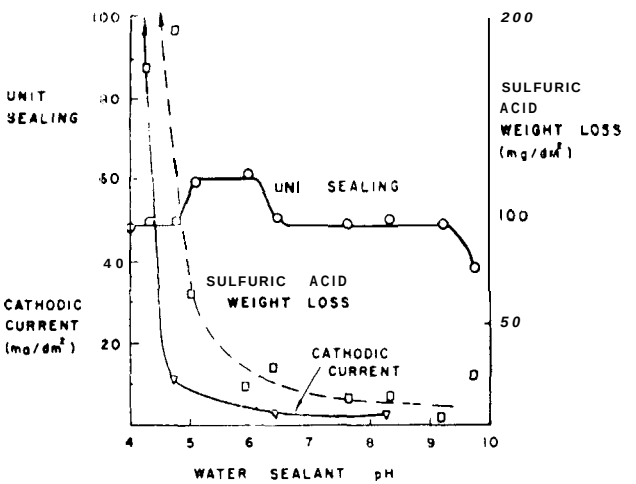


Fig. 11-21. Effect of water sealant acidity on anodic film properties (anodizing 30 min. in 15% (wt) sulphuric acid, 21°C, 15 amp/sq. ft. sealed 30 min. at 98-100°C)

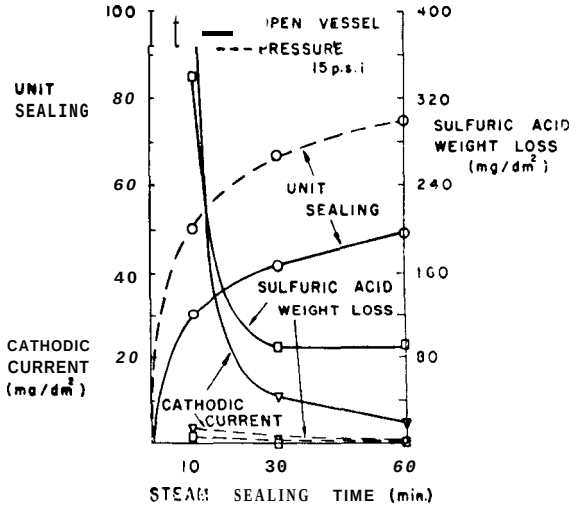


Fig. 11-22. Effect of steam sealing on anodic film properties (anodizing 30 min. in 15% sulphuric acid, 21°C, 15 amp/sq ft)

The outdoor exposure tests showed that hot water sealing at pH 6.1 in deionised water gave equal or better resistance to pitting corrosion than either dichromate or sodium molybdate sealing and was equivalent to nickel acetate sealing. Pressure steam sealing is slightly better than open steam sealing, although not to the extent predicted by accelerated tests.[74] Of the laboratory tests, the sulphuric acid leach test *(5%* (vol) sulphuric acid at room temperature for periods of 6 hours) was expected to show resistance to pitting in industrial atmospheres, while the cathodic current flow test, in which the current was measured flowing to a test panel immersed in 2% (vol) nitric acid at 10 volts, was designed to measure the electrical resistivity of the coating, which is increased by sealing.

Fig. 11-21 shows that, in water sealing, the optimum pH is between 6 and 9, and these results were confirmed by acetic acid salt spray tests, while, in Fig. 11-22, steam sealing at atmospheric pressure is shown to be more-or-less complete after 30 minutes, sealing at 15 p.s.i. being both quicker and more effective.

Table 11-15 shows that the best acetic acid salt spray resistance is given by dichromate sealing, followed by sodium molybdate. The silicone did not prove very successful while attempts to improve the sulphuric acid coating by boric acid anodizing to enhance the barrier layer thickness failed to give any significant improvement. Table 11-16 shows the effect of various sealing and anodizing treatments on outdoor exposure.

TABLE 11-16

Effect of various sealing and anodizing treatments on pitting penetration of anodic oxide filnns on exposure in an industrial atmosphere (Montreal)[30]

Treatment	Pit Ratings of Oxide-stripped Panels'					
	Front			Back		
	Exposure Period (years)					
	1	3	5	1	3	5
Film thickness						
15 min	8(M)	7(M)	5(M)	7(C)	6(C)	5(C)
30 min	9(M)	9(M)	9(M)	9(MC)	9(C)	9(C)
60 min	10	9-10	10	9	9-10	10
Anodizing temp						
15°C	9(M)	9(MC)	8(M)	9(M)	8-9	8(MC)
21°C	9-10	9	9(M)	9-10	9(MC)	9(MC)
25°C	9-10	9-10	9-10	9-10	9(M)	8(MC)
Water sealing time						
0 min	9-10	8-9(M)	7(M)	9	8(MC)	7(C)
10 min	9(M)	8	8(M)	8-9(MC)	8-9(M)	8(C)
30 min	9-10	9	9	9(M)	9(C)	9(C)
60 min	9	9(M)	7(M)	9(C)	8(C)	8(C)
(Tap) 30 min	9(M)	9	7(M)	9(C)	9(MC)	8(C)
Sealing watrr pH						
4	9-10	10	10	9-10	9(M)	9-10(MC)
5	9-10	9	8-9(M)	9(M)	9(C)	9(MC)
6	9-10	9	9(M)	9(M)	9(M)	9(MC)
7	9-10	9	9	9-10	9(M)	9(MC)
8	9-10	9-10	9(M)	9(M)	9(C)	9-10(MC)
9	9-10	9-10(M)	9	9-10	9-10(M)	9(C)
Steam sealed (open)						
10 min	9-10	9	7	9	9	7(MC)
30 min	9-10	9	9	9(M)	9(MC)	9(MC)
60 min	9-10	9(M)	8-9	9(MC)	9(MC)	8(MC)
(15 psi)						
10 min	9-10	9	8-9	9(MC)	9(MC)	9(MC)
30 min	9-10	9	9	9(M)	9(C)	9(MC)
60 min	9-10	9	9	9(M)	9(C)	9(MC)
Miscellaneous						
Potassium dichromate 5%	9-10	9(M)	9(M)	9-10(M)	9(MC)	8(MC)
Potassium dichromate 0.1%	9-10	9(M)	9(M)	9(MC)	8-9(C)	8(MC)
Potassium dichromate + sodium carbonate	9-10	9(M)	8(M)	9-10	8-9(MC)	8-9(C)
Sodium molybdate	9-10	9(M)	8(M)	9-10(M)	9(MC)	8(C)
Boric acid anodizing	9-10(M)	9(M)	8(M)	9-10(M)	9(C)	8(C)
Nickel acetate	9-10(M)	9(M)	9(M)	9	9(M)	9(MC)
Barium nitrate	9-10	9(M)	7(M)	9-10	8-9(MC)	8(C)
Silicone	9-10(M)	9	9	9(M)	9(M)	9(C)
Silicone + water	9-10	9	9	9(M)	8-9(MC)	8(C)
Ferric oxalate + water	9-10	9	8	9(M)	9(M)	8(C)

* Pitting attack was evaluated on a 10, 9, X..... 1 (most severe) basis. Pit was designated as follows: M – moderate. C – coarse. Fine pitting was noted to some degree on all pitted surfaces and therefore is not included in the pit size designation given here

Spooner also showed that resistance to acetic acid salt spray as well as to outdoor exposure is improved appreciably by increasing the temperature of the anodizing solution from 15 to 21°C and slightly by a further increase to 25°C.

There is a long history of experience in various countries to demonstrate that deterioration or failure in service occurs most readily with anodized specimens which are unsealed or poorly sealed. Other things being equal the exposed work most resistant to any change for the worse from its initial appearance is the one where sealing has been carried out in pure water at the right temperature, correct pH and for an adequate time, while gross deterioration has often but not always been correlated with treatment conditions known to inhibit effective hydration. The exceptions to this arise from the fact that films of adequate thickness in a relatively mild environment can become sealed naturally in the course of time once sealing has been commenced, and provided no inhibiting factors are present, but it is now axiomatic that sealing of the anodic coating is a most important requirement.

Deterioration in service may take one or more of the following forms:

(a) Corrosion pitting where the film has been perforated and the basis metal attacked, but not necessarily with any general attack on the film surface.
(b) The formation of a chalky white bloom over much of the surface (chalking).
(c) The formation of iridescent or smut-like layers on the film surface.
(d) The formation of a white irregular bloom within the coating itself.
(e) **A** change in the colour or shade of dyed work.

Pitting attack represents the long-term deterioration of an anodic coating and is confined to weak sites in the coating which are usually of random distribution and not clearly connected with known metallurgical features, although the form of the intermetallic constituent is obviously connected with them, because pitting declines as the purity of the metal is increased. It is more dependent on alloy and anodic film thickness than on sealing quality, and is frequently the final mode of deterioration of a well sealed film. It occurs most readily in polluted industrial and urban environments and in industrial-marine conditions, though marine environments alone are not particularly hostile to anodic coatings.

An extensive chalky white surface bloom however is a sign that the oxide itself is the subject of chemical attack or physical degradation and it usually occurs when too much film attack has taken place in the sulphuric acid anodizing electrolyte. It is mainly a problem with thick coatings (above 15 microns), and occurs if too high an electrolyte temperature or concentration, or too low an anodizing current density is used (see also page 477). It represents a cracking and flaking of the surface layers of the film and leads to a loss of coating thickness. This and other short term weathering effects on anodic coatings have been described by Furneaux ***et al.***[21] Chalking is most likely to happen wherever

the atmospheric pollution contains acidic or alkaline constituents capable of producing such attack..In most cases the attack will be associated with sulphur dioxide gas forming sulphurous acid in solution, and most accelerated tests for corrosion introduce sulphur dioxide in some form. Once the basis metal is exposed these environments will also produce pitting.

Iridescence is a common phenomenon on coloured anodic films during the early stages of weathering, and it is associated by Furneaux[21] with residual sealing smut. Smut formation during the early stages of weathering is again most visible on coloured coatings, and it develops as the surface layer weathers due to etching of the film surface. Both effects occur in all environments, but are most visible in marine or urban situations, and they can be removed by cleaning.

Weathering bloom, on the other hand, is very much a function of sealing quality, and is the type of effect occurring when adequate sealing has been prevented by contaminants such as phosphate or silicate. It is an etching action occurring within the cell structure of the film and cannot be removed by simple cleaning methods.

Resistance to attack can be conferred in two manners. By the physical action of filling up or plugging the porous structure so that the basis metal is better protected and the surface area of the oxide available for attack reduced, or secondly by converting the aluminium oxide to a hydrated form which is inherently more resistant to attack by chemical agents. The latter is the more desirable because it also contributes towards the pore closure.

The resistance of coloured work to fading or weathering is notably improved by sealing, but this effect is more a function of physical confinement and protection of the dye molecules from external influences than any chemical modification, since the performance of many dyes in unsealed but lacquered films is the same as for sealed films, that is as long as the lacquer maintains its protective effect. In fact in cases when boiling water tends to leach or bleed the dye from the film, then the sealing temperature must be dropped and an alternative sealing mechanism based on nickel or lead acetate resorted to as noted above.

Discussions on the sealing of anodic films can become so academic and rarefied that the main point is sometimes overlooked, and this is the improvement of performance in service, which usually implies prolonged exposure in more or less corrosive environments. In general the short term laboratory measurements of impedance, porosity or the resistance to chemicals in accelerated tests count for nothing unless it can be clearly demonstrated that such results correlate in some measure with the performance in service. For instance, although impedance and other measurements will demonstrate that the hydration process continues for 24 hours or longer it has also been found that such films may deteriorate more quickly than similar films sealed for only 30 minutes. One should also mention in this context that the difference between sealed and unsealed work in outdoor exposure is frequently much less dramatic than corrosion or other tests would indicate that it is going to be.

This concern about the correlation between accelerated test performance and outdoor exposure performance was the basis of much of the uncertainty over the use of cold impregnation systems in exterior architectural applications. As a result many exposure tests were carried out before the systems were generally accepted. Sheasby[135] reported the results of 5 years exposure in the Qualanod evaluation tests, which showed no general difference in appearance between those panels which had been cold impregnated and those conventionally sealed.

Recent work in Spain[218] has looked at the effect of up to 20 years exposure of conventionally sealed samples on seal quality tests, and their results are shown in Fig. 11-23 and Table 11-17. These samples were anodized conventionally to 18-20 microns, sealed in deionised water, with or without the presence of sodium or ammonium acetate, and exposed at a site in Madrid. They also examined the specimens with electrochemical impedance spectroscopy and concluded that films continue to age for many years, eventually attaining a sealing quality well above that required by standards.

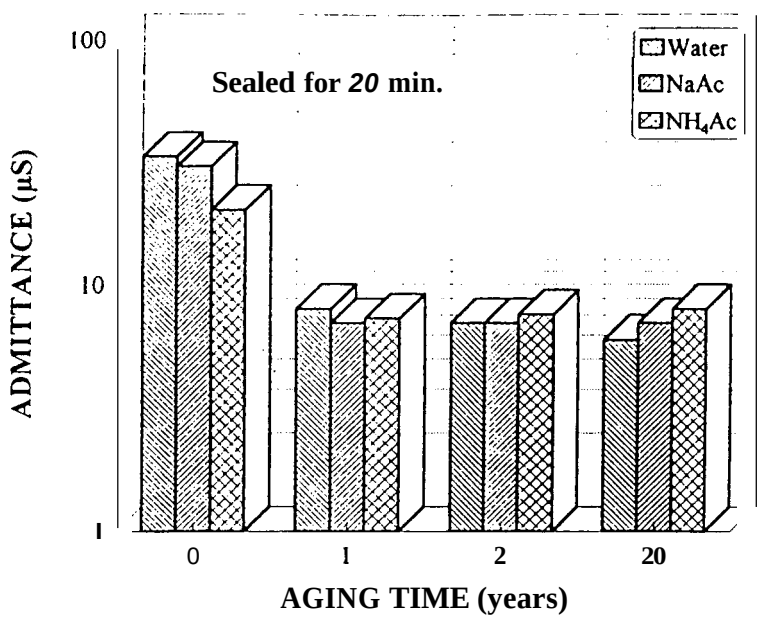


Fig. 11-23. Changes in admittance with the time of exposure to the atmosphere of Madrid of specimens sealed in boiling de-ionized water and in sodium or ammonium acetate solutions containing 0.5 g/l acetate for 20 tnin

TABLE 11-17

Effect of sealing time, bath composition and aging time on the results of the dye spot and acid dissolution tests

Conditions	Dye spot (level)			Acid dissolution (mg/dm^2)		
	0 years	2 years	20 years	0 years	2 years	20 years
H_2O						
1 min	5	0	0	425	3	12.9
5 min	2.5	0	0	128	2	12.3
10 min	2	0	0	44	1.6	11
20 min	1	0	0	5.2	1.5	10.5
NaAc						
1 min	3	0	0	250	2.8	13.5
5 min	1.5	0	0	6	1.7	8.9
10 min	0.5	0	0	2	1.4	8
20 min	0	0	0	5	1.5	7.3
NH_4Ac						
1 min	4	0	0	6	2	11.9
5 min	1	0	0	4	1.2	9.2
10 min	1	0	0	2	1	8.5
20 min	0.5	0	0	7	0.9	7.5

Light-fastness

Although nickel and/or cobalt acetate is the usual sealing medium for dyed coatings, other salt solutions may yield better light-fastness. This is shown in Table 11-18 for a number of commercial aluminium dyes.”””

Heat resistance

The heat resistance of anodic oxide coatings, particularly when dyed, may vary considerably with the sealing method used. Table 11-19 shows that nickel-cobalt acetate is often superior to other sealing solutions in this respect, though not in the case of Aluminium Blue LLW.

TABLE 11-18

Effect of different sealing salts on light-fastness of dyed aluminium[220]

Colorant	SEALANT								Recommended sealing ion in preferred order
	Nickel acelale	*Calcium acelale*	*Lead acetate*	*Copper acetate*	*Sodium acetate*	*Barium chloride*	*Cobalt chloride*	*Zinc chloride*	
	LOSS IN LIGHT-FASTNESS AFTER 200 HOURS								
Metal Bright Gold **AT**	15%	Complete	10%	Slight shade change	No change	Slight	10%	Complete	Na^{+}, Ba^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}
Metal Red R	75%	**80%**	10%	20%	35%	45%		Complete	Pb^{2+}, Cu^{2+}, Na^{+}, Ba^{2+}
Metal Bright Red BB	75%	10%	5%	Complete	10%			Complete	Pb^{2+}, Ca^{2+}, Na^{+}
Metal Bright Blue PT	5%	10%	10%	No change	20%	20%	15%	30%'	Cu^{2+}, Ni^{2+}, Ca^{2+}
Metal Bright Orange BG	90%	90%	Slight change	80%	70%				Cu^{2+}
Metal Golden **Yellow** 3GP	5%	Complete	70%	60%	Complete	90%	No colour	Complete	Ni^{2+}
Metal Blue B	40%	20%	5%	No change	-	5%	No change	5%	Cu^{2+}, Pb^{2+}, Ba^{2+}
Metal Black Special	30%	Complete	Complete	20%		90%	Slight change	85%	Co^{2+}

TABLE 11-19

Heat resistance of dyed anodic oxide coatings after various sealing treatments

Sealing process (30 minutes, 100°C)	*Dyeings of 2 g/l Aluminium Bronze G (15 minutes, 60°C)*		*Dyeings of 2.5 g/l Aluminium Blue LLW (15 minutes, 60°C)*	
	Not exposed to heat	*Heated to 300°C for 1 hour*	*Not exposed to heat*	*Heated to 300°C for 1 hour*
Distilled water, pH 4.5	Dark brown	Light brown	Dark blue	Weak brown
Nickel/cobalt acetate, pH 5.4	Dark brown (rather more yellow than above)	Medium brown (rather darker than above, same shade)	Strong blue	Weak brown (as distilled water)
Lead acetate 5 g/l, pH 5.6	Dark brown (as distilled water)	Light brown (as distilled water)	Strong blue	Weak brown (as distilled water)
Sodium chloride 2.5 g/l, pH 5.8	Dark brown (as distilled water)	Medium red-brown (clearly redder than colour by distilled water)	Strong blue	Weak brown (as distilled water)

Abrasion resistance

Next to its effect on corrosion resistance the other principal effect of sealing is the well known reduction in hardness or wear resistance of the anodic coating which accompanies it. This has been referred to in Chapter 9 on Hard Anodizing where measurements by Harris and Oechslin (p. 782) have indicated that a thick hard-anodized coating after normal sealing may be expected to have about 60% of the hardness of the as-formed unsealed coating.

Using the abrasive jet method of BS 1615: 1972 (Method L), now BS 6161: Part 10, which involves directing a jet of silicon carbide powder at the surface under carefully controlled conditions until the surface is worn down to the basis metal, Thomas[62] examined the progress of 20 μm films formed in 180 g/l sulphuric acid at 20°C after sealing in boiling distilled water and in steam at 100°C. The total weight of silicon carbide required for penetration for various times of sealing is given in Table 11-20. Under these conditions the abrasion resistance drops rapidly to about 60% of its original value in about 10 minutes and the decline continues over a very long period, so that after 4 hours it is only about 35% of the original value, and continues to decline very slowly for a further 20 hours.

The effects of steam and water sealing are practically identical and the slow change seems to parallel results obtained in impedance tests, but the abrasion test is equally reliable for comparing coatings which are dyed, pigmented or impregnated with any other materials, on which an impedance measurement can be quite unreliable.

TABLE 11-20

Effect of sealing at 100°C on abrasion resistance of 20 μm film

Time of sealing (minutes)	*Grams of SiC for penetration*	
	Distilled water	*Steam*
0	130	130
5	86	86
10	–	13
15	71	–
20	–	66
30	64	63
60	54	58
120	51	56
240	45	48

The same effect is shown in work by Göhausen with the Erichsen abrasive wheel apparatus.[221,222] Typical results are shown in Fig. 11-24. In this case an increasing loss of thickness as a result of abrasion, indicates a reduced abrasion resistance.

It has been suggested that, owing to the different mechanism involved, cold impregnation has less; effect on abrasion resistance of the unsealed anodic coating than does conventional sealing, but this was not shown in the work of Ellard and Morita,[144] who measured abrasion resistance using the Suga abrasive wheel test apparatus (BS 6161:Part 10).

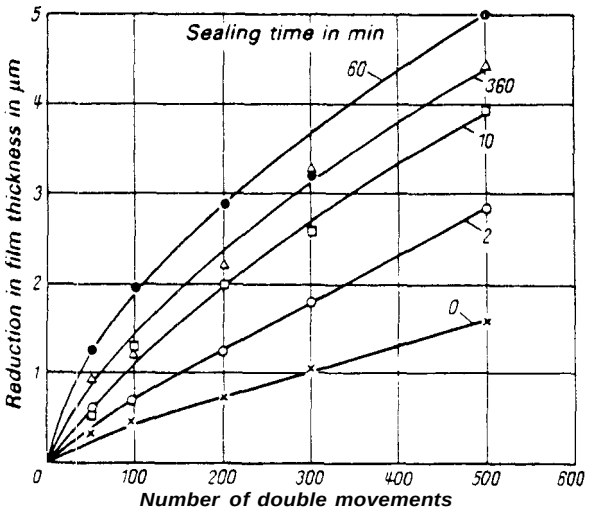


Fig. 11-24. Influence of sealing time on abrasion resistance: **Alloy** AlMg1; anodizing 200 g/l H_2SO_4, 1.5 A/dm², 18-19°C; film thickness 20-22 µm; sealing: deionised H_2O + 1 g/l ammonium acetate'"

Impedance

Impedance is the resistance offered by a component to the passage of an alternating current. It is expressed in ohms and is identical with the resistance when a resistor is the only component in question. However, when inductance or capacitance effects are also present, the impedance is related to their combined values in a complex manner, which is dependent on frequency. The ability of the anodic film to conduct or transmit an alternating current, when in contact with an electrolyte, depends upon its thickness, structure, composition, method of formation and type and degree of sealing; in this connection the impedance refers to the current passed through a specified area, when the film is immersed in a neutral or weakly acid electrolyte and a very low voltage alternating current is applied.

Bridge analysis

An exact measurement of impedance in such a situation calls for a Wheatstone Bridge circuit of the type shown in Fig. 11-25 where the unknown component, in this case the cell composed of the aluminium specimen immersed in an electrolyte with a platinum counter-electrode, is balanced against the variable components R_s and C_s in the other arm of the bridge until a zero current is indicated in the detector. A typical electrolyte is 35 g/l potassium sulphate but others have been used. In the balanced position the well known relation applies, $Z_1 / Z_2 = Z_3 / Z_4$ where Z represents the impedance of each arm for the particular frequency used. What **is** actually obtained with a bridge of this type is a reading for R_s and C_s at frequency f which is related in some manner to the properties of the coating. The bridge could equally well be balanced with R_p and C_p, the parallel combination.

If the anodic film in the cell could be adequately represented by a capacity C and a resistance R in series, then the bridge could be used to relate their values to the measured or known values by the equations:

$$R = k.R_s = k.R_p \sqrt{\left(\frac{1}{1 + 4\pi^2 f^2 R_p^2 C_p^2}\right)}$$

$$C = \frac{l}{k}.C_s = \frac{C_p}{k} \sqrt{\left(\frac{1}{1 + 4\pi^2 f^2 R_p^2 C_p^2}\right)}$$

where **k** is the ratio R_3 / R, and R_s , C_s and R_p , C_p refer to the series and parallel combination of the variable components respectively.

Measurements of this type have been made on a number of occasions. Thomas made a quite extensive but unpublished survey of the impedance of variously produced coatings at frequencies between 30 Hz and 6×10^6 Hz in 1951, but these related to coatings which were not sealed and they revealed quite a complex state of affairs. Wood, Cole and Hoar[223] described a variable frequency bridge designed for carrying out impedance measurements which was applied amongst other things to the study of anodic films, and in a subsequent paper[4] they analysed the results making use of an electrical analogue circuit for the anodic film, which had been suggested earlier by Jason and Wood.[224] In Fig. 11-26 is given the electrical circuit used to represent an unsealed film, while Fig. 11-27 indicates a circuit which states more accurately the behaviour of a partially sealed film where the various capacities and resistances reproduce the functions of barrier, pore, oxide plug near surface, etc. The analogue is most nearly correct when, for one set of components, it enables the bridge to be balanced over a wide range of frequencies, for then a virtual identity has been established between the film and the network of components.

The accuracy with which Hoar and Wood were able to establish this relationship between 10 and 10^6 **Hz** is quite impressive as their paper shows, and Table 11-21 gives the values assigned to the various components in Fig. 11-27 which enabled this identity.

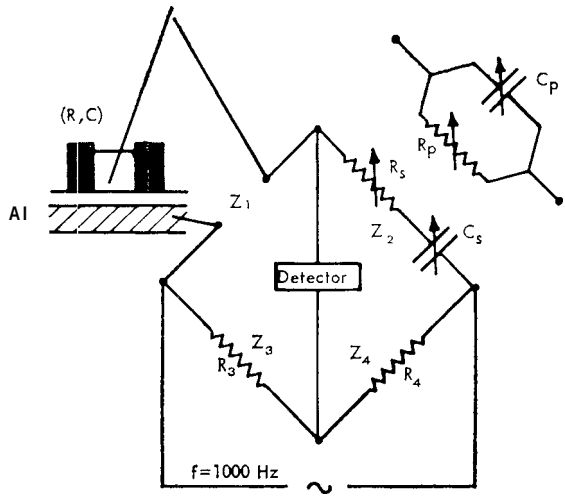


Fig 11-25. Circuit for measurement of impedance

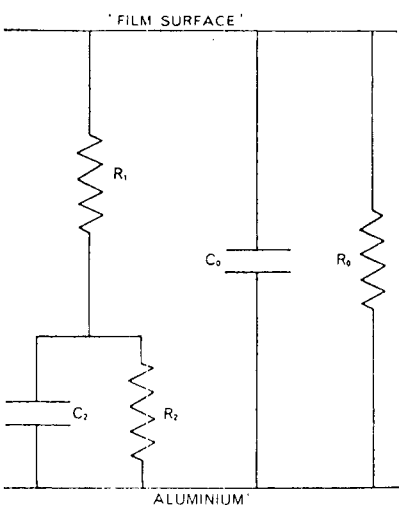


Fig. 11-26. Simple electrical analogue for unsealed porous film (after T.P. Hoar and G.C. Wood')

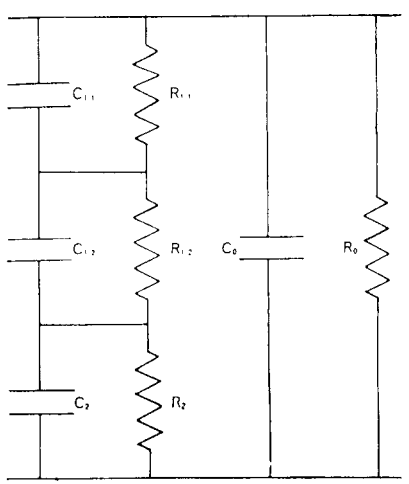


Fig. 11-27. Modified electrical analogue for partially sealed porous films'

TABLE 11-21

Values of components in analogues according to Fig. 11-27[4]

	Analogue for 30-min sealed film	*Analogue for 24-h sealed film*
C_0 (μF/cm²)	0.001*	0.00094
$R_{1,1}$ (kΩ/cm²)	2.34	83
$C_{1,1}$ (μF/cm²)	0.195	0.0167
$R_{1,2}$ (kΩ/cm²)	1.66	17
$C_{1,2}$ (μF/cm²)	0.005	0.0003
C_3 (μF/cm²	0.45*	0.32

$R_{1,1}$: 5 MΩ/cm² (estimated; precise value immaterial).
$R_{1,1}$: 700 kΩ/cm² (experimental, from simple analogue for unsealed film, precise value immaterial).
* Value held fixed. **All** other values adjusted by trial and error for best balance with R_b and C_b previously obtained by balancing with film impedance during sealing.

These results lead to the following general interpretation:[4]

30-minute sealing. The pore resistance is increased from 25 Ω/cm² to 4 kΩ/cm². This obviously indicates a very considerable filling of the pore volume – if filling is uniform from the sides inwards, the pore sectional area is decreased by a factor of 160, i.e. to 0.6% of its initial area. However, the analogue of Fig. 11-27 (with components as in Table 11-21) gives considerably better agreement with the frequency dependence of the film impedance than does the analogue of Fig. 11-26 containing a simple non-capacitative pore impedance. We may thus suppose that a substantial part of the 4 kΩ/cm² of R_1 is concentrated as $R_{1,1}$ in a very short length of the pores, across which length there is a quite large parallel capacitance $C_{1,1}$. This strongly suggests that 30 minutes sealing consists of a general reduction of sectional area of each pore to perhaps 2% of its initial area, together with the formation of a very short 'plug' in the pore of much higher average specific resistance than that of the pore electrolyte. This could well be a plug of semi-solid material, containing nevertheless a good deal of water to give it a high dielectric constant, at the outer end of the pore; its early formation or partial formation would explain the non-entry of dyestuffs into films 'sealed' for a few seconds only.

24-hour sealing. The pore resistance is increased to 100 kΩ/cm². Again analogues on the scheme of Fig. 11-27 are in much closer agreement with the frequency dependence of the film impedance than is the simpler analogue. As compared with the analogue for the 30-minutes sealed film, $R_{1.1}$ is increased from 2.34 to 83, and $R_{1.2}$ from 1.66 to 17 kΩ/cm², so that $R_{1.1}$ becomes the major part of the

pore resistance. C_{11} is decreased sharply, and C_{12} is also considerably reduced. Thus both the resistance and capacitance changes on long sealing are consistent with a substantial increase in the solidity and length of the plug and a further decrease of the diameter of the main length of the pore. Finally, C_2 the barrier layer capacitance, is reduced about 30%, consistent with a 30% increase of the thickness of the barrier layer.

The results of impedance measurements are clearly related more to sealing than to any other feature of the film. Wood and Marron[14] also extended this work to the examination of films sealed in nickel and chromium salts, also making use of electron probe micro-analysis on cross sections of the coatings to measure the distribution of the absorbed material through the thickness of the coating.

Admittance 'value and loss factor

The bridge network is of course in the balanced condition when the impedance ratios are equal, or $Z_1/Z_2 = Z_3/Z_4$. In the case of the variable components R_s, C_s (series) or R_p, C_p (parallel) the impedance Z at the operating frequency f is:

$$Z = \sqrt{R_s^2 + \frac{1}{4\pi^2 f^2 C_s^2}} = \sqrt{\frac{R_p^2}{1 + 4\pi^2 f^2 R_p^2 C_p^2}}$$

The admittance value is the reciprocal of the impedance or 1/Z, and another factor of importance: is the loss factor, Y, or tan d which is the ratio between the resistive and capacitative parts of the impedance. Thus:

$$Y = \tan\delta = R_s / \frac{1}{2\pi f C_s} = 2\pi f R_s C_s$$

Single frequency analysis

In most later work investigators have eschewed the finer points of bridge analysis and concentrated on a single frequency, usually 1000 Hz, to measure either the impedance Z, the admittance $1/Z$, or the loss factor Y.

Predictably, the device was soon to appear as a test instrument; this made its debut in America as the Alcoa Z-Scope where it was used to indicate the quality of sealed work. Englehart and Sowinski[225] described its use as a pass or fail test for bright anodized trim components. Fig. 11-28 shows the values of the impedance obtained for unsealed, poorly sealed and adequately sealed work for various thicknesses of coating, which indicates that there is quite a substantial gap between poor and adequate sealing. There is no doubt that when used in a commercial plant whose products lie within a narrow range of anodizing conditions, this type of .instrument will pick out any departures from normal practice very quickly.

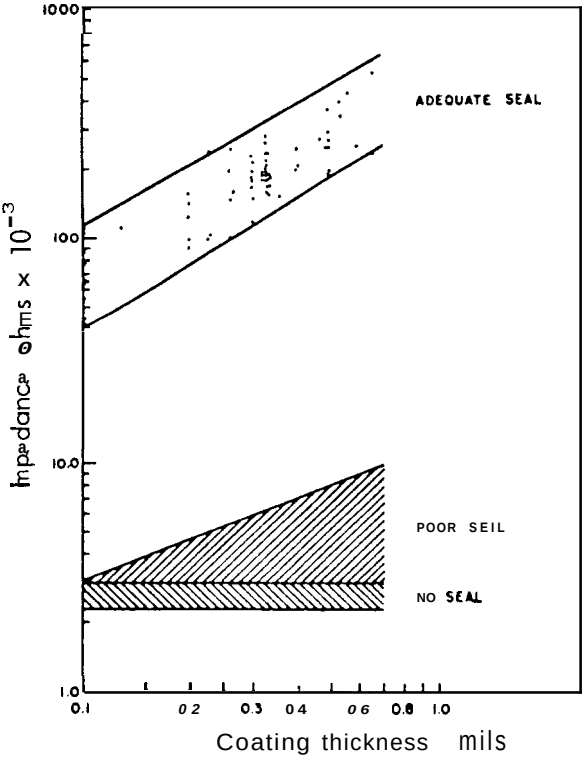


Fig. 11-28. Results obtained using the Alcoa quality control test for anodized aluminium."' 1 mil = 25.4 μm

Other investigations

Birtel and Leute[15] also investigated the use of impedance techniques for monitoring sealing, by using a bridge circuit operating at 1000 Hz. Some of their results are shown in the graphs of Figs. 11-29, 11-30 and 11-31, which indicate the effect on impedance of sealing time and temperature and the thickness of the anodic film. They were associated with the development of the instrument which was known as the Testal-4, which was of course a method for direct measurement of the impedance on a meter and not a null-point method.

Birtel and Leute[226] were later to suggest that the loss factor constituted a better index of sealing than the admittance, because it was almost independent of the thickness of the film and was less affected by anodizing conditions and ageing of the film. A further commercial instrument was soon launched under the name of Anotest-DY[227] which indicated both admittance and loss factor, and a British version appeared in 1971 under the name of the 'S' Tester, and later the 'Anospec S'.[228]

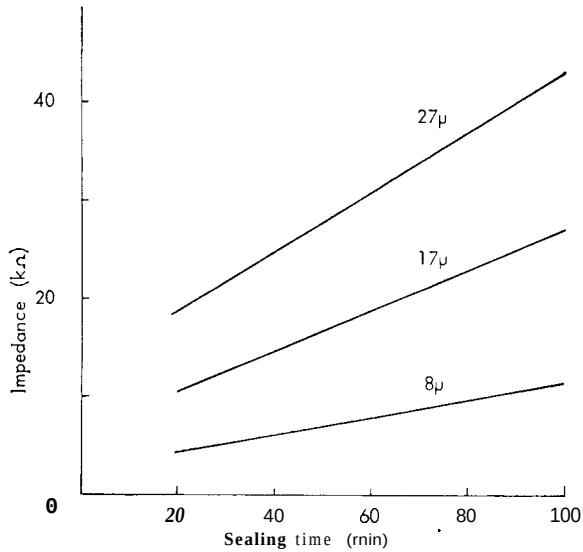


Fig. 11-29. Effect on impedance of sealing time (in saturated steam at 100°C) and anodic film thickness. (Alloy AlMgSi 0.5, anodized at 1.5 A/dm²)[15]

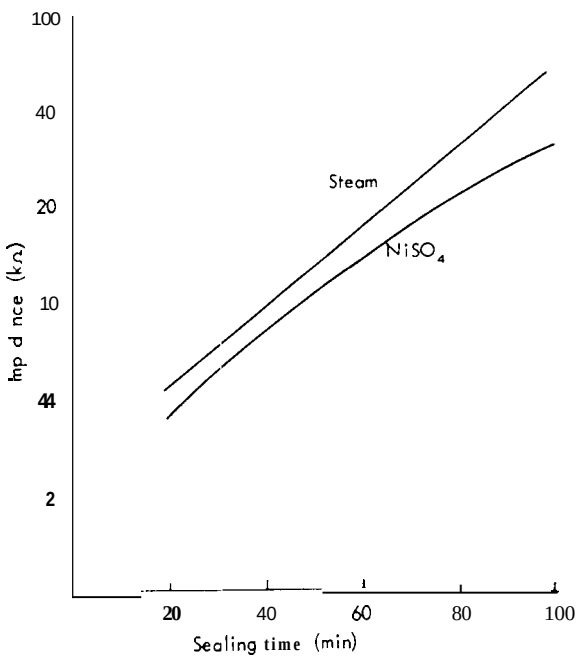


Fig. 11-30. Effect on impedance of sealing time and sealant. Films sealed in steam and in nickel sulphate solution. (Alloy AlMgSi 0.5, anodized at 1.5 A/dm²)[15]

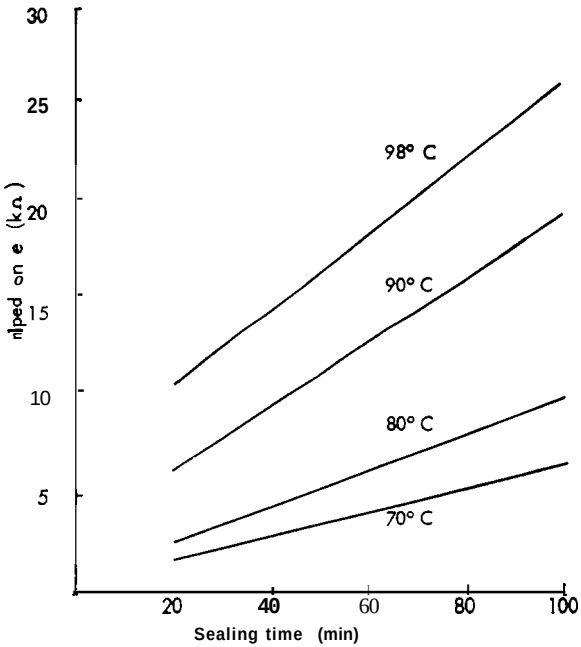


Fig. 11-31. Effect on impedance of sealing time and temperature. (Alloy AlMgSi 0.5, anodized at 1.5 A/dm^2, anodic film thickness 20 µm, sealed in nickel sulphate solution)"

Admittance measurements are now widely used as a production control test for sealing in either water, steam or nickel acetate, but the method is considered less suitable for coloured or pigmented work: the loss factor or dissipation factor was not found reliable with normal British sealing practice.[54] Admittance or impedance measurements for seal quality evaluation are covered by an International Standard (ISO 2931: 1983) and most countries have their national version of this (e.g., B.S. 6161: Part 6: 1984). The new European Standard (EN 12373-5:1999), however, only covers the use of admittance, as impedance measurements are no longer used in this area. The standards caution that the results may be affected by the presence of sealing additives, or contaminants such as silicate, and therefore results must be used with care. Electrolytic colouring processes, particularly when producing dark finishes, have a strong effect on admittance results, and this has been referred to in Chapter 8 (Table 8-27). This makes admittance measurements difficult to use for the control of such dark finishes. Similar problems have occurred with cold impregnated finishes.

Electrochemical impedance spectroscopy

The use of electrochemical impedance spectroscopy, where impedance is measured over a range of frequencies, is increasingly being suggested as an evaluation method for degree of sealing.[28,229] The use of a wide frequency range is said to allow probing of the various contributions to the impedance, and their

influence on the overall sealing process, and it is suggested that this could be the basis of an on-line monitoring technique.[28] These studies have led to suggestions of more complex electrical models for the sealed and unsealed film, and these are shown in Fig:;. l 1-32 and l 1-33. However these ideas have not yet been incorporated into any testing standards.

Research workers in many countries are starting to use electrochemical impedance spectroscopy. In Spain the method has been used to examine the ageing behaviour of cold impregnated films[136] as well as conventionally sealed films.[218,230] In U.S.A. it has been employed with films produced in the Boeing boric acid / sulphuric acid anodizing process and sealed in cerium acetate solutions,[29] and in India the work has been on sulphuric acid anodized material sealed in deionised water, triethanolamine or dichromates.[231] However all workers agree that this is a very sensitive way of following the sealing and ageing processes.

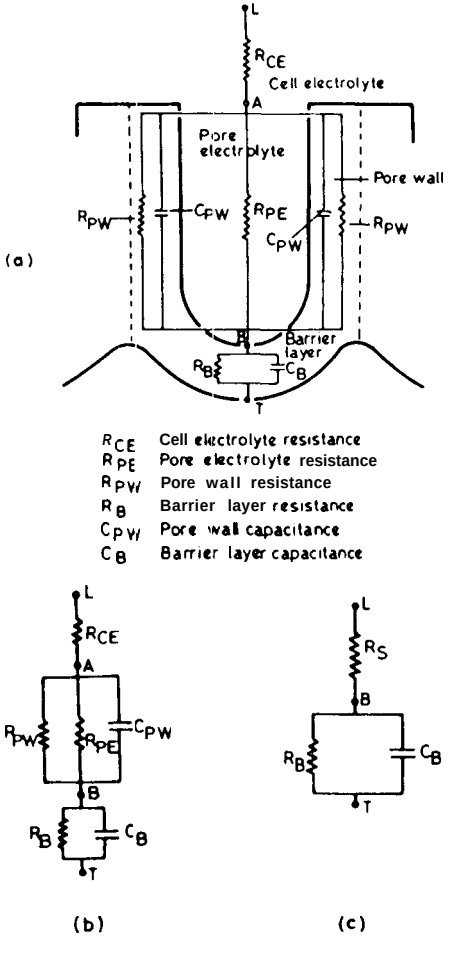
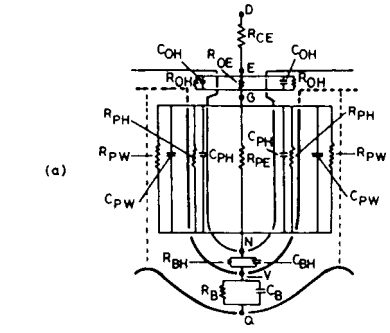


Fig. 11-32. Equivalent circuit models for the initially formed porous anodic film:

(a) circuit indicating possible contributions to the impedance response;

(b) simplified circuit



R_{OH} : Surface crystals and intermediate layer resistance
R_{OE} : Surface crystals and intermediate layer electrolyte resistance
R_{BH} : Barrier layer hydration resistance
R_{PH} : Pore filling material resistance
C_{OH} : Surface crystals and intermediate layer capacitance
C_{PH} : Pore material capacitance
C_{BH} : Barrier layer hydration capacitance

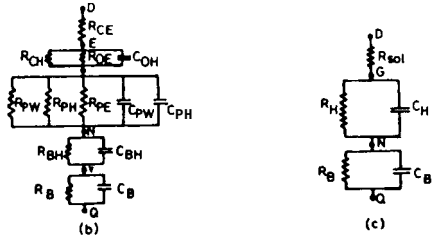


Fig. 11-33. Equivalent circuit models for the sealed anodic films:
(a) schematic diagram of the porous anodic film;
(b) equivalent circuit of (a);
(c) simplified circuit

Dielectric strength

The dielectric strength of dry films is measured as the voltage, between the basis metal and an auxiliary probe in light contact with the coating, at which the coating becomes conducting or disrupts with the formation of an arc. It varies from 50 to 250 V/μm and is a complex property depending on the history, composition and structure of the coating as well as the ambient humidity and external circuitry of the test apparatus. Ruff[232] and Weeks[233] have noted that the breakdown voltage is initially reduced by sealing but that subsequent ageing for two months increases it to more than the unsealed values. Working with sulphuric coatings of about 10 μm (20% w/v, 20°C, 1.3 A/dm^2, 30 min) Sacchi[234] has reported the following breakdown voltages, which indicate an improvement by both sealing and ageing: unsealed coating - 600 V; sealed at 70°C - no change; sealed 100°C, 10 min - 750 V; sealed 100°C, 30 min - 950 V; sealed in nickel acetate at 100°C - 1200 V. By ageing at 74-78% humidity for 1000 hours each of the coatings reached 1400 V or more except one sealed in tap water which reached only 1050 V (see also pages 970 and 1052).

Emissivity and heat reflectivity

Both the emissivity and the heat reflectivity of anodized aluminium are affected by sealing, chiefly because water has pronounced absorption bands in the near infra-red region of the spectrum. This can be a disadvantage for heat reflectors owing to either their reduced efficiency, or in some applications by an excessive temperature rise of the reflector itself. It is the usual practice to reduce the anodic coating thickness in such applications since the oxide coating itself is quite a potent heat absorber and sealing merely adds a little more to it. The emissivity of the surface has been proposed and developed as a method for assessing both the coating weight and the degree of hydration by Lawler and Pirzadeh[235] of the Boeing Company. Bright aluminium surfaces have a very low emissivity and this is increased on anodizing by an amount which, up to a point, is closely proportional to the weight of aluminium oxide formed on the surface. A further increase is brought about by hydration of the oxide because of the characteristics of the hydroxyl groups.

Using a commercial Lion Emissometer, Model 25B, they discovered that by working anywhere in the temperature range 21-27°C the instrument was sensitive enough to determine both the coating weight of the unsealed film and the degree of hydration after sealing. An area of the anodized surface is dried and two standards are firmly attached to it so that they can reach thermal equilibrium with the surface. One of these is a piece of bright uncoated aluminium foil and the other is a similar black foil. The instrument is adjusted to read zero on the bright surface and 1 on the black surface and a measurement **is** then taken on the anodized but unsealed aluminium. After sealing, the procedure is repeated. By reference to a graph of the type reproduced in Fig. 11-34 both the coating weight and degree of sealing can be ascertained.

Crazing of anodic oxide coatings

One of the unwanted side effects of sealing is its tendency to reduce the temperature at which thermal crazing can occur. With hard anodizing carried out at low temperatures in the region of 0-5°C, the increase to room temperature is sometimes sufficient to cause the film to fracture under tension, and a dip in hot water is almost certain to cause it. This tendency is often present with thick films of about SO microns produced in sulphuric acid at ambient temperatures or in integral colour processes.

The normal sulphuric acid coating produced at about 20°C and less than 25 microns in thickness can be heated to about 150°C in the unsealed condition before thermal crazing will occur. Sealing will progressively reduce this temperature until with thorough sealing of good quality a temperature of 103-105°C produces sufficient expansion of the basis metal to fracture the coating. Michelson[236] considered that the only way in practice to mitigate crazing was to restrict the coating thickness to 3 microns or less and to restrict the sealing time.

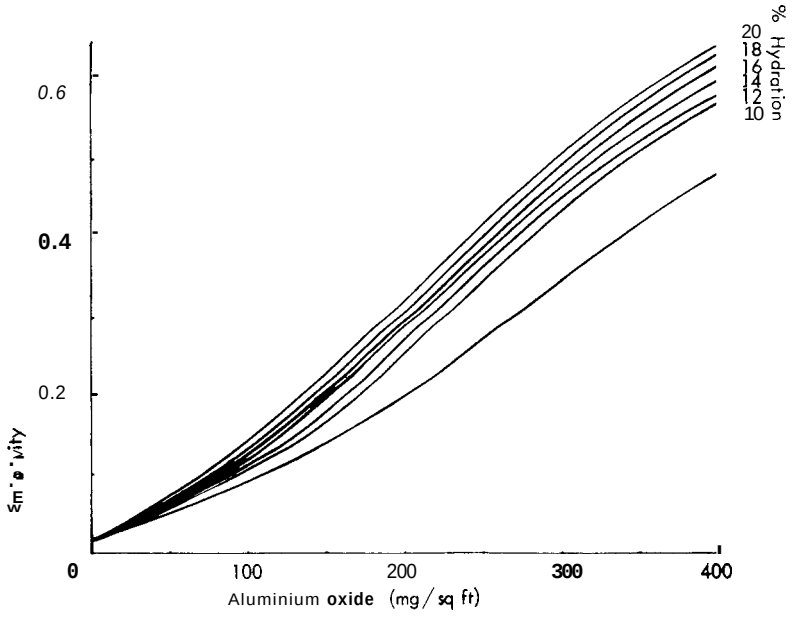


Fig. 11-34. Developed plot of aluminium oxide and per cent hydration versus emissivity.[?] Alloy 6061-T6. The lowest curve is for the unsealed oxide. 9.3 mg/sq ft = 1 mg/dm^2

One method considered by Harris[51] for overcoming this was to seal in water or steam at a high temperature. He sealed coatings in both water and steam at temperatures up to 150°C, producing sealed films that were not crazed, but on drying they still crazed at 105°C. Also, films sealed at 100°C could be heated in water or steam up to 150°C without crazing although they would craze at 105°C in dry air. This sort of observation has obviously led to the patent by the Ford Motor Company[237] which enables anodized aluminium to be heated without crazing by ensuring that the water content of the furnace atmosphere has a dew point of 100°C for temperatures of 135-140°C and a dew point of 66-71"C for heating up to 120°C.

One disconcerting feature of crazing is the way that it sometimes disappears after a few days. Spooner[238] reported that crazing could occur as a result of exposure of a sealed film to a dry atmosphere (0% R.H.) for a period of several months. On removal from this atmosphere and exposure to higher relative humidity conditions the cracks disappeared. Re-exposure to 0% R.H. again caused crazing. The effect was restricted to thick (25 micron) films produced at higher anodizing temperatures and sealed for 30-60 minutes, so resulting in a high water uptake and good sealing. Clearly there is still much to be found out about the relationship between sealing and crazing.

Kaiser Aluminum Co.[183] have suggested adding 0.02-0.04 g/l of *p*-toluene-sulphonamicle to the sealing water to increase the temperature at which crazing takes place, but the improvements claimed are not as much as one would wish for, for instance, in a paint curing cycle.

More recently the problem of crazing has come to the fore with cold impregnation systems, which were shown to have a strong tendency for crazing, particularly in hot, dry climates such as those in the Middle East.[142,143] This problem was reduced by the double sealing treatments now generally used, where cold impregnation is followed by a short period of hot water sealing.

Paint adhesion

Whether anodized surfaces should be sealed or not before painting is a question on which there are differing opinions, and very little attention has been given to the effects of sealing on paint adhesion. Garwood[239] says that paint adhesion problems are no greater with anodized aluminium than they are with stainless steel or chromium plate, but that sealing was a major factor in the adhesion of 20 different paints which he examined. He found it necessary however to use curing temperatures below 113°C in order to avoid problems of thermal crazing. When curing temperatures of 150°C are used with sealed films there is blistering and. lifting of the paint because of release of water from the oxide coating, and under these conditions one obtains better adhesion by painting the unsealed coating.

The most damaging addition to the sealing bath was a wetting agent. Adhesion was consistently poor if any wetting agent at all had been added. This is an unfortunate occurrence since nickel acetate sealing baths require a wetting agent if the sealed surface is to have a good appearance. Nickel acetate when used as the only additive to the sealing water produced good paint adhesion. Chloride was harmful at 20 ppm, and sulphate at 200 ppm but not 20 ppm, while variable results were obtained when phosphate was present so that a maximum of 15 ppm was deemed wise. But results with 20 ppm of phosphate were good when iron acetate was present also.

Another beneficial addition from the point of view of paint adhesion was ammonium molybdate, which gave consistently good results even when added at 1000 ppm, and this seemed also to counteract the effect of phosphates.

It is clear that what constitutes a good sealing treatment for subsequent paint adhesion is not necessarily the treatment which is best for corrosion resistance, and this is an area where further investigation is needed.

Adhesive bonding

Allied to the question of paint adhesion is that of adhesive bonding, which is becoming **of** increasing importance because bonded joints are now used more frequently. The strength of a bonded joint is affected not only by sealing but also

by degree of etching before anodizing, and by the anodizing conditions themselves. Friedemann ***et al***.[96] found that, when bonding with Metalon K (1 pt of hardener to *2* pts of monomer), the strength of bonded joints increased with sealing and this effect was more pronounced with bright surfaces than with those which had been pretreated by etching. They also found that the sealing smut impaired adhesion, but that this could be overcome by wiping off the smut before bonding. In their tests they also examined their 'Products **A'** (a weakly alkaline polyhydroxy compound) and 'B' (the alkali salt of polycarboxylic acid), and found that by using these to suppress smut formation, the adhesive bond strength was considerably higher than could be obtained with water sealing, even after the sealing smut had been removed (Table 11-22).

TABLE 11-22

Influence on glueing of additions for prevention of sealing bloom in conjunction with various pretreatments[96]

			Strength	
Etch	***Seal***	*Water*	*Product A*	*Product B*
Matt	Water	0.82f0.34		
Matt	Water *	1.13±0.30		
Matt	0.2% Product		1.35±0.25	1.33±0.18
Matt	0.5% Product		1.44±0.14	0.94±0.24
Matt	None		(1.01+0.07)	
Bright	Water	0.60±0.10		
Bright	Water *	0.72±0.13		
Bright	0.2% Product		1.42±0.10	0.80±0.13
Bright	0.5% Product		1.64k0.19	0.76f0.09
Bright	None		(1.16+0.20)	
None	Water	0.54±0.10		
None	0.5% Product		1.73±0.30	1.07k0.08

Strength of joint according to DIN 53 281 in kp/mm^2.
Sealing at boiling temperature in de-ionised water with or without addition of 0.5% or 0.2% Product **A** or B, 60 minutes.
* = sealing smut wiped off.

O'Connor and Zimmermann[240] have reported an investigation of adhesion of organic coatings and adhesives to bright anodized surfaces. In contrast to Garwood,[238] they found that a buffered nickel acetate/surfactant seal gave consistent seal quality and good bond durability particularly with cyanoacrylate adhesives. However the condition of the sealed surface was critical, and the main function of the nickel acetate was to make sealing conditions less sensitive to contaminants such as phosphate and silicate.

Silicone sealing

With the increase in the use of structural silicone glazing systems in architectural applications. the problem of adhesion of silicone sealing materials to sealed anodized aluminium arises frequently. Little has been published on this subject, but once again the best sealing practices are not necessarily those that provide the best basis for a silicone sealant, and results are often very variable. However an ASTM paper[241] shows that critical parameters are the degree of surface sealing of the anodized aluminium, the nature of the cleaner used to prepare the surface for silicone bonding, and the time period between cleaning and sealant application. Of the cleaners examined a siloxane based cleaner gave the best results, whilst a water based cleaner containing ammonia and surfactants gave the poorest results. The best adhesion was obtained when the anodized aluminium was not quite sealed, and was giving a value of 1.5 in the dye spot test (ISO 2143). The workers concluded that the cleaning solvents conditioned the surface of the anodic coating, and were probably retained by it, but this benefit was only maintained for a few hours.

Ageing of sealed coatings

One feature of sealing is the way that it seems to proceed in a humid atmosphere, once the process has been properly initiated, at a faster rate than if it receives no sealing at all, so that in the long run indifferent sealing performs as well as good sealing provided that the conditions of exposure are not severe enough to cause pitting at an early stage. On the other hand if sealing has been commenced in water containing contaminants that inhibit sealing. the surface will deteriorate and not improve with time. The phenomenon of ageing was examined in some detail by Sacchi, Paolini and Prati[242] who considered the implications for accelerated testing, which does not permit the spontaneous improvement that can occur with natural exposure. Since then many other workers have studied the effect of ageing, and much of this work has been referred to in earlier sections of this Chapter.[27,218,229,230] It is generally concluded that the sealed film continues to take up water in humid atmospheres, with further crystallisation and solidification of the gel-like material in the pores. Most of the recent studies have used electrochemical imp(-dancespectroscopy to follow this phenomenon, and it seems to be a particularly suitable technique.

Corrosion tests

It has always been realised that accelerated corrosion tests can be a fallible guide to what will happen under conditions of long term service. They are certainly useful in sorting out good from bad work. Carter[243] has observed that the CASS test, which is a good one in many respects, shows a remarkable lack of

discrimination between sealed and unsealed coatings. This may not be a valid criticism of the test because as noted above on long term exposure there is also less discrimination than one might anticipate between sealed and unsealed coatings because of natural ageing.

Thomas[244] has suggested that the CASS apparatus could be producing a sealing effect on the specimens in it, and demonstrated that by exposing unsealed coatings for various periods and then testing them by means of a dye spot test (ISO 2143: 1981) and by measuring the weight loss in nitric acid, an appreciable sealing effect of some type was occurring (Table 11-23).

Thomas and Jackman[62] followed up this observation by thoroughly cleaning out a **CASS** cabinet and operated it with sprays of deionised water at 45°C only, and confirmed by three tests that sealing was occurring, and one of these was the abrasive jet test which is not an easy one to explain away. The tests were also repeated at 52°C where the sealing rate was more rapid, and at 31°C where there was no sealing effect at all (Tables l 1-24 and 11-25).

TABLE 11-23

Sealing effect of the CASS test

Sealing	*Spot test (Scott)*	***Weight** loss **25** min in 50% HNO_3*
None	deep red	160 mg/dm^2
5 min at 85°C	pink	71
25 min at 100°C	slight pink	14
18 h in CASS	no colour	28

These results demonstrate that there is a hydration effect well below the temperatures often thought to be essential for it to occur, and are the more surprising since control tests in water at 52°C and in vapour at the same temperature for 8 hours produced no effect, but there was considerable sealing effect in vapour when the temperature was cycling between 42 and 48°C. Thomas and Jackman also confirmed that, by operating the CASS test at 35°C instead of 45°C when testing unsealed work, there was a greater incidence of pitting on 5 and 10 μm films.

Conditions in the CASS test are critically important in determining whether the results are more dependent on anodic film thickness or seal quality. Sheasby and Clarke[245] in an unpublished investigation, showed that under standard conditions (pH 3.2 and 50°C) the CASS test was not sensitive to seal quality, but that at pH *2* the test became more seal sensitive.

TABLE 11-24

Sealing in CASS apparatus at 45°C with waterspray only

Time in cabinet	*Spot test (Scott)*	*Abrasion test*	*Weight loss 25 min in 50% HNO_3*
5 min	Deep red	20.3 g/µm	25.6 mg/dm^2
15 rnin	Deep red	21.6	28.3
30 min	Red	18.7	22.2
1 h	Pink	16.4	7.2
2 h	Light pink	13.5	4.8
4 h	No colour	13.7	6.0
22 h	No colour	12.4	8.0
48 h	No colour	11.3	10.8
Boiled	No colour	10.0	

TABLE 11-25

Sealing in CASS apparatus at 52°C with waterspray only

Time in cabinet	*Spot test (Scott)*	*Weight loss 25 min in 50% HNO_3*
5 min	Deep red	24.3 mg/dm^2
15 min	Red	17.8
30 min	Light red	6.0
1 h	Pink	2.0
1½ h	Pink	1.9
2 h	Pink	1.5
2½ h	Light pink	1.2

Ellard and Morita[144] showed how important it was to test cold impregnated work under acid conditions. They used the ASS test rather than the CASS test, but demonstrated a significant difference in acid resistance between cold impregnated and conventionally sealed samples, though the former improved with ageing.

Summary

To summarise, then, sealing is of profound practical significance and also theoretically complex, and the following effects are produced:

1. Prevents the absorption of dyes or other materials by closing up the pore structure.

2. Improves the resistance to weathering.
3. Increases the resistance to attack by a wide range of chemicals, both acid and alkaline.
4. Increases the impedance as measured in an electrolyte.
5. Increases the breakdown voltage when dry – after an ageing period.
6. Increases the emissivity and the heat absorption.
7. Reduces the hardness and resistance to abrasion.
8. Reduces the temperature at which thermal crazing occurs.
9. Creates a removable 'smut' on the surface.

Tests for sealing

In theory any property which is altered by sealing can be expected to provide a basis for assessing the effectiveness of the sealing operation.

In practice a simple dye-stain test was for years the principle test of sealing, and occasionally it is still employed. But this indicates whether sealing has been omitted and is not good for discrimination of sealing quality.

The most frequently used tests are based on chemical attack in which any of a number of reagents may be employed, liquid or gaseous. The assessment may be:

1. Visual by judging the extent of surface 'milkiness'.
2. Visual and qualitative by judging the depth of colour on immersion in dyestuff solution after attack by a chemical.
3. Quantitative as in (1) or (2) but with the amount of etching or the depth of colour assessed photometrically.
4. Quantitative by determining the loss of weight during chemical attack under standardised conditions.
5. Quantitative by measurement of admittance or impedance values.

In practice the quality control tests that are internationally recognised are those based on:

(a) Dye retention after localised treatment with sulphuric acid and potassium fluoride or with fluorosilicic acid (ISO 2143: 1981, B.S. 6161: Part 5: 1982, and EN 12373-4: 2000).
(b) Measurement of admittance or impedance values (ISO 2931: 1983, B.S. 6161: Part 6: 1984, and EN 12373-5: 1999).

For referee purposes, and for control purposes where the other tests are not suitable, the acid dissolution tests are used as shown below:

(a) Nitric acid pretreatment followed by immersion in acidified sodium sulphite or in sodium acetate/acetic acid solutions (ISO 2932: 1981 and B.S. 6161: Part 4: 1981).

(b) Immersion in chromic acid/phosphoric acid solution without a nitric acid predip (ISO 3210: 1983, B.S. 6161: Part 3: 1984, and EN 12373-6: 1999), anti with a nitric acid predip (EN 12373-7: 1999).

Tests for sealing are dealt with in more detail in Chapter 12.

10. CONTROL OF SEALING BATHS

Dichromate baths[42]

(a) Make up 25 ml sealing solution to 250 ml. To 25 ml of the diluted solution add 100 ml distilled water, 5 nil analytically pure sulphuric acid and 10 ml 30% potassium iodide solution. Stand for 5 minutes, and titrate against N/10 sodium thiosulphate, using starch to determine the endpoint.

$$1.96 \times \text{ml N/10 } Na_2S_2O_3 \equiv \text{g/l } K_2Cr_2O_7$$

(b) For the rapid Tomashov and Tyukina method: measure pH with glass electrode and make additions of $K_2Cr_2O_7$ or Na_2CO_3 according to whether the pH is high or low. Alternatively, crush up 0.1 g dibromothymol sulphophthalein in an agate mortar with 3.2 rnl N/20 NaOH and make up to 100 ml. Add 6 drops of this indicator to 20 ml sealing solution. A brownish-green colour shows the pH to be between 6 and 7.5. If there is no colour change, the pH is below 6 and sodium carbonate is added. If a blue or greenish-blue colour is obtained, the pH is above 7.5 and dichromate is added. The solution may be titrated to determine the quantities of' additions required.

Sodium Silicate baths

In these the concentration may be determined by density measurement provided the same quality sodium silicate is always used. The $Na_2O:SiO_2$ ratio should be checked either by analysis or, more simply, by pH meter.

Nickel or cobalt sealing baths

(a) Test the pH, which should preferably be 5.7, and make up with 10% acetic acid if the pH is high, or with dilute ammonia or borax if the solution is too acid.

(b) Nickel content. This may be determined electrolytically or by volumetric or gravimetric analysis.[42] In the last, to 5 ml sealing solution add 2-3 ml of 50% tartaric acid and 240 ml distilled water and make just alkaline with ammonia. Heat to 70°C, stir and add 50 ml of a hot 1% alcoholic solution of dimethyl-glyoxime. Stand for one hour at 70". Cool, filter through a weighed Gooch or sintered glass crucible, wash with distilled water at SO-60°C. Dry at 120°C and weigh as nickel dimethyl-glyoxime $[Ni(C_4H_7O_2N_2)_2]$.

Grammes $Ni(C_4H_7O_2N_2)_2$ x 12.25 = % nickel acetate in sealing bath.
Grammes $Ni(C_4H_7O_2N_2)_2$ x 4.06 = % Ni in sealing bath.

A similar test has been described by Stiller.[246]

In the volumetric method, pipette 25 ml of the solution into a 200 ml beaker and add 100 ml water. Titrate against 50 g/l E.D.T.A. solution, reading the pH after each 0.5 ml. Plot a graph of pH against ml E.D.T.A. The pH goes through a minimum, which corresponds to the end point:

$$\%\ \text{nickel acetate}\ (Ni(CH_3COO)_2.4H_2O) = \text{E.D.T.A.} \times 0.126$$

(c) Cobalt content. Estimate gravimetrically by precipitating cobalt with a-nitroso β-naphthol. Pipette 10 ml of the sealing solution into a measuring flask and make up to 100 ml. Pipette 10 ml of this solution into a beaker, add 5- 10 drops of IO0 volume H_2O_2, and add 0.2N sodium hydroxide until a precipitate forms, keeping the beaker covered. Add 10 ml glacial acetic acid, warm gently to dissolve the precipitate, dilute to 200 ml with boiling water, and treat with 10-20 ml of the reagent freshly prepared by dissolving 4 grammes α-nitroso β-naphthol in 100 ml acetic acid. Add 100 ml hot distilled water, and filter. Heat to boiling, stirring vigorously until the precipitate settles out. Test whether precipitation is complete by adding more reagent solution, and filter through a weighed Gooch or sintered-glass crucible. Wash with hot acetic acid and boiling water and dry at 130°C to constant weight.

Weigh as $Co(C_{10}H_6O_2N)_3.2H_2O$
Weight of ppt x 8.285 = % Co

Hot-water sealing baths

These must be checked for pH which should be 5.5-6.5, and discarded and renewed when required. Alternatively, slight alkalinity or acidity may be counteracted by additions of 10% acetic acid or ammonia solution, or preferably by using a 1 g/l ammonium acetate addition in the seal.

11. STRIPPING ANODIC OXIDE COATINGS

Four stripping solutions are in common use for removing anodic oxide coatings. These are:

1.	phosphoric acid (d. 1.75)	35 ml/l
	chromic acid	20 g/l
	used at boiling point	
2.	sulphuric acid (conc)	100 ml/l
	potassium fluoride	4 g/l
	used at room temperature	
3.	sulphuric acid (conc)	100 ml/l
	hydrofluoric acid	
	(commercial 50/60% HF)	10 ml/l
	used at room temperature	
4.	nitric acid	27% (wt)
	hydrofluoric acid	2% (wt)
	used at room temperature	

In general the chromic-phosphoric acid solution is in the widest use as attack on the basis metal is insignificant and the bath needs less control than fluoride containing solutions.[247] This solution is also used in the stripping and weighing method of measuring coating mass or average coating thickness (ISO 2106: 1982, B.S. 6161: Part 1: 1984, and EN 12373-2: 1999).

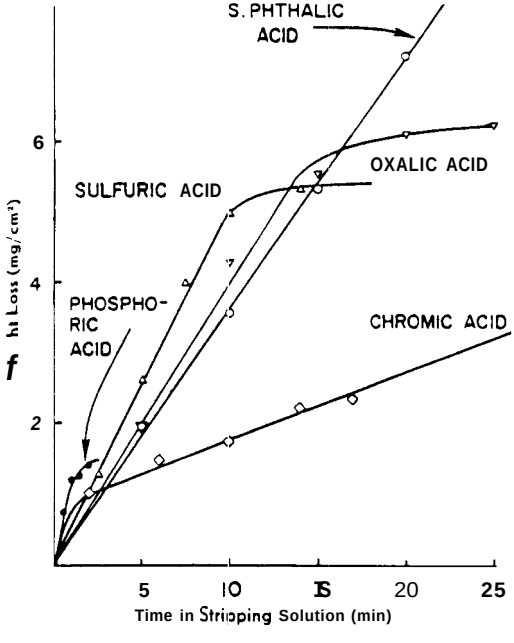


Fig. 11-35. Dissolution of sealed porous anodic films in a chromic-phosphoric acid solution (water sealed 120 min)[36]

The rate of stripping of anodic films produced in different anodizing electrolytes has been studied by Spooner,[36] and his results are shown in Fig. 11-35. Rate of stripping is, to some extent, an indication of seal quality, and again phosphoric acid anodized samples were least resistant to attack.

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CHAPTER 12

Properties and Tests of Anodic Oxide Coatings

As discussed previously, the properties of the coatings obtained by the various anodizing processes may vary considerably, and depending on the specific application for which the work is to be treated, it is often possible by varying the solution, the operating conditions, the after-treatment, or even the composition of the basis metal or alloy, to obtain improvement in the properties aimed at. This chapter comprises a general discussion of the physical and chemical properties of anodic coatings together with some of the testing methods employed, certain of which might with advantage be incorporated in routine control and inspection in industrial practice, particularly where work is to specification.

1. APPARENT DENSITY

The apparent density (specific gravity) of anodic oxide coatings may vary within quite wide limits depending upon the operating conditions and the basis metal. The variations are due to differences in porosity and in foreign inclusions in the film, for which reason the term apparent density is more appropriate and is now generally preferred.

Table 12-1, which shows the apparent densities of anodic oxide films produced in different treatment times and on different alloys, is due to Elze.[1]

TABLE 12-1

Variation of apparent density of sulphuric acid anodic oxide coatings with anodizing time and basis metal composition'

	Apparent density (g/cm³)				
Anodizing time (min)	*99.99% Al*	*99.5% Al*	*Al-3% Mg*	*Al-Mg-Si*	*Al-Cu-Mg*
5	3.3	3.5	3.4	3.5	2.9
10	3.2	2.9	3.3	3.1	2.4
20	3.0	2.8	2.6	2.8	1.9
30	3.0	**2.6**	2.5	2.4	1.8
40	2.6	2.4	2.5	2.3	1.6
50	2.4	2.6	2.3	2.4	–
60	2.2	2.4	2.3	2.3	–

In a very detailed series of measurements covering all of the common American alloys, Kissin, Deal and Paulson[2] carried out determinations of apparent density on specimens anodized for up to two hours in 15% by weight sulphuric acid (165 g/l) at 12 amp/sq ft (1.29 A/dm²) at 20°C and 25°C. The term apparent density is preferred to specific gravity because the latter concept is a property of the alumina which makes **up** the coating and strictly would only apply to a perfectly homogeneous pore-free coating. Their determinations were carried out on unsealed coatings because it was found that measurements on sealed coatings were much less reproducible. **A** selection from their results, which covers the normal anodizing conditions, is given in Table 12-2.

TABLE 12-2

Apparent density in g/cm³ of unsealed coatings on various alloys[2]

		Anodized in 165 g/l H_2SO_4 at 1.29 A/dm² and					
Alloy and		*20°C*			*25°C*		
nominal composition		*20 min*	*60 min*	*80 min*	*20 min*	*60 min*	*80 mi*
1099-HI4	99.99% AI	2.59	2.44	2.36	2.59	2.29	2.14
1100-H14	99.0% **AI**	2.52	2.45	2.32	2.69	2.23	2.09
5005-H18	0.8 Mg	2.65	2.45	2.37	2.45	2.19	2.03
5052-H32	2.5Mg, 0.25Cr	2.67	2.36	1.29	2.47	2.05	1.78
6063-T5	0.7Mg, 0.4Si	2.48	2.40	2.36	2.27	2.26	2.11
3003-H14	1.2 Mn	2.85	2.56	2.40	2.52	2.25	2.08
4043-HI4	5.0 Si	2.89	2.48	2.36	2.57	2.30	2.19
2014-T6	4.4 Cu	2.10	1.53	1.37	1.72	1.25	1.28
7075-T6	5.6Zn, 2.5Mg 1.6Cu, 0.3Cr	2.37	1.83	1.63	2.09	1.49	1.40

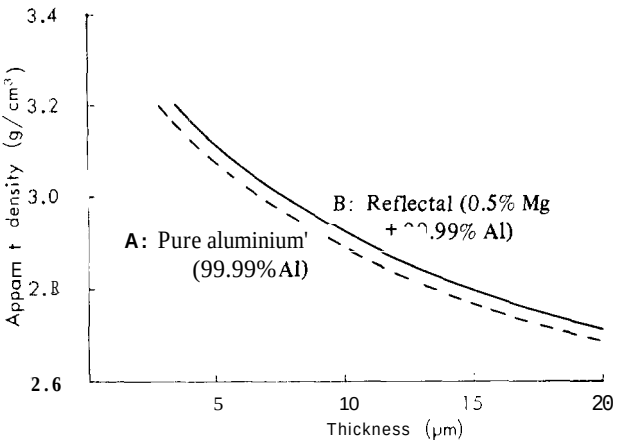


Fig. 12-1. Apparent density of anodized film on Reflectal (0.5% Mg) and on pure aluminium sheet as a function of film thickness.' Electrolyte 250 g/l H_2SO_4, bath agitated by air, temperature 17-18°C. Film sealed 20 minutes in saturated steam at 100°C.

The Aluminum Association Standard for anodized aluminium in architectural applications' specifies a minimum apparent density for coatings of 2.32 g/cm³, and a minimum coating weight for a Class I (18 micron) film of 27.0 mg/in² (4.18 mg/cm²). The Architectural Aluminium Manufacturers Association specifications for electrolytically coloured[5] and integral colour coatings[6] are similar, but, in the case of the integral colour specification, no minimum apparent density is specified, but the equivalent minimum coating weight is 32.0 mg/in² (4.96 mg/cm²).

Accurate determinations of apparent density were also made by Lenz[3] using 99.5% aluminium and Reflectal, an alloy of 0.5% magnesium with 99.99% aluminium. He investigated coatings up to 20 μm thick formed in 250 g/l sulphuric acid at 17-18°C and found that the density decreased with film thickness, as shown in Fig. 12-1, from 3.1 for 5 μm films to 2.7 for 20 μm films. Reflectal had a very slightly higher density than pure aluminium, but the effect of current density from 0.7 to 2.5 A/dm² was negligible. These coatings had all been sealed in saturated steam for 20 minutes and the findings are in good agreement with those obtained by Elze.[1] By extrapolation of Fig. 12-1 to very thin films a value of 3.41 g/cm³ is obtained, which is in agreement with values obtained for air-formed or boehmite films by other methods.

More recent work by Dowell and Gabe[7] has looked at a range of anodizing conditions used with a variety of alloys. Their results are shown in Tables 12-3 and 12-4. Again the most consistent results were obtained with unsealed work, and they clearly showed that it was conditions that lead to pore wall attack, and hence

an increase in overall porosity, that gave reduced density values. In particular long sulphuric acid anodizing times at higher than normal temperature (25°C), or anodizing Al-Cu or Al-Zn-Mg alloys, had the greatest effect on film density. However use of conventional anodizing conditions on the alloys most commonly anodized (e.g. Al-Mg or Al-Mg-Si) gave relatively constant values of apparent density. They concluded that values of about 2.6 for unsealed films and 2.7 for sealed films were appropriate, but pointed out that their work was done on relatively high purity based alloys. Related work at Loughborough University of Technology[8] confirms these conclusions.

TABLE 12-3

Variation of apparent density of sulphuric acid anodic oxide coatings with anodizing time and basis metal composition

	Apparent density ($g.cm^{-3}$)				
Anodizing time (min)	*99.99% Al*	*99.5% Al*	*Al-3% Mg*	*Al-Mg-Si*	*Al-Cu-Mg*
5	3.3	3.5	3.4	3.5	2.9
10	3.2	2.9	3.3	3.1	2.4
20	3.0	2.8	2.6	2.8	1.9
30	3.0	2.6	2.5	2.4	1.8
40	2.6	2.4	2.5	2.3	1.6
50	2.4	2.6	2.3	2.4	–
60	2.2	2.4	2.3	2.3	–

TABLE 12-4

Apparent density in $g.cm^{-3}$ of unsealed coatings on various alloys

		Anodized in 165 g/l H_2SO_4 at 1.29 A/dm^2					
Alloy and nominal composition		*20°C*			*25°C*		
		20 min	*60 min*	*80 min*	*20 min*	*60 min*	*80 min*
1099-H14	99.99% Al	2.59	2.44	2.36	2.59	2.29	2.14
1100-H14	99.0% Al	2.52	2.45	2.32	2.69	2.26	2.09
5005-H18	0.8 Mg	2.65	2.45	2.37	2.45	2.19	2.03
5052-H32	2.5 Mg, 0.25 Cr	2.67	2.36	1.29	2.47	2.05	1.78
6063-T5	0.7 Mg, 0.4 Si	2.48	2.40	2.36	2.27	2.26	2.11
3003-H14	1.2 Mn	2.85	2.56	2.40	2.52	2.25	2.08
4043-H14	5.0 Si	2.89	2.48	2.36	2.57	2.30	2.19
2014-T6	4.4 Cu	2.10	1.53	1.37	1.72	1.25	1.28
7075-T6	5.6 Zn, 2.5 Mg 1.6 Cu, 0.3 Cr	2.37	1.83	1.63	2.09	1.49	1.40

It is clear then that there is a degree of uncertainty about the precise density of the anodic oxide coating, and when values of 2.4 and 2.6 are quoted for the unsealed and sealed coating respectively this is something in the nature of an agreed convention for uniformity. Errors or variations can arise for the following reasons:

1. The inherent difficulty of making an accurate thickness determination by micro-section, with the error variously estimated as from ¼-½ micron.
2. The film weight is determined over an area, whereas a microsection is a very limited sample at a few points, and in the case of some alloys an 'interpretation' is needed.
3. Small changes in anodizing conditions can affect the film thickness locally.

2. COATING THICKNESS

The thickness of coatings normally produced by the different anodizing processes has been described in previous chapters. As has been seen, the increase in film thickness is not linear with the treatment time, but a maximum, or limiting, film thickness may often be reached when an equilibrium is established between the rate of film growth (which at constant voltage decreases with the thickness of the film) and the rate of dissolution of the film in the electrolyte. The operating time is often critical, however, in that the metal will continue to decrease in thickness after the maximum film thickness has been obtained, while in the case of some alloys, e.g., certain aluminium-magnesium and aluminium-magnesium-zinc alloys, there may even be an actual decrease of the film thickness after the maximum is reached.

In general, the limiting thickness and the rate of film growth increase with rise in current density and pH of the solution, with vigorous agitation and with greater homogeneity of the alloy, and decrease with rise in temperature and the presence of heterogeneous phases of alloying constituents which accelerate dissolution of the film in the electrolyte. The most effective method of producing thicker coatings is to use low temperatures (see Chapter 9). In the case of dielectric non-porous films, which are practically insoluble in the solution, such as are produced in the boric acid eleclrolyte, the film thickness is limited mainly by the electrical resistance of the film, and film growth of the barrier type film ceases when the breakdown voltage is equal to the voltage applied (Chapter 7).

In most cases anodizing first increases the dimensions of the work and then reduces them again after reaching a maximum. In general, the sulphuric acid film itself has a volume approximately 1.5 times that of the metal from which it is formed but this ratio is slightly higher in oxalic acid anodizing, and hard anodic films may be 2.0 times the volume of the metal removed during their formation.

Dimensional change with a range of black dyed materials has been reported by Morse[9] and his results are shown in Table 12-5. He makes the point that dimensions are also changed by pretreatment, and suggests conditions for cancelling out the increase due to anodizing with suitable etching or chemical brightening conditions.

TABLE 12-5

Selected features of anodic coatings produced at 68-70°F (20-21°C) in 15% sulfuric acid at a current density of 12 A/ft² (1.2 A/dm²)[9]

Alloy	*Anodizing time (minutes)*	*Coating weight*	*Thickness (mils)*	*Buildup/Surf (mils)*	*Dimensional change (mils)*
2024-T4	20	1104	0.27	0.09	0.18
	40	1888	0.51	0.17	0.34
	60	2370	0.74	0.25	0.50
6061-T6	20	1758	0.28	0.093	0.19
	40	3370	0.56	0.19	0.38
	60	4990	0.87	0.29	0.58
	80	6392	1.16	0.39	0.78
7075-T6	20	1594	0.29	0.097	0.19
	40	2861	0.59	0.197	0.39
	60	3837	0.89	0.297	0.59

1 mil = 25.4 microns

In practice measurement of anodic film thickness is one of the most important control parameters, but relating the film thickness produced to the anodizing conditions used can also be a useful control of the solution conditions and equipment employed. Thickness control is of particular importance where the work is to be dyed or where close dimensional tolerances have to be obtained together with adequate protection. It is, of course, essential where a specification is to be maintained.

Determination of coating thickness

Numerous methods have been suggested, but no technique which is both simple and accurate has been evolved suitable for all types of coatings. Methods for determining the thickness of anodic coatings in routine inspection should preferably not destroy the film, and at least should not affect the basis metal. Most film thickness meters are now accurate and dependable, but the referee methods in cases of dispute inevitably involve destruction of the coating.

A. Non-destructive methods

Interference microscopy[10,11,12]

The principle of interference between two coherent beams of light to produce a pattern of light and dark fringes can be applied to the determination of the thickness of transparent films on a reflecting surface with great accuracy in the range where it can be applied, that is from 500 Å (0.05 μm) up to several times the wavelength of light, or about 3 μm. There are several techniques for accomplishing this, and in the most easily understood a beam is separated into two components, one of which is reflected from a reference surface, and the other from the surface under test, before combining them in the field of view of the microscope eyepiece. When correctly set the fringe pattern will be visible, along with a secondary pattern produced by the part of the beam reflected from the film surface. By selecting a small feature of the surface which produces an easily recognisable distortion in the fringe pattern, the corresponding pattern initiated by the beam from the film surface can be identified near to it or made to appear by movement of the reference mirror. The distance between these two must then be assessed in terms of the number of fringes between them; this value n is obtained either by dividing the physical distance by the width of one fringe, or moving the pattern across the eyepiece wires and counting the number of fringes. If λ is the wavelength of the light employed (thallium light is convenient) and μ is the refractive index of the film, then the film thickness t is:

$$t = \frac{n.\lambda}{2\mu} \text{ or } \frac{\lambda}{3.2} \ \mu\text{m per fringe.}$$

Various optical arrangements can be employed and it is possible to use white light and techniques of multiple beam interferometry, which have been discussed by Tolansky.[13] The method can also be applied to the determination of the refractive index of the coating, which has been found to be 1.6 ± 0.1, which is in good agreement with that for α-$Al_2O_3.H_2O$ (1.62). Generally accepted values for refractive index are 1.59 for unsealed films and 1.62 for sealed coatings.

The interference microscope is an expensive piece of equipment and scarcely justifiable for the limited range of film thicknesses with which it can cope if this were to be its only use, but it can give the thickness on rough or profiled surfaces of any curvature and even on edges." Michelson[14] has described a more simple interference device which uses a reasonably narrow illuminating band which can be adjusted in frequency over a range of 200 μm, a reflection-diffraction grating and a meter to identify the peaks in the response curve. He compared the method with others and found that it gave results which were quite acceptable for quality control in the range 2.5-5 μm and could be extended up to 9 μm with an empirical calibration curve.

Breakdown voltage[15,16]

The application of this method is limited as differences occur not only between coatings produced by different methods and operating conditions and on different alloys, but also within the different layers of the coating, i.e., it will vary with the thickness of the coating. The method thus requires calibration by determining the value for each alloy treated and with each change in operating conditions. As a result it is rarely used today.

By a technique developed by Compton and Mendizza,[16] a chromium plated steel ball of 3 mm diameter was used as the electrode and was pressed against the surface with **a** load of 1,000 or 2,000 grammes. Alternating current was applied and the voltage raised slowly until breakdown occurred. An accuracy of ±10% could be obtained with d.c. coatings with an approximate value of 93 volts per 0.0001 inch (37 volts/μm).

Electrical breakdown is an exceedingly complex phenomenon and little understood. Not only is it affected by anodizing conditions and metal composition, but sealing and subsequent ageing have an effect, as also does the surface roughness. It is affected by the material of and the pressure on the contact electrode, by the polarity, wave form and rate of voltage rise, by the humidity and temperature, and by other factors. These are discussed later on page 1052, but as Compton and Mendizza demonstrated and as others have found, for coatings produced under more-or-less standard conditions and similarly tested there is mostly a linear relationship between film thickness and breakdown voltage, so that the property could be used as an indication of thickness in production tests as well as being used where a minimum breakdown voltage was required. The linear relationship is most readily produced when using an alternating current source. The principles of the test were set down in BS 1615: 1972, but it was not approved as a general method for film thickness determination.

A meter built according to these principles was available in the U.S.A. as the Rohco Anodicator[17] in which the requisite slow rate of voltage increase was applied to a probe in contact with the surface under uniform pressure. A similar portable instrument was also described at about the same time.[18]

A commercial instrument known as the 'Testalu Walter' was also described in France.[19 20] It was unusual in employing a bipolar probe of two adjacent metal spheres spring loaded to SO-100 g, and the voltage applied to these was steadily increased by means of a motorized control until a signal lamp indicated breakdown; a mono-polar probe could also be used if required. A rather simpler mono-polar instrument was also produced at about the same time at the Ranshofen Research Institute," and a further one has been described by Nachtigall.[22]

Ruff of I.S.M.L. (Light Metals Research Institute, Italy) probed more deeply into the mechanics of electrical breakdown than other investigators to see what factors determined it, and also studied the events in the film prior to breakdown.[23] His 'Resistometer' also used a pair of contact spheres under light pressure of 100 g but instead of waiting for disruptive breakdown with the consequent arcing

across the film he used a magic-eye device to indicate when a pre-breakdown current of 100 μA was passing, and found that the corresponding voltage related better to film thickness than any other value. Thomas[24] also made detailed studies of breakdown voltage with particular attention to the pre-breakdown phenomena and found it, except on the thinner films, to be a very variable and unpredictable property, but the best indication of film thickness was obtained with alternating current applied to a single probe, preferably made of graphite and with external impedance of not more than 500 KW. Dependable results were obtainable up to 10 μm but for thicker films the results became more scattered, dependent on the circuit constants and affected by ionisation of the air in the vicinity of the probe. Use of the method has also been noted in Czechoslovakia.[25]

In practice, with the availability of the more accurate eddy-current meters, this method of measurement is rarely used today.

Eddy-current measurement

The most reliable non-destructive thickness tests are those carried out with meters based on the eddy current principle, which are designed so that the strength of a high frequency current flowing through the search coil is dependent on the distance of the coil from a conducting surface.

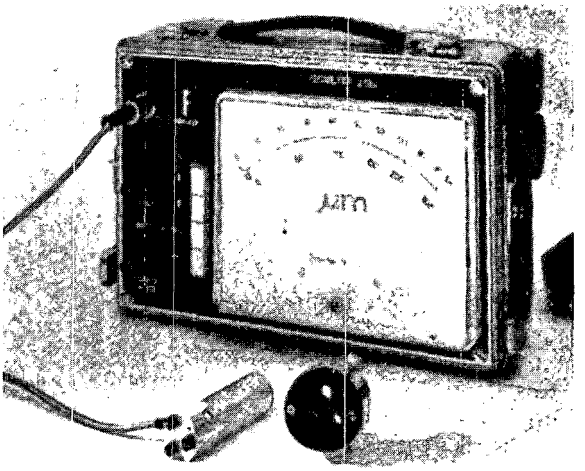


Fig. 12-2. Isometer Type 2.082 for measuring anodic oxide coating thickness

[Courtesy Institut Dr. Forster]

One of the earliest commercial instruments was the Isometer, in which the test head is a small coil energized by a high-frequency oscillator. The associated magnetic field induces eddy currents in the basis metal. The depth of penetration of the current is inversely proportional to the square root of the frequency and directly proportional to the conductivity of the basis metal. Thus, when the conductivity of the coating differs from that of the basis metal the coating thickness (i.e., the distance between the probe and the basis metal) is linear to the output of the amplifier, which is measured on a dial. In order to prepare calibration curves for the specified aluminium alloy, non-metallic foil of known thickness is placed on the uncoated metal.

The American 'Dermitron' instrument, developed by Brenner and Gottia, operates on a similar principle. Fig. 12-3 shows the circuit diagram.[26] The instrument is calibrated in the same way as the Isometer.

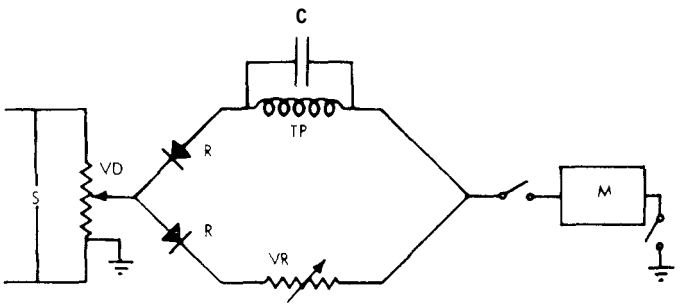


Fig. 12-3. Circuit diagram for the Dermitron. **S** = oscillator used as power supply. VD = voltage divider. **R** = germanium rectifiers. TP = test probe. C = mica condenser. VR = helipot potentiometer, 0-100 ohms. M = d.c. microammeter

In Europe a variety of eddy-current thickness meters have become available over the last 20 years. These range from relatively simple hand-held instruments (which may or may not be microprocessor controlled) to quite sophisticated instruments which print out the measurement results, and can provide product statistics and trend charts. Both mains and portable battery versions are usually available.

Eddy-current instruments have been used for a good many years, principally as flaw detectors, as alloy sorters or resistivity-measuring devices; in the last case the exploring head is not very sensitive to the distance from the metal

surface. In designing a distance-measuring device the circuit must be arranged so that the current is not affected (within limits) by the resistivity of the basis metal but is very sensitive to the distance of the coil carrying the current. The electrical circuitry is in fact much easier to construct than the test coil itself. This must be a carefully engineered coil which sits very gently on the surface under light pressure, is dimensionally stable, with its electrical axis precisely vertical, not subject to tilting or friction, temperature-stable and introducing no inductive changes by movements of the leads. Most instruments require a zero setting on uncoated metal of the same composition or alloy type as the anodized metal to be measured, and standardising on coatings of accurately known thickness, which are supplied as plastic films or calibrated anodized samples. The use of microprocessors in conjunction with eddy-current instruments has allowed the effect of substrate conductivity to be minimised.

The commercial instruments have varied in accuracy, stability and dependability with the course of time. Defects of the earlier models were associated with zero drift requiring very frequent rechecking, a high sensitivity to temperature changes, a response that was not always linear, and probes whose characteristics were not always stable, but the modern instruments are such that eddy current testing is the standard method of thickness measurement for most anodic coatings.

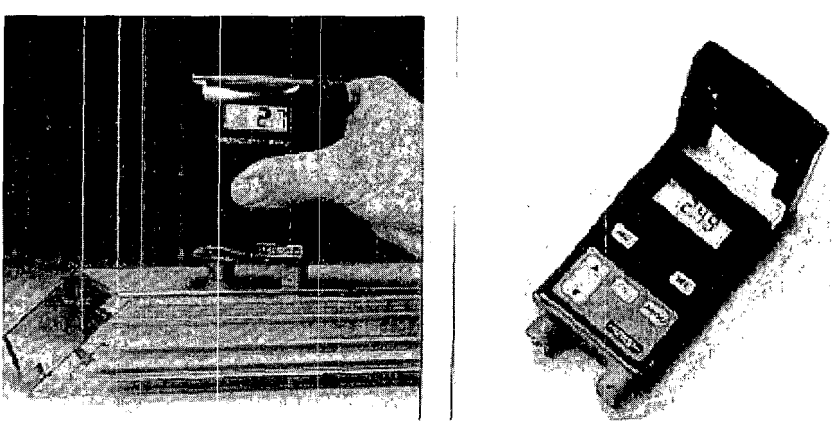


Fig. 12-4. Fischer Isoscope MPOD with inregrated constant pressure probe

[Courtesy of Fischer Instrumentation (G.B.) Ltd.]

R.S. Young, who was responsible for three patents on the subject,[27,28,29] demonstrated that a stable circuit could be made which showed no zero drift over long periods and was compensated for normal temperature changes; it could be made practically independent of basis metal resistivity so that the error in changing from 99.99% aluminium to a high copper or zinc alloy was no more than 0.5 microns, and a linear response over a wide range could be maintained.

The design of eddy current instruments has been reviewed by Latter,[30,31] Gühring[32] and Ott,[33] and their use is covered in an International Standard (EN ISO 2360) and in national equivalents (e.g., B.S. 5411: Part *3:* 1984 and ASTM B244-97). The introduction of microprocessors has allowed the instruments to be pre-programmed for the effects of factors such as surface curvature, so they can now be used on the curved surfaces of such components as tubes and rods. Miniaturisation of the instrument circuits has produced highly portable units such as the Fischer Isoscope (Fig. 12-5).

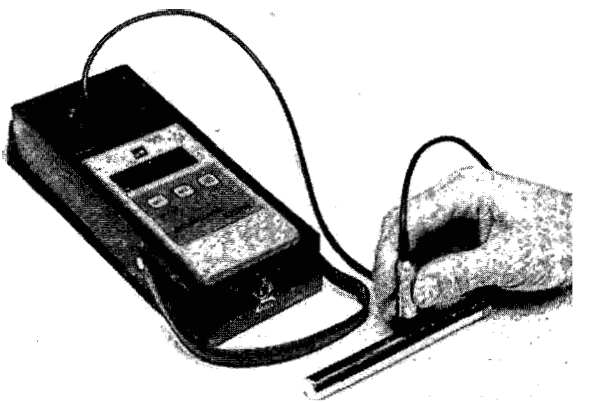


Fig. 12-5. Portable Isoscope being used to measure thickness on a curved surface

[Courtesy of Fischer Instrumentation (G.B.) Ltd.]

Radiation methods

The availability of radioactive isotopes has resulted in a large number of frequently very sophisticated instruments for thickness determinations of all types on practically any material. These may employ α, β, or γ-rays, continuous radiation from β-radiation or X-rays. In the case of oxide coatings on aluminium the most convenient source of radiation is one which emits β-rays in the direction of the

surface under test, and the reflected radiation is measured with a Geiger-Muller tube. The instruments require calibration with standards of known thickness and can measure coatings from 500 Å to 300 μm, giving digital read-out directly in any desired units, millionths, microns, angstrom units, or weight per unit area. However, in order to obtain accurate readings with thin coatings, they require a significant difference in density between the coating and substrate. This does not occur with anodic coatings on aluminium and, in practice, a thickness of about 7 microns is the minimum that can be measured with the beta backszatter method. Commercial models are the Betascope[34] and the Microderm.[35] Again their use is covered in standards (EN ISO 3543).

Peisach, Poole and Röhm[36] have determined the thickness of the oxide film on aluminium by measuring the difference between the energies of α-particles scattered from the surface of the oxide layer and from the underlying metal. Films ranging in density from 10-130 mg/cm^3 were analysed with a coefficient of variation of 3.5%.

The back reflection of X-rays can also be used for thickness determination, a commercial instrument being the EKCO Fluoroscopy Gauge N683[37] and the Fischerscope XR.[31] Ramous[38] has discussed the application of the X-ray fluorescence method to anodized aluminium. It is appropriate to coatings in which the same element is present as in the basis material but at a different concentration. The intensity of radiation of the common element can be expressed as a function of the thickness and composition of the coating. Lihl, Ebel and Struszkiewicz[39] have given a theoretical treatment of the relation between the yield of fluorescence due to aluminium and the thickness of the anodic layer of aluminium oxide which permits the evaluation of the density and composition of the layer. By experimental investigations it was found that the layer was composed of $Al_2O_3.H_2O$ with the corresponding density of 3.1 g/cm^3.

Split-beam microscope

A quick non-destructive method for determining the thickness of transparent coatings on relatively smooth surfaces is by means of the split-beam microscope, which is also known as the Schmaltz method.[40] **A** parallel light beam is incident on the surface at an angle of 45° as shown in Fig. 12-6, and part of the beam is reflected from the film surface while the rest is reflected at the metal/oxide interface so that it emerges with a lateral displacement. In the field of view of the eye-piece therefore there appear two images of the illuminated slit which are separated by the apparent thickness of the transparent film (Fig. 12-7). If T is the actual film thickness and T_1 is the apparent thickness (Fig. 12-6) it can soon be shown that these quantities are related by the equation:

$$T = T_1 \sqrt{2n^2 - 1}$$

where n is the refractive index of the coating. The values for this are considered to lie between 1.59 and 1.62, which makes T about 2.04 T_1. It is sufficient therefore to take T as twice the apparent thickness.

The method (ISO 2128: 1976), B.S. 6161: Part 2: 1981 and EN 12373-3: 1999) is comparable with the microsection method in that the film thickness is directly observed through a microscope, and its accuracy depends on having a sufficient magnification available (× 500) to see the film, and the ability to measure the reflected image exactly. This is done by means of a vernier screw controlling a calibrated reticule which indicates the thickness of the coating in microns.

A commercial instrument made by Carl Zeiss (Fig. 12-8) functions on either flat or curved surfaces and may also be used on lightly dyed coatings, but it is unsuitable for heavily pigmented coatings and it is difficult to use with precision on surfaces that have been heavily etched because of the blurred image, but even in these cases a very good estimate is obtained for the thicker coatings. Thin coatings of less than three microns are subject to the same problem as with the microsection method, namely, that there is insufficient separation of the two surfaces to make an accurate determination.

Four calibrated scales are used to cover the ranges 1-3.5 μm, 2-10 μm, 5-30 ym and 10-100 μm.

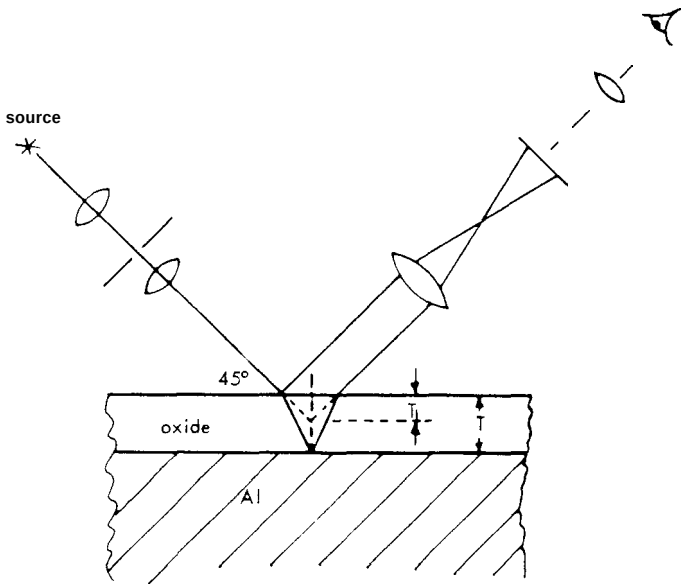


Fig. 12-6. Principle of the split-beam microscope

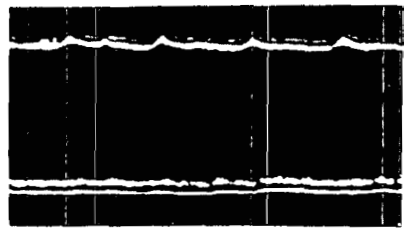


Fig. 12-7. Split beam photomicrographs of an anodized layer (upper) and a transparent lacquer coating (lower illustration)

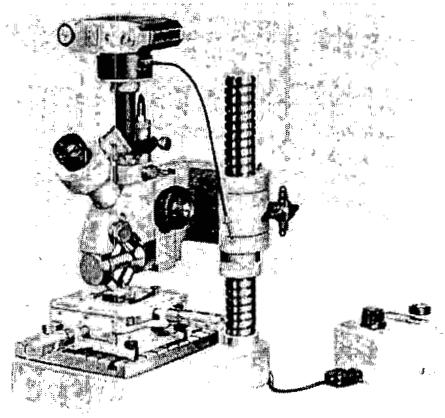


Fig. 12-8. Split-beam microscope[41] [Courtesy Carl Zeiss]

Ellipsometry

An ellipsometric method of measuring oxide film thickness of aluminium has been described by Norman.[41] A source of plane polarized light is used, and when the light strikes an optically transparent film on a reflective substrate, it is reflected with elliptical polarization. This change in polarization is dependent on the refractive index and the thickness of the surface film. Norman used a Gaertner model L119 ellipsometer with a laser light source. This method is suitable for measuring very thin oxide films, and it can in fact be used for measuring natural as well as thin anodic oxide coatings. It is particularly suitable for measuring the type of film produced in barrier anodizing electrolytes. The subject has been extensively reviewed by Neal.[43]

With all optical measurements a knowledge of the refractive index of the oxide being measured is essential, and workers in Taiwan[44] have used ellipsometry to indicate how it can vary with thin oxide films. For a top surface layer on a substrate with given optical properties, the evaluation of both thickness and refractive index requires the numerical solution of two complex simultaneous equations, and the accuracy of the thickness results depends sensitively on the calculated refractive index. If, however, either the thickness or the refractive index of the film is known precisely, then the numerical solution of the other parameter can be greatly simplified, and its accuracy significantly increased. The Taiwan workers used cross-sectional electron microscopy to accurately determine the thickness of a range of anodic oxides, and then used ellipsometry to determine their refractive index. Results of their own and other studies are shown in Table 12-6. They concluded that, except for one study with an ammonium tartrate electrolyte, the refractive index of anodic alumina fell within a narrow range of 1.62 to 1.70 over a thickness range of 120-4700 nm, and the value seemed to be insensitive to the electrolyte used for anodizing.

Workers at Brussels University have also used this method to determine the thickness and refractive index of barrier films.[45]

TABLE 12-6

Refractive index of anodic Al_2O_3 films[44]

Electrolyte	*Thickness (nm)*	*Refractive index n*	*Measurement method*
Tartaric acid / propylene glycol	133	1.67	Ellipsometry
Tartaric acid / propylene glycol	120	1.62	Ellipsometry
Ammonium pentaborate	400	1.65	Ellipsometry
Ammonium pentaborate ethylene	400	1.67	Ellipsometry
Ammonium tartrate	91	1.71 - 1.75	Ellipsometry
Ammonium tetraborate	402	1.66	Spectrophotometry
Oxalic acid	1300 - 4700	1.66 - 1.70	Photoluminescence
Sulphuric acid	350	1.63	Ellipsometry
Tartaric acid	150 - 200	1.62	Ellipsometry

U.V. reflectance

A method of measuring thin anodic coatings using a U.V. reflectance method has been described by Khan *et al.*[46] This method uses a scanning spectrophotometer to measure the U.V. radiation reflected from an oxide covered surface. As the

wavelength of the incident radiation is varied, the oxide film acts like a diffraction grating, and the intensity of the reflected radiation passes through maxima and minima. It is possible to derive an expression which relates the oxide thickness to the spacing of the maxima and minima, and also to the refractive index of the oxide. As the refractive index of the film varies with wavelength, particularly in the U.V. region of the spectrum, it must be measured, and this has been done with barrier layer oxides by Khan *et al.*[46]

The technique is rapid and non-destructive and, with U.V. radiation, can be used over an oxide thickness range of about 0.25-5 microns, but it is not suitable for rough substrates. Infra-red radiation can also be used for thicker films (3-30 μm) but spurious peaks due to the presence of water can create problems.

Electron microscopy

Whilst not being; a generally applicable method of anodic film thickness measurement, research laboratories are increasingly using electron microscopy as a method of measuring the thickness of coatings, particularly when they are less than a few microns in thickness.

In the case of anodic coatings, the anodized sample is normally immersed in liquid nitrogen and then bent sharply through a small radius in order to crack the film. The edge of the fractured film can then be examined directly in the scanning electron microscope and the thickness measured directly. This method has the advantage that it is not dependent on other factors such as refractive index or film density, and, with a suitable SEM, it can be used with films down to about 0.1 microns.

B. Destructive methods

By microsection

The traditional method for determining the anodic coating thickness without equivocation is the preparation of a standard metallurgical microsection which can be viewed with a high power microscope fitted with a calibrated micrometer eyepiece, or which is equipped with a projection screen on which direct measurements at a known magnification can be made. It remains the sole reference method for thicknesses greater than **AA5** in British Standard 1615, as it is in EN 12373-1, because it does not require a knowledge of density or refractive index, and on the principle that seeing is believing. It is destructive, very time consuming, allows only a small portion of the surface to be examined, and requires some skill and experience because of the tendency for the edge of the coating to bevel or chip. In fact, in inexperienced hands it can be less certain than the eddy current method.

The method is covered in EN ISO 1463 (formerly BS 5411: Part 5), but some special precautions are needed with anodized aluminium. Guidance has been provided by the British Non-ferrous Metals Research Association as follows:

'Sections should be cut using a fine jeweller's saw to avoid deformation and burring of cut edges. The cut edges of anodic coatings require support to retain a true profile during polishing and for ease of differentiation between coating and mounting medium. This may be achieved in a variety of ways, the following method being recommended.

'The anodized surface of the specimen should be tightly wrapped with a single layer of smooth aluminium foil and folded at one end to retain in place. The wrapped specimen is mounted using a suitable thermosetting resin. Fine particles of resin powder should be first packed around the specimen to ensure the complete filling of voids and the press finally filled using the coarser resin particles. The anodized specimen should be perpendicular to the face of the completed mount, a deviation of 10° introducing, however, only an error of 2% in the thickness. After mounting the specimen must be free from voids between the section and the mounting medium.

'Mounted specimens are ground on emery paper using water or white spirit lubrication, and the minimum pressure applied to avoid bevelling of the surface. Initial grinding should employ 100 or 180 grade emery to reveal the true specimen profile and remove any deformed areas. Subsequently grades 240, 320, P500, and P800 should be used without exceeding 30-40 seconds grinding on each paper, and altering the direction of grinding by 90° for each change of paper. A final polish for 2-3 minutes on a rotating wheel charged with 4-8 μm diamond paste particles and white spirit lubrication should suffice to remove emery scratches for final examination. Where a specially high degree of finish is required a further treatment using up to 1 ym paste may be employed.

'Where very soft aluminium substrates are being prepared emery particles may become embedded during grinding. This may be minimised by totally immersing emery papers in lubricant during grinding or by using a copious flow of lubricant. If emery particles do become embedded they may be removed by applying a short, light hand polish with metal polish after grinding and before diamond finishing.'

The most convenient microscope magnification for viewing the section is 1000 because 1 mm on the screen is then equal to 1 micron film thickness. The accuracy with which the coating can be measured is generally about ± 0.5 ym, and the average of several determinations is taken.

It should be noted in passing that most other methods of film thickness determination are calibrated by means of standards which have, or should have, been measured by microsection. They cannot therefore be any better in absolute accuracy than the microsection method, and determinations of density are subject to a proportionate error which obviously becomes greater when applied to thinner films. The most accurate calibrations require the techniques of interferometry and expensive equipment.

The method of wrapping the sample in foil is to an extent a matter of personal preference. Some operators obtain better results with a normal mounting technique which seems to be a question of selecting the correct resin and using rather a high temperature in the mounting press. Casting in type metal has also been a technique employed. Calabra[47] has suggested that the addition of pelletised aluminium oxide filler to the mounting medium makes for excellent edge retention when preparing metallographic specimens.

The microsectioning technique is also described in the A.S.T.M. Standard B 487-85 (1990), in BS 5411: Part 5: 1984 and in EN JSO 1463.

Gravimetric determination[48,49]

Strictly speaking this is a method for determining the total weight of the coating over an area, from which the average thickness is calculated by assuming a value for the density. The test piece must be cut from the sample and after carefully cleaning off any organic material by tneans of a solvent it is weighed on a chemical balance and the coating then stripped in a boiling solution containing:

o-phosphoric acid (d. 1.75) 35 ml/l (or 70 ml/l)
chromic anhydride, CrO_3 (A.R. quality) 20 g/l (or 40 g/l)

The coating is removed very quickly, often in a minute or so, but up to 10 minutes may be allowed for very thick coatings. After washing, drying and reweighing, the difference gives the weight of coating W in milligrams from which the thickness is calculated using the formula:

$$T = \frac{10W}{a.d} \text{ microns} = \frac{0.39W}{a.d} \text{ mils}$$

where a is the total area of the surface in cm^2 and d is the density. According to most standards the latter is now taken to be 2.4 for unsealed coatings and 2.6 for sealed coatings. (Variations in density are discussed on page 964). The method is described in EN ISO 2106, EN 12373-2: 1999 and BS 6161: Part 1: 1984, as well as in ASTM B 137-95.

This is a very simple method which can usually be carried out quickly, but there are a number of points to be noted. The sample size should exceed $1000\mu m^2$ if possible for the greatest accuracy, and it is frequently necessary to remove the coating from the non-significant surface first. This can be done by masking the top surface with adhesive PVC tape (electrician's tape) and dissolving the coating from the reverse side, desmutting and drying; any adhesive remaining after removing the tape should be carefully wiped off with solvent. Sometimes it is convenient to grind the reverse side. The stripping solution must be contained in a glass or stainless steel vessel, and it is important that the aluminium should not contact the steel, nor must it be suspended in the tank by a wire or jig of any other metal. Any dissolved heavy metals will lead to attack on the aluminium.

The active agent is the phosphoric acid, and the chromic acid prevents attack of the aluminium substrate. The ratio of these acids is therefore important, but mixtures containing very much more chromic acid have been proposed, e.g., 200 g/l chromic acid and 20 ml per litre of phosphoric acid.[48] Alloys which are high in magnesium, copper or zinc are slowly attacked by the stripping solution and care must be taken especially when trying to determine very thin coatings; in these cases Scott has recommended replacing part of the phosphoric acid with boric acid to give:

o-phosphoric acid	40 ml/l
boric acid	30 g/l
chromic acid	40 g/l

The gravimetric method is applicable to all anodic coatings and in BS 1615: 1987 and EN 12373-1 it serves as a referee method for coatings thinner than AA5 (5 microns), but the microsection method is still the reference test for thicker grades.

Dial gauge method

In a method describedby Kutzelnigg,[50] the oxide coating is penetrated by a zincate solution prepared by dissolving 260 g sodium hydroxide in 750 ml water, adding 50 g zinc oxide and making up to 1 litre. In this test the specimen is firmly located on the instrument shown in Fig. 12-9. A drop of the zincate solution is applied, and when the end point is observed by the appearance of a grey-black spot the thickness is read off on the dial. On coloured coatings the end point is observed through a lens. The wire contact (e in Fig. 12-9) can also be used to determine the end point of thicker coatings. The method is based on one used by Müller[51] for determining zinc or cadmium coatings on steel. In the case of aluminium the deposition of a thin layer of zinc prevents attack of the basis metal after the coating has been removed.

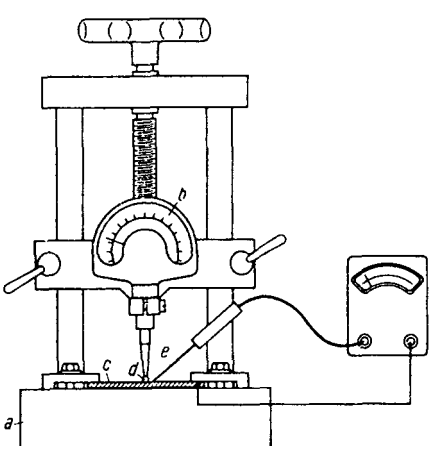


Fig. 12-9. Diagram of dissolution test instrument

a	Foot	c	Panel		
b	Measuring dial	d	Probe	e	Wire contact

By loss of thickness on stripping

Stalzer[52] successfully measured the thickness of hard anodic oxide coatings by cathodic stripping in the anodizing bath itself at 20 A/dm^2 (200 amp/sq ft) and 4 volts. A similar direct measurement can also be made after removing the coating in the stripping solutions described in the gravimetric method.

In these stripping methods, the film is destroyed but the basis metal may generally be anodized again, though this naturally applies only where the shape of the work is such that the surface area may be determined without deformation.

By dissolution of the metal

(a) An early technique was developed by Wernick.[53] It consisted in first abrading the oxide film at a suitable point and treating this with mercury. The sample was then placed in a solution of mercuric chloride, resulting in the continuous dissolution of the aluminium. The oxide coating was thereby released in the form of small flakes which were retrieved, dried and examined. Thickness could be measured directly (Figs. 12-10 and 12-11).

(b) The following method was developed by W. Treadwell and A. Obrist[54] and was claimed to give a high degree of accuracy. A sample of sheet 1 cm square and 0.6 mm thick is anodized and placed on a platinum gauze approximately 1 cm above the bottom of a small beaker. The vessel is filled half full with dried ether and is kept cold in running water; it is fitted with a tightly-fitting glass lid through which a tube is led which reaches down to about 1 cm over the specimen and a condenser is fitted around the exit tube. Completely dry hydrochloric acid gas is led into the ether at the rate of 1 to 2 bubbles a second. The excess gas then escapes through the condenser, which holds the ether. The sheet is dissolved in 3-4 hours and the oxide film is taken out and washed in ether. The thickness is measured by micrometer and may, if desired, be subjected to chemical analysis or to X-ray or electron diffraction.

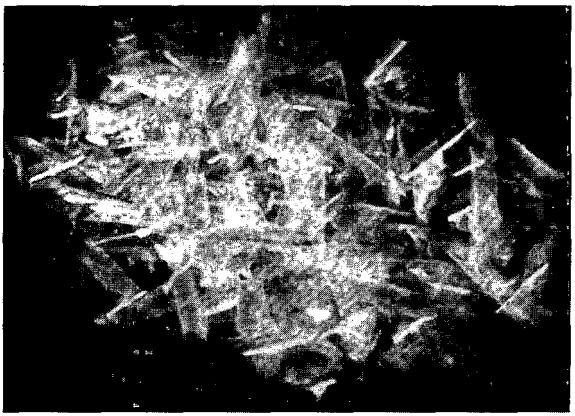
(c) Anodic films may also be isolated by dissolving the aluminium in a 10% w/v solution of iodine in absolute methyl alcohol at *50°C*. In the case of alloys containing more than 1% copper, 3% sulphosalicyclic acid ($C_7H_6O_6.2H_2O$) is added.[55]

(d) Unsealed anodic coatings can also be detached by anodic treatment in a solution containing:[56]

perchloric acid (70%)	1 pt (vol)
methanol	5 pt (vol)

at 50-65 volts and 21°C for 1-4 seconds using an aluminium cathode. For sealed films this method is not so suitable, although a solution containing 4.5% perchloric acid, 77.5% methanol and 18% water is fairly successful.

Fig. 12-10. Method of detaching oxide film (mercuric method).[53]
Fig. 12-11 (below) Detached film



(e) Other stripping solutions which have been suggested include bromine in methyl alcohol and a sulphuric acid solution containing antimony.

(f) Thomas[57] has also suggested an electrolytic stripping method based on an a.c. anodizing treatment after normal anodizing. He reduced the voltage progressively under a.c. conditions to about 4 volts and switching off the power supply at that stage, and allowing a short period for chemical dissolution, completely detached the film.

Determination of barrier films

The thickness determination of barrier type coatings, or barrier layers beneath porous coatings, presents special problems because of their extreme thinness

amounting to only 14 Å (0.014 μm) per volt. True barrier films formed in neutral electrolytes can be determined by a capacity measurement made in the forming electrolyte simply by connecting the cell to a capacitance bridge and using the formula:

$$C = \frac{8.84KA}{10^3 d} \text{ microfarads}$$

where K is the dielectric constant of the oxide (about 8.5), **A** is the area of the sample and d is the thickness of the film. This method demonstrates the accurate linear relation between film thickness and forming voltage. It cannot be applied so simply to barrier layers of porous type films formed in the usual anodizing electrolytes because their behaviour cannot be equated with a capacity and resistance in parallel.

Hunter and Fowle[58] have measured barrier layers of both types by the simple technique outlined on page 333, which in effect is to continue the anodizing treatment from where it was terminated, noting carefully the current-voltage curve to see where the current begins to increase rapidly. The voltage at which this occurs is related to the barrier thickness by the well-known ratio 14 Å/volt, and since the voltage can be determined to ± 0.1 volts, the barrier thickness will be known to about 3 Å. By subtracting this from the total film thickness determined by another method the thickness of both parts of the coating is then known.

There are still problems however where the porous coating itself is too thin for any method other than interferometry, the apparatus for which is not generally available, and Hunter and Towner[59] have extended their technique to cover this situation, so that films which are little thicker than the natural oxide film on aluminium can be evaluated. The film is stripped from a part of the specimen with chromic acid/phosphoric acid stripping solution and a barrier film is applied to the whole specimen of sufficient thickness to produce interference colours. By comparison with known standards the thickness of film on both areas can be determined, and since the applied coating is a function of the voltage, by subtracting this from the combined coating the original porous film thickness is obtained. An electrolyte suitable for applying the barrier film is 3% oxalic acid adjusted to a pH of 5.5 with ammonia.

Ellipsometry is a useful technique with such thin films, and Alcan are using it for production control with their coil electrolytic cleaning line in Nachterstedt, Germany.[60]

3. POROSITY

There are semantic problems associated with applying the concept of porosity to anodic oxide coatings because we are dealing with a material whose nature is inherently porous, while at the same time superimposing on this a secondary

concept borrowed from the terminology of electrodeposits, which is related more to discontinuities in an essentially homogeneous medium. These two properties are sometimes distinguished by referring to them as micro- and macroporosity, but this is not altogether unambiguous because the microporosity is on a scale far below the reach of any microscope and can only be imperfectly seen at magnifications approaching 100,000 with an electron microscope, while macroporosity can be associated with a number of factors, including intermetallic constituents, which are of truly microscopic dimensions.

The porosity which is part and parcel of the inherent structure of anodic coatings formed in acid electrolytes has been discussed in considerable detail in Chapter 6, where it **is** shown to arise from dissolution of the coating in the electrolyte so that continuous film formation becomes possible, and the dimensions of these pores are a function of the electrolyte, the operating conditions and the thickness of the coating. The nature and magnitude of this porosity is important because it affects the resistance to abrasion, to corrosion, the ease with which a coating may be dyed or otherwise impregnated, and the efficiency with which it can be sealed. In very thin anodic coatings the pores can be produced to an extremely uniform size, e.g. to within ± 10% and much of our knowledge of pore structure has come from observation of such films, while in practice they have been used for the filtration of gaseous colloids or colloidal suspensions[61] and as porous membrances (see Chapter 7). It has also been shown that microporosity can be influenced by the texture of the metal surface,[62] decreasing with the smoothness of the surface, and being less in electropolished surfaces than in mechanically polished surfaces after anodizing.

While microporosity is closely linked with the physical properties of the coating as noted above, the continuity or macro-scale features are related to corresponding features or faults in the basis metal, or to extreme operating conditions, and these may be detrimental to appearance or corrosion resistance. These will be discussed later.

Quantitative tests

The quantitative estimation of porosity will vary to an extent with the method of definition or test because the dimensions involved are such that they will admit some molecules and not others so that gaseous absorption or theoretical calculation of the void space may not correspond with what can be absorbed in the nature of a solid pigment.

Lead acetate absorption

A number of methods have been devised which are based on impregnation of the anodic coating. One such test was described by Kubaschewski and von Krusenstjern[63] in which the specimen is anodized, dipped for 10 minutes in

distilled water in order to remove traces of electrolyte, dried at 110°C for 30 minutes, and weighed. Subsequently the specimen is immersed for 2 hours in lead acetate solution, again washed in distilled water, dried and re-weighed. The gain in weight caused by impregnation with lead acetate is then determined and the porosity calculated.

Oil absorption

Reliable results can be obtained in such methods if the anodic coating is separated from the basis metal and weighed. In a method described by Tomashov and Byalobcheski[64] the pores are impregnated with light oil at 150°C, the specimens are cooled in the oil and the excess wiped off. Subsequently the oil is extracted with acetone and weighed and the oxide film dissolved in a solution containing:

phosphoric acid (d. 1 SO)	45 g
chromic acid	45 g
water	1 litre

at 93°C. The porosity can then be calculated from the volume of the coating and the weight of the oil absorbed. The percentage porosity is:

$$P = \frac{W_0 \times 10^6}{d_0 \times T \times A}$$

where W_0 is the weight of the absorbed oil in g, d_0 is the density, T the coating thickness in μm and A the area of the oxide in cm^2.

Gas absorption

The absorption of gases at very low temperature is a function of the accessible surface area rather than the volume of porosity, but the latter may be calculated. Cosgrove[65] measured the uptake of n-butane at 0°C and of krypton gas at –195.8°C to determini: the surface area, pore volume and pore diameter of coatings formed in sulphuric chromic and oxalic acids, applying the Brunauer, Emmett and Teller equation[66] which, on the assumption of complete wetting, gives the pore radius as:

$$r\,(\text{Å}) = -6.30/\log p/p_0 \text{ for krypton}$$

and

$$r\,(\text{Å}) = -5.42/\log p/p_0 \text{ for n-butane}$$

where p is the equilibrium pressure and p_0 is the saturation pressure. Results on sulphuric acid films anodized for up to 30 minutes were in fair agreement with other methods, but for thicker films or pore diameters greater than 160 Å krypton sorption gave results inconsistent with n-butane sorption because of pores not completely filled, but there was better agreement by using solid rather than extrapolated liquid vapour pressures for krypton calculations.

Toluene absorption (Real density)

Mason[67] calculated the pore volume by immersing coatings in toluene and using Archimedes principle to measure the real density as opposed to the apparent density. With unsealed coatings formed on 99% aluminium in sulphuric acid he found a density of 2.96 which corresponded to a pore volume of 15.8%, while after sealing the real density became 2.65. Using 2024-T6 alloy (4.5% Cu, 1.5% Mg) he calculated a pore volume of 47%. In an oxalic acid electrolyte there was very little change in real density with rise in anodizing temperature and only a slight increase in porosity, which is different from sulphuric acid where the role of temperature **is** very important.

This was also done by Miyata *et al.*[68] using transformer oil as a medium, measuring both the real density and the dielectric constant (see below).

Schenkel and Speiser[69] used a simple form of this type of test when evaluating the porosity of anodic coatings used for dyeing. They measured porosity in terms of the volume of pores compared to the volume of the total film by gravimetric determination of the increase in weight after filling the pores with polyethylene glycol. A cloth impregnated with 'polyglycol 200' was rubbed over the surface of the film and excess removed afterwards with a dry cloth.

Electrolytic pore-filling method

Dekker and Middelhoek[70] developed an electrochemical method of determining porosity by filling the pores with a barrier oxide. After anodizing a specimen in a normal acid electrolyte, they reanodized it in a neutral borate-glycol solution at a constant current density and recorded the variations in cell voltage with time. They suggested that the pores of the porous layer were gradually filled with non-porous oxide and that the increase in applied voltage directly reflected the increase in barrier layer thickness. They then estimated a value for porosity of the original film from an analysis of the voltage-time curve.

The method was further investigated by Takahashi and Nagayama[71] who found that the borate-glycol solution was not ideal, because of anodic decomposition of glycol. They used a boric acid-sodium borate solution, and using thin films produced in an oxalic acid electrolyte, estimated porosity of about 22%.

These pore filling techniques have been used by many research workers, particularly in the basic study of anodizing mechanisms, and are referred to in Chapter 6.

Refractive index

In an ingenious piece of analysis and experimentation Huber[72] made a calculation of the pore volume of anodic oxide coatings by starting from a proposition due to Wiener[73] that a mixed body consisting of parallel cylinders of isotropic material of refractive index n_1 penetrating through the whole thickness of

another material of refractive index n, will behave as a uniaxial positive crystal if the structure element!; are smaller than the wavelength of light, and in particular will exhibit double refraction where:

$$n\varepsilon - n\omega = \frac{\delta_1 \delta_2 (n_1^2 - n_2^2)}{(\delta_1 + 1)n_2^2 + \delta_2 n_1^2}$$

$$\delta_1 + \delta_2 = 1$$

The double refraction $n\varepsilon - n\omega$ will depend on the volume fractions 6, and 6, of the components. Using thick coatings prepared in oxalic acid, Huber detached wedge shaped fragments and, by viewing these in polarized light in a direction parallel to the plane of the film, he was not only able to measure the refractive indices, but also to do this at various points through the thickness by means of the differential birefringence of the prismatic fragment. His results indicated a pore volume of4.3-4.4% adjacent to the aluminium, increasing to 15.5-16.9% near the electrolyte side.

Dielectric constant

Miyata, Isawa, Furuichi and Takamura[68] estimated the porosity of coatings formed in sulphuric acid by making measurements of the apparent density and the apparent dielectric constant and then assuming values for the real density and the real dielectric constant, which they took to be 2.95 and 8.7 respectively. They found that the porosity of oxide formed in 15% sulphuric acid at 4 A/dm^2 and 30°C for 30 minutes was 24-26%, while the porosity of a film formed at l"C was 10-14%. When aluminium was anodized at more than 20°C there was a rapid increase in porosity. Their investigations covered temperatures from 1 to 30°C and current densities from 2 to 4 A/dm^2. They also confirmed their results by measuring the amount of transformer oil which could be absorbed by the unsealed coating.

Electron micrograph method

An interesting method for determining microporosity was used by Keller, Hunter and Robinson[74] in their work on the mechanism of coating formation. These authors showed on theoretical grounds that each micropore formed the centre of an oxide cell and confirmed this by comparing cell base patterns obtained by the electron microscope using polystyrene impressions and silica replicas of cross-sections of the anodic coating, with the pore pattern obtained under identical conditions of anodic oxidation by examining the coating itself by transmission in the electron microscope. The overall cell size can be measured directly from micrographs of the cell base pattern and, as seen on page 360, a linear relation exists between cell size and forming voltage.

Assuming that the pore diameter remains constant, its value is given by the amount by which the plot of cell size against voltage is transposed from the origin, i.e., in the condition represented in Fig. 6-26 (page 360).

The pore diameters of coating obtained in phosphoric acid, oxalic acid, chromic acid and sulphuric acid were 330, 170, 240 and 120 Å respectively. The pore value can then be calculated from the relation:

$$V = 78.5 \frac{p^2}{c^2}$$

where V is the pore volume in %, p is the pore diameter and c the cell size.

The pore volumes obtained by this technique are lower than the true values as they do not take into account the widening of the pores by solvent action in the surface layer.

Permeability

Allied to porosity, of course, is the question of permeability of the porous fraction of the coating, and this has been less frequently examined because of experimental difficulties. Burwell and May[75] studied the osmosis of 0.2M sucrose at 25°C through chromic acid coatings by using completely oxidized foil which was allowed to stand in chromic acid for periods of 22 and 76 minutes after the termination of anodizing. Their results are shown in Fig. 12-12.

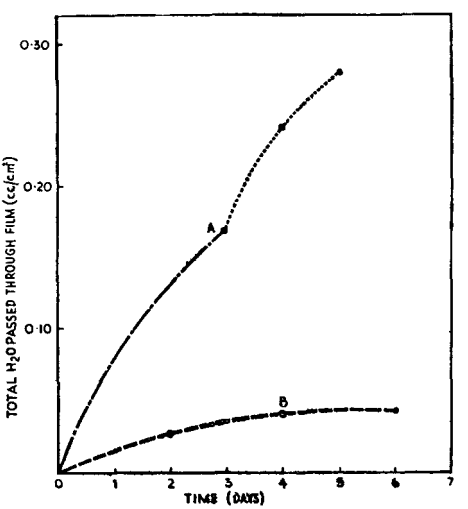


Fig. 12-12. Permeability of chromic acid-anodized coatings. Osmosis in 0.2M sucrose at 25°C. A and B are curves for completely-oxidized Al foil remaining 76 and 22 minutes respectively in the anodizing bath after electrolysis was complete[71]

Continuity of coating

It is frequently important to make some assessment of the continuity of the anodic coating or to have some method which will readily indicate minute bare spots. This can also be regarded as a test of the macro-porosity. The coating can always be expected to be homogeneous and continuous when formed on high purity aluminium, but in the case of commercial purities, or alloys which contain other metals or intermetallics which respond differently to anodizing, the coating will contain many microscopic areas containing oxides of other metals and voids where highly soluble materials were present or metals such as silicon remain unchanged. While the coating will frequently engulf such discontinuities, in the case of large particles in thin films or coarse segregates, there can be paths of low resistance or points of weakness in the coating. In addition there may be discontinuities associated with foreign inclusions, with mechanical damage especially on rough surfaces where asperities which are difficult to coat anyway can be easily abraded, with mechanical or thermal stresses, with corrosion or with faulty anodizing.

One method suggested by Fischer[15] for assessing the extent of defects in the coating depends on using an acid solution containing a copper salt which will deposit copper when it can come into contact with the bare metal. The solution contains:

acetic acid	6%
copper sulphate	0.1-0.5%
zinc chloride	1.5%

The pores are shown after a few minutes by red-brown spots of copper. The larger ones appear first, while small micropores appear later. The process can be accelerated by replacing the acetic acid by 0.5% hydrochloric acid. International Standards (ISO 2085: 1976 and EN 12373-16:2000) describe this general method of test. These methods use a solution of 20 g/l copper sulphate and 20 ml/l of hydrochloric acid at 20 ± 5°C for 5 minutes, and are only applicable to anodic coatings of less than 5 microns.

An electrographic method which gave somewhat similar results was also developed by Fischer. Here, the anodized specimen, which should be perfectly flat, was covered with a filter paper impregnated with barium chloride solution and phenolphthalein. On top of the paper a copper sheet was placed and a current was passed, the aluminium being the cathode and the copper the anode. Wherever the current passed through pores in the oxide coating, the filter paper became coloured due to the alkaline reaction products formed. In practice, however, it was found[62] that the number of 'pores' made visible by the method increased with time, due probably to the fact that the electric current itself creates pores. Again only macropores were revealed.

Macroporosity can be determined by salt spray or other corrosion tests (see below) or, alternatively, by making the sample anodic in a solution containing

0.25% sodium alizarin sulphonate and 10% hexamethylene tetramine, $(CH_2)_6N_4$, for 40 seconds at 13.5 volts using aluminium cathodes. If the coating is sound, no current will flow; at defective places current flows and decomposes the electrolyte causing a red deposit.[76]

Electrophoretic test

An electrophoretic test for showing up macropores was developed in Germany.[77] Called the Duffek Porosity Tester, it used colloidal solutions of organic dyestuffs which migrate electrophoretically to the anode under the influence of an electric current. If the anodized aluminium was made anodic, the dyestuffs were precipitated at defect sites, showing up their location.

4. ADHESION

The adhesion of the oxide coating is normally much better than that of electrodeposits, but the film tends to be weak vertically to the surface, i.e., the film is apt to crack transversely to the direction of rolling. When bent, the coating cracks in parallel lines but will not strip as electrodeposits do. Film adhesion can be affected in electrolytic colouring processes, though this is usually on a very localised rather than a general basis. Incorrect electrolytic colouring conditions can lead to localised spalling of the film and this has been described in Chapter 8 (page 711).

As the coating is an integral part of the surface, no adhesion test is used for anodized aluminium in normal circumstances.

5. HARDNESS AND ABRASION RESISTANCE

The oxide film itself is very hard but is generally too thin to increase the effective hardness of the metal itself. It will not protect the metal from strong pressure though it will resist surface scratches and thus protects the appearance and reflectivity of a polished surface.

In general, the hardness of a coating is increased by decrease in temperature of the electrolyte and in acid concentration, or the use of less 'aggressive' electrolytes, by increase in the homogeneity of the alloy structure, and by increase in current density. In addition, d.c. coatings are rather harder than coatings produced by a.c.

The hardness of the film varies throughout its depth and is inversely proportional to the porosity; thus it is softer in the surface layers due to the solubility of the film in the electrolyte and to hydration of the outer layers of the coating. In extremes of operating conditions, i.e., when the temperature, acid concentration or current density are too high, the outer layers may become powdery or spongy as the

solubility of the film in the electrolyte increases. This fault is therefore avoided by adjusting the operating conditions.

Sealing has been shown to decrease the abrasion resistance of hard anodic coatings to 50-70% of the unsealed value and to even less on some alloys, e.g., 2024. To a lesser extent the effect of ageing, which causes slow hydration, also reduces abrasion resistance (Chapter 11).

Hardness tests

The usual methods of determining hardness, i.e., Brinell, Vickers, etc., are not applicable to anodic coatings as they give the hardness of the basis metal. Nor is the Rockwell scratch method or the method developed by Martens, who used a diamond point, entirely satisfactory. In these methods the object is moved horizontally against the weighted point and the hardness calculated from the width of the scratch. The results obtained are only approximate and do not take into account variations in hardness of the basis metal or variations occurring throughout the coating itself.

Various modifications of this process have been developed and interesting comparative results obtained for the different anodizing processes on the same basis metal. In this way Fischer[15] determined the hardness of the standard Eloxal coatings on an aluminium-magnesium-zinc alloy (Table 12-7).

TABLE 12-7

Hardness, and abrasion resistance of Eloxal coatings[15]

*Process**	*Thickness*		*Hardness*		*Abrasion resistance (double movements)*	*Hardness/ thickness (kg/μm)*	*Specific abrasion resistance (h)(double movements/μm)*
	(μm)	*(mil)*	*(kg)*	*(lb)†*			
GX	35.3	1.4	105	231	400,000	2.9	12,500
GXh	29.0	1.2	41	90	300,000	1.4	10,300
GS	14.7	0.6	38	84	85,000	2.6	5,800
WGh	14.7	0.6	14.5	32	57,000	1.0	3,900
WX	5.9	0.2	5.2	11	4,000	0.9	600

* For explanation of Eloxal designations, see p. 428.

† The hardness is given in terms of kg (lb) wt required to make a scratch penetrating the film.

Although conventional hardness testing is unsatisfactory on anodized surfaces for indicating the properties of the coating, it is possible to carry out microindentation tests on cross sections of the coatings which have been mounted

in resins and polished by metallographic techniques. The load applied to the diamond indenter in such tests is generally very low and may be as little as 50 or 15 g, the impression being measured at relatively high magnification. By this method it is possible to test the hardness at various positions through the depth of the coating, and it can be shown that under normal anodizing conditions in sulphuric acid there is an appreciable drop in hardness from about 350 kp/mm^2 at the metal surface to about 100 kp/mm^2 at the outer surface. Results obtained by Sautter[78] have been given on page 790, which show the effects of anodizing temperature, and that under hard anodizing conditions the coating is of practically uniform hardness through the thickness. Results by Oechslin using loads of 15 and 50 g on hard anodized coatings on various alloys have been referred to on pp. 751 and 783. Campbell" has pointed out that these hardness measurements are a fallible guide to the performance of the coating in service which is frequently much better than they would seem to forecast. The method of carrying out microhardness tests on coatings is described in EN ISO 4516 and BS 5411: Part 6: 1981.

Workers in Japan[80] have developed a scratch test for anodized aluminium and this uses a loaded sapphire pin. It is again most suitable for testing thick, hard films, as with thin films the metal substrate is penetrated.

Abrasion resistance tests

An early method[76] for determining abrasion resistance obtained values which were almost independent of the basis metal. In this method, the work was moved to and fro under a hard metal pointer which pressed on it with a constant load (300 g). When the film was penetrated, an electric relay circuit was closed, stopping the motor operating the device. The number of double movements (H) was then taken as the abrasion resistance, though the specific abrasion resistance (h) was the better comparative value, where h = H/d (d is the thickness of the film in microns).

The specific abrasion resistance tends to increase with anodizing time, though here too there is a maximum value when the limiting film thickness is reached. These authors also investigated the effect of alloy on abrasion resistance with both d.c. and a.c. sulphuric and oxalic acid anodizing electrolytes. In general, the maximum abrasion resistance was obtained on pure aluminium and AI-Mg alloys. Oxalic acid electrolytes produced more abrasion resistant films than sulphuric acid, and the a.c. films were softer than the d.c. films.

Campbell[79] has described an instrument for non-destructive testing of the scratch resistance of hard anodic oxide coatings. This consists of a diamond stylus with a 1 mil (25 ym) radius and a load of 70 g which traverses a small area of about 0.01 **sq** inch (6.5 mm^2) until it raises debris at the ends of the area. The shadow of the debris, as shown by a lamp set at a low angle, is used as a measure of the wear resistance. With this instrument, Campbell found that the hard anodic oxide coating performs particularly well at low loadings, and under light conditions

metals with high hardness values will show more wear when in contact with hard anodized aluminium.

Another method for determining the abrasion resistance of anodic coatings consists in blasting the surface using a fine abrasive powder (silicon carbide No. 180, carborundum or alundum 190) by means of compressed air under controlled constant pressure. The pressure controls the blasting velocity and is varied to suit the specific experiment. The end point of one such method[81] is when a surface of 2mm diameter is worn through. The end point can also be given by electrical contact, a metallic spring pointer being used to close the circuit when the metal is exposed. Besides pressure and powder size, the diameter of the mouth of the blasting tube and humidity and temperature should all be controlled.

The analogous British Standard method (see below) has been developed from an apparatus by Schuh and Kern[82] with an abrasive flow (carborundum or alundum of 150 mesh) of 50-60 grammes per minute, and bases its results on the weight used until visual inspection shows breakthrough of the film and formation of a black spot. This test is a measure of the internal cohesion of the coating which is a function of both its hardness and thickness. Using this method on 1200 (commercial Al) and 5454 (Al-Mg 1, Arit[81] showed that, as compared with the scratch methods, little difference in the specific abrasion resistance was found with variation of coating thickness. Appreciable differences were found in the abrasion resistance of coatings sealed by various processes, the abrasion resistance in general decreasing with the degree of hydration of the anodic coating, i.e., with the efficiency of sealing (see Fig. 12-13), but these coatings were formed at what would now be considered **an** undesirably high temperature.

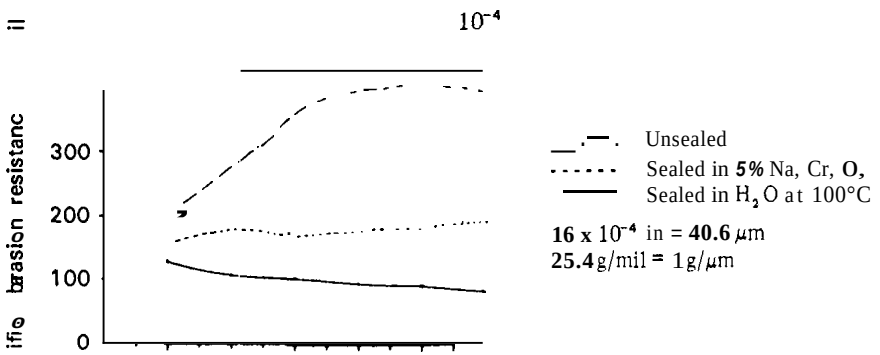


Fig. 12-13. Effect of sealing and anodizing time on the abrasion resistance of sulphuric acid coatings formed in 10% H_2SO_4, 1.5 A/dm². 35°C, on aluminium[81]

This method has been used with success for the determination of the abrasion resistance of anodic films obtained under various operating conditions[83] and also of hard anodized components, results of which have been given in Chapter 9.

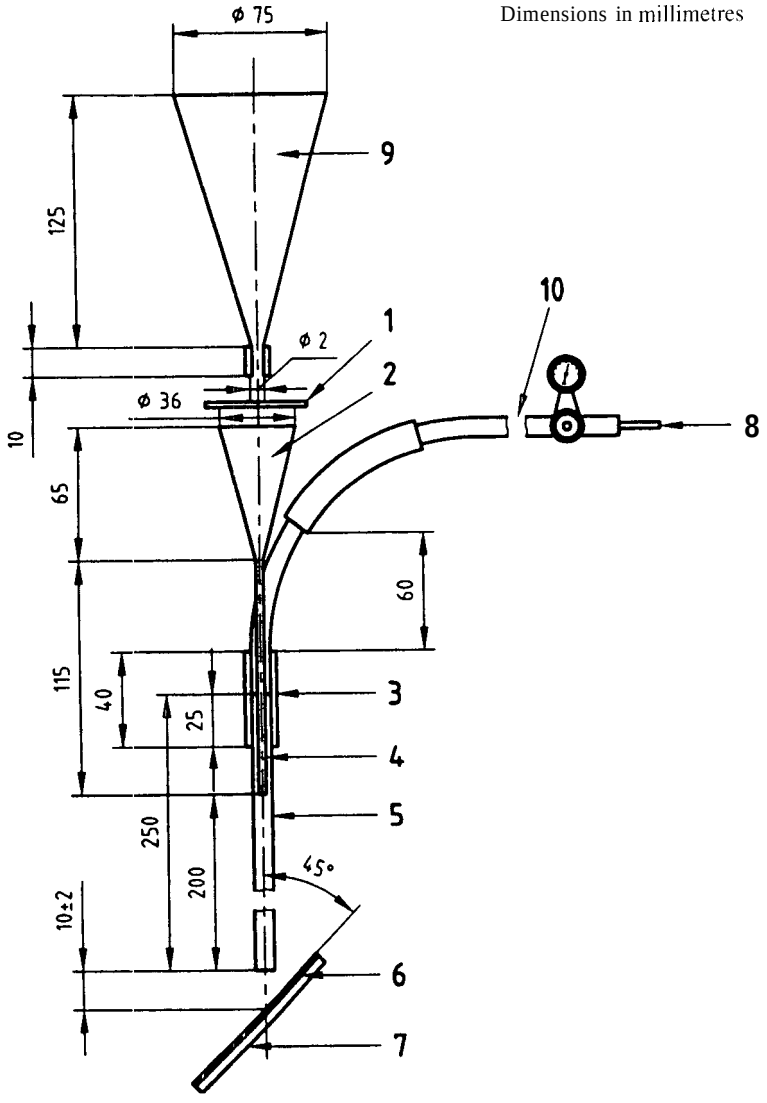
Apparatus of this type has not in general been commercially available, though equipment constructed along these lines became available in the U.K.[84] and Japan.[85] This method for determining abrasion resistance has, however, appeared in a number of national standards, such as BS 6161: Part 10, and now internationally as ISO 8252: 1987 and EN 12373-10: 1999.

Abrasive jet tests

The abrasive jet method originally proposed by Schuh and Kern[82] in 1931 was adopted in the first edition of the British Standard 1615 in 1949. Modifications introduced into the 1958 edition were made by Thomas, and in the 1961 edition the jet assembly was completely redesigned on the basis of work carried out by J. Edwards[86] at the British Non-Ferrous Metals Research Association. Nevertheless, it was still emphasised that different users could obtain widely varying results and that no two versions of the apparatus would necessarily agree, but that it could enable an accurate comparison to be made between any two samples tested under identical conditions. It remained a comparative test because it was not possible to prescribe with any confidence a method for obtaining a standard sample. Much of the uncertainty concerning the test was due to the fact that it had been so little used and the sources of variability did not become apparent until the apparatus had been used consistently over long periods. The design by Edwards, with slight modifications in procedure resulting from the work of Harris,[87] is still the basis of the international test.

Alternative designs of the apparatus and jet assembly are shown in Figs. 12-14, 12-15 and 12-16, the first being the British design and Figs. 12-15 and 12-16 being the designs used in Japan. The general arrangement of the apparatus is shown in Figs. 12-14 and 12-15. The abrasive hopper is designed to deliver abrasive at a rate of 20-30 g per minute, which falls through the central tube, is picked up by the air stream and accelerated along the very important mixing length to impinge on the specimen which is held rigidly at an angle of 45" to the jet. The jet is clamped with the abrasive hopper directly above it in a cabinet designed to contain the used abrasive while providing support for the specimen in such a position that it can be observed during testing. The side tube of the jet is connected to a supply of compressed air through a valve, a drying tube containing silica gel, and a flow-meter of range 10-100 litres of air per minute.

The abrasive powder is silicon carbide of 120 micron mesh size (ISO 565: 1990), free from moisture and passed through a coarse sieve to ensure freedom from any large particles or fibres which would interfere with the rate of flow. The use of dry abrasive is very important, and the European Standard requires drying at 105°C in a shallow tray before use. The air must also be dried.

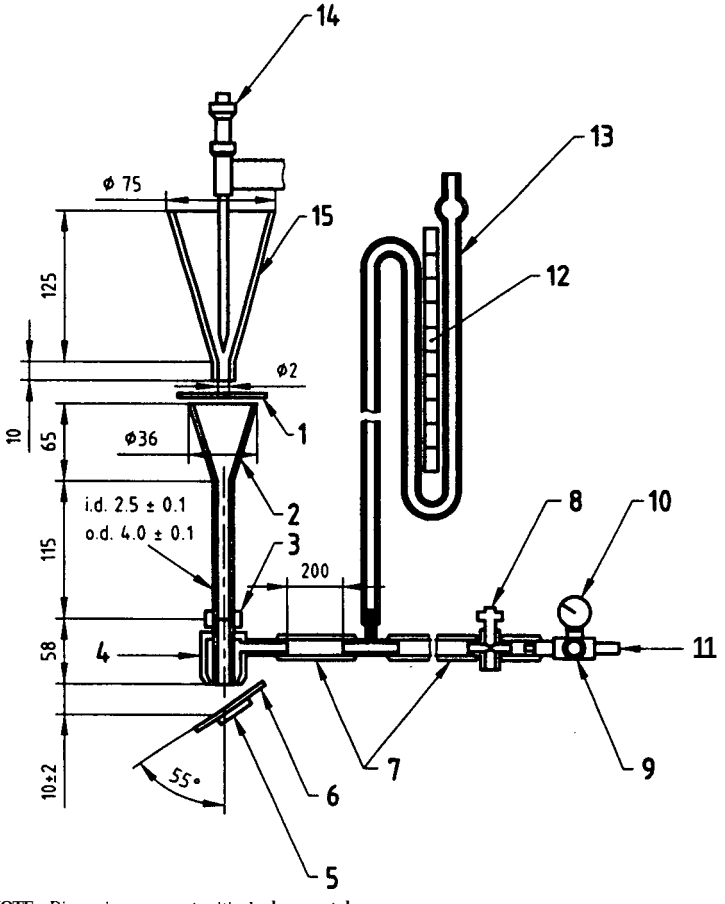


NOTE Dimensions are not critical where no tolerances are given

1 Shutter
2 Funnel
3 Metal collar
4 Inner tube
i.d. 2.5 ± 0.2
o.d. 4.0 ± 0.2
5 Outer tube (push fit into metal collar)
i.d. 6.5 f 0.1
o.d. 8.5 minimum
6 Test specimen
7 Sample supporting stage
8 Air or inert gas supply
9 Hopper for abrasive powder
10 Manometer or gas flow meter (not shown)

Fig. 12-14. General layout of alternative abrasive jet test apparatus[88]

Dimensions in millimetres

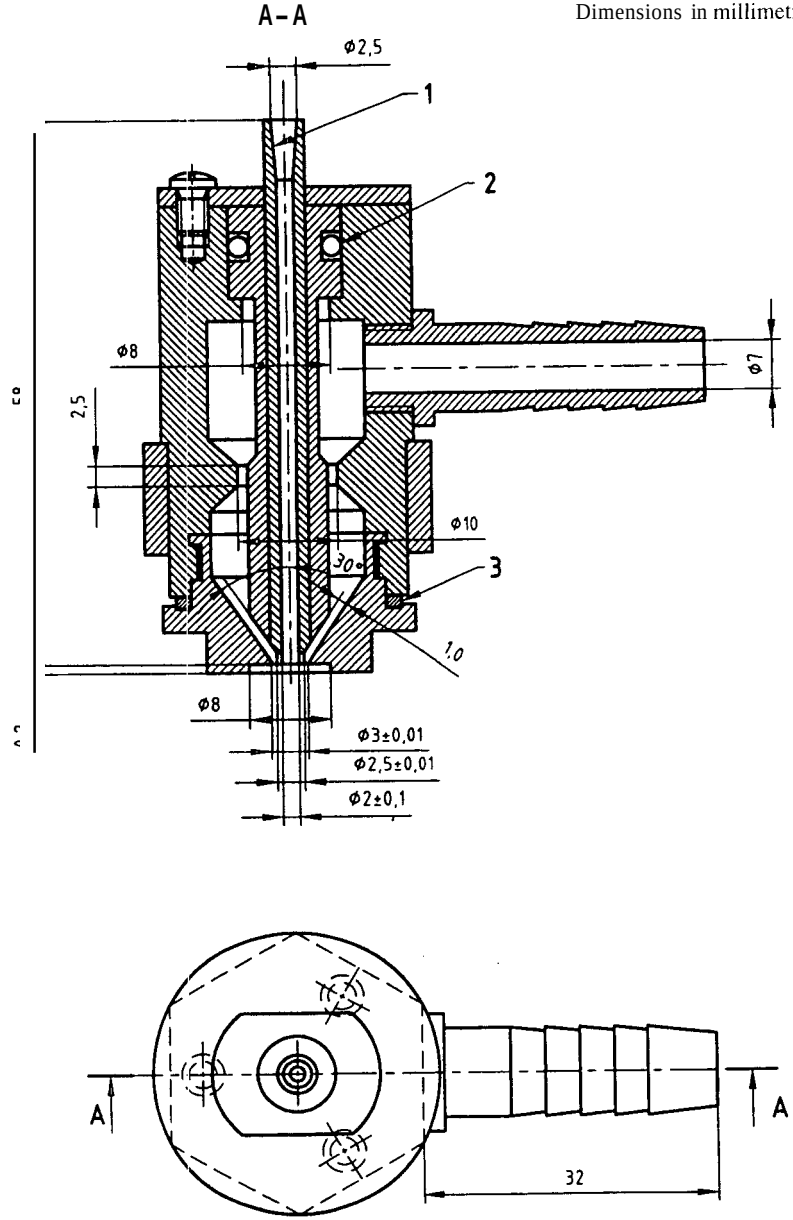


NOTE Dimensions are not critical where no tolerances are given

1 Shutter
2 Funnel
3 Joint
4 Nozzle
5 Sample supporting stage
6 Test specimen
7 High pressure resisting rubber tube
8 Stop cock
9 Control valve
10 Pressure gauge
11 Air or inert gas supply
12 Scale
13 Water manometer
14 Abrasive flow rate adjuster
15 Hopper

Fig. 12-15. General layout of abrasive jet test apparatus[R8]

Dimensions in millimetres



1 1:20 tapered
2 O-ring, usually of elastomeric material
3 Packing

Fig. 12-16. Details of suitable jet nozzle[XR]

The air flow is set and maintained accurately at the specified value (normally 40 litres/minute, but up to 70 l/min may be needed in the case of hard anodic coatings) and dry air is used. A weighed amount of abrasive is placed in the hopper. The air flow is adjusted if necessary during the test. When a small dark spot appears in the centre of the abraded area, the test is terminated by covering the delivery tube of the hopper with the thumb. The abrasive remaining is weighed and the weight used to penetrate the film is calculated. The time required to penetrate the film is also noted in order to verify that the rate of flow of abrasive is correct. The end point can also be checked by an electrical conductivity test to ensure that the film is penetrated, but the probe must be very lightly applied. The funnel should never have a build-up of abrasive.

At least three determinations are made. The average result is normally expressed as grammes per micron of the coating thickness, which is the specific abrasion resistance. With thick coatings the weight removed per unit weight of abrasive may be a more convenient measure of the surface abrasion resistance, but it should be noted that the abrasion resistance can vary through the thickness of the coating.

The test can be carried out in a few minutes on normal anodized surfaces but tends to become very lengthy for hard anodized surfaces, and also for those produced in some integral colour anodizing processes. In this case the air flow can be speeded up to 70 litres/minute to enable the test to be carried out in a short time, but there are some difficulties in changing from one rate to another as noted below.

The slight modifications in procedure have resulted from work at the British Aluminium Co. by P.G. Harris who has made the following observations about the test:[87]

'*Abrasivepowder*. The abrasive powder is found to vary from batch to batch. In fact by separating various fractions from the batch they all gave the same results which were different from the various fractions of another batch.

'*Consistency of abrasive*. The abrasive becomes more effective after the first or second usage so that measured values appear to fall (by 3% in one case). Thereafter there is a slow decline in abrasive power towards a steady value; in one test the measured abrasion value altered from –3% to +2% between the second and sixteenth usage, and remained unaltered throughout the period of test which was up to the fiftieth time. If the initial excursions are tolerated – and they can be in a test which is comparative and where one is not seeking an accuracy of much more than 10% – then there is no reasonable limit to the life of the abrasive, and certainly no need, as is sometimes suggested, to use fresh abrasive for each test. In fact, the opposite should be the case.

'*Roughnessof tube interior*. The interior finish of the outer delivery tube can have a marked effect on the abrasion value. A polished interior leads to a low value but the interior surface rapidly becomes roughened by the action of the abrasive. With a copper tube initially smooth, the abrasion value rises rapidly during the first few

tests and continues to rise for some time. This change is more slow with a glass tube. **A** rough interior can proceed initially in the opposite direction because of the abrasive action. In changing from one rate of air flow to another there is a period of drift during which the tube interior becomes stabilised with respect to the new conditions. It is preferable for this reason to keep to one assembly at 40 litres/minute for normal anodizing and another at 70 litres/minute for hard anodizing. It may be difficult with some tubes to maintain consistency for long enough to compare a specimen with a standard; for this reason it is recommended that at least the mixing length of the tube should be constructed in glass.

'*Wear of jet assembly*. The most serious variation is a long term drift due to the delivery tube slowly becoming tapered outwards by the action of the abrasive to form a cone rather than a cylinder, with consequent increase in the apparent abrasion value. The long term drift and the short term effects of surface finish are the principal factors which require the test to be comparative by nature.

'*Rare of abrasive flow*. The mass flow rate (g/min) has a big effect on the result. If the normal value is 25 g/min, then each divergence of 1 g/min from this value causes the apparent abrasion value to alter by 0.9%. Variations in mass flow rate of a considerably larger value than this can occur spontaneously with the hopper arrangement for delivering abrasive. For an accuracy of +3% the abrasive flow rate should be maintained between 22 and 28 g/minute. The Standard covers this point by sieving out coarse particles, ensuring no interruption of abrasive supply and checking time for each test. Harris has designed means of maintaining a constant abrasive supply rate by using **a** V-shaped wheel driven by a synchronous motor to monitor the supply.

'*Air flow rare*. It is vitally important to control the air flow. Variations of 1% or ±0.4 at 40 litres/minute cause the abrasion value to alter by about 3.5%, and 1% at 70 litres/minute has the same effect (±0.7 l/min). The control is therefore more effective at the higher rate but for much anodized work the test is too short at this speed, and the increased effects of apparatus wear would probably embarrass users more in this region.

There is a more-or-less constant ratio between results at the two speeds (x 5 on one apparatus) so that results can readily be converted to a common scale by means of a factor, but one cannot change indiscriminately from one flow rate to another without observing the proper 'running-in' procedure. Control to ±0.1 litres/minute has been found possible.

'***Air** temperature*. The effect of temperature is not great. About 5°C causes a change of about 1% in the measured result but this may well be the effect of temperature on the flow meter itself.

'*Water content of air*. The humidity of the air is a very important feature now incorporated into the standards. There is a 30% difference between the abrasion values obtained when using dry and saturated air. Tubes of silica gel are used for

drying the air and on a humid day these can cause a considerable rise in temperature of the air passing through them.

'Water in silicon carbide. This too can have quite disastrous effects. The abrasive should be dried before use and when using properly dried air it keeps that way, but before this modification the effect of trying to carry out abrasion tests on a very humid day was to introduce gross variations.

Given all the above sources of variability, it is not surprising that the search for a method of producing a standard specimen for comparison purposes should have proved exceedingly difficult. Having established many of the critical test parameters, however, it was possible to agree such a method and this is an essential part of the International Standard. The method described is as follows:

aluminium specification	EN AW-1050A (Al min. 99.5%)
temper	HE 14
nominal test specimen size	140 mm x 70 mm
thickness	1.0 mm to 1.6 mm

carefully observing the following conditions:

pretreatment	degreasing only (light caustic etching, electropolishing or chemical polishing is permissible)
free sulphuric acid concentration	180 ± 2 g/l
aluminium content	5 g/l to 10 g/l
temperature	20 ± 0.25°C
current density	1.5± 0.1 A/dm^2
agitation	with compressed air
anodizing time	45 min
anodic coating thickness	20 ± 2 μm
sealing	60 min in boiling deionised water containing 1 g/l ammonium acetate at pH 5.5 to 6.5

'The standard test specimen shall be anodized vertically with the longer axis horizontal in the bath, maintaining vigorous agitation over the anode surface, and smooth direct current with not more than 5% ripple. Not more than 20 standard test specimens shall be anodized at one time, and the volume of the electrolyte shall not be less than 10 litres per standard test specimen.

Note 1: The standard test specimens are most accurate and reproducible if anodized singly with careful control of all the conditions.

Note 2: Standard Specimens have inherent variations of ± 10%.

The use of a Standard Specimen allows calibration of the apparatus, the jet and the abrasive, and takes away many of the uncertainties previously found with this equipment.

Developments in Japan also reduce the problem of tube wear, as in this jet design (Fig. 12-16) the abrasive falls through a central tube, and on emerging, it is picked up by a converging, air stream and directed onto the test surface. Although the principle is the same as for the British apparatus, there is much less wear of the jet components and it gives rapid abrasive action and a sharp end point. It is the basis of the Japanese Standard JIS H8682, and has been described by Nakayama, Suga and Thomas.[89] The general apparatus layout is shown in Fig. 12-15 and the jet design in Fig. 12-16. This work confirms the lack of drift, due to wear of the jet tubes, in this design of apparatus. Another feature is the rapid rate of wear produced, in comparison with the British design. The method can be used on small sample areas and even on curved surfaces. Both methods are covered in the International Standards.

National Bureau of Standards test

A similar abrasive jet apparatus was developed at the National Bureau of Standards in the U.S.A.[90] Here abrasion resistance was measured in terms of the time required for the abrasive (alumina propelled from a vibrating chamber under controlled gas pressure) to break through the coating. Specific abrasion resistance was expressed in seconds per mil.

The apparatus was in fact a great deal more sophisticated and expensive than the simple abrasive *jet* of the British Standard. The work covered the effects of gas pressure, specimen-to-nozzle distance, flow rate of abrasive, angle of impact and thickness of the coatings. The abrasion time depended strongly on the test conditions. It increased almost linearly with increasing nozzle-to-coating distance, decreased with increasing pressure, and decreased markedly with decreasing angle of abrasion from 90° down to about 30"; at lower abrading angles the abrasion time rose again. Values were obtained with an average coefficient of variation of about 5%. It is possible that different abrading angles may give different correlations with actual service. It is postulated that a 90" test may simulate leading edge corrosion erosion, while a 45" test may more nearly simulate the scuffing type of wear encountered during maintenance operations.

Deal'" found that the most consistent results were obtained with this method if a single spot was abraded for only 4 seconds after which the jet was turned off briefly before resuming. Operating conditions were important and the optimum conditions were found to include a jet angle of 60° to the surface, a CO, gas pressure of 50 p.s.i. (345 kN/m^2) and a distance of 0.4 inches (10 mm) from the nozzle to the coating. **A** microscope of 20 diameters magnification was used to view the endpoint.

This method was very suitable for hard anodized specimens and gave a good comparison of the abrasion resistance of coatings produced on different alloys in different electrolytes. Using this method, Deal found that the abrasion resistance of hard anodized aluminium increases linearly with coating thickness (Fig. 12-17).

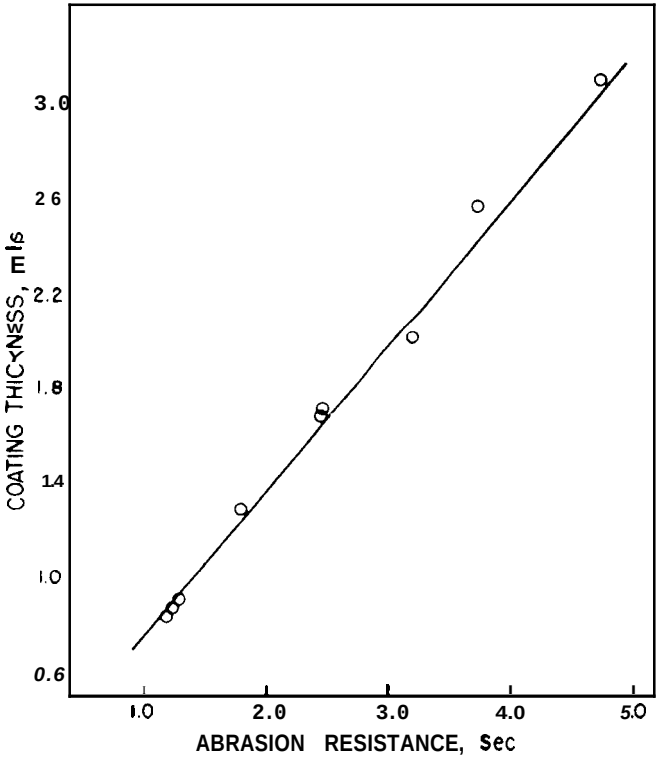


Fig. 12-17. Abrasion resistance and hard anodic oxide coating thickness on 1100 alloy.[91] 1 mil = 25.4 μm

It would appear however from a later account[92] that the design left considerable room for improvement and reference panels were introduced to enable data obtained under different conditions to be reduced to a common basis for comparison. Close control of the amplitude of vibration was needed to assure uniform flow of abrasive and constant abrasive rate. The amplitude changed with gradual drop in the level of abrasive as the operation continued due to shift in the centre of gravity of the electro-mechanical vibrator system. This gradual change could be compensated by periodic readjustment of the regulated line voltage applied to the vibrator, to maintain the standard abrasion rate on the reference panel. In the vibratory storage chamber undesirable turbulence and interference effects were minimised by redesign, so abrasive particles sifted into and were propelled along a straight tube instead of through a circular chamber. New devices for setting and adjusting nozzle-to-coating distances were added, with which the distance was

easily set to within 0.05 mm. Several subtle sources of error in the basic method were identified and eliminated. The method could be applied to aluminium sheet as well as to anodized and other coatings. However, in practice, the next method, the Taber Abraser, is much more widely used in the U.S.A.

Taber Abraser

In the American Taber Abraser" the abrasion resistance is given as the number of revolutions to penetration of a flat coated surface by two weighted abrasive wheels. Alternatively, weight loss per 1,000 cycles may be determined. The specimen, which must be in the form of a flat sheet 8 cm square, is carried round with the wheels so that the abrasion is in the form of two arcs criss-crossing each other over an area of approximately 30 cm^2. For anodized aluminium, a coarse resilient wheel at 1,000g loading or a fine-grain non-resilient wheel at 500 g loading is used. Typical values for sulphuric acid and chromic acid coatings of different thickness are given in Table 12-8.[94]

TABLE 12-8

Taber Abraser values for anodic coatings[94]

Load: 1,000 g. **Wheel:** CS 175, 70 r.p.m.
1 mil = 25.4 μm

Alloy	*Anodizing time* ***(min)***	*Sulphuric acid coatings*		*Chromic acid coatings*	
		Film thickness ***(mil)***	*No. of revolutions*	*Film thickness (mil)*	*No. of revolutions*
3003	20	0.24	855	0.04	57
	40	0.5I	2480	0.08	I43
	60	0.81	4748	0.14	278
2024	20	0.21	688	0.04	39
	40	0.46	1745	0.08	114
	60	0.73	3460	0.12	176

The Taber Abraser (Fig. 12-18) has been widely used with anodic coatings, particularly those produced by hard anodizing, and it is specified in many military and aerospace standards For example the U.S. Military Specification, MIL-A-8625F, requires a Taber test of 10,000 cycles for hard anodic coatings, in which

the anodic coating loss shall not exceed 40 mg for copper bearing alloys, and 20 mg for other alloys. The aerospace specification AMS-2468E specifies abrasion resistance in terms of thickness loss, and the average loss should not be more than 1 mil (25.4 microns) with a Taber test of 5000 cycles. This is a very long test as 10,000 cycles take about 2½ hours to run.

In an excellent general survey of abrasion and hardness testing, Thomas[95] points out that the time required for Taber testing, the expense of frequent wheel replacement, and the size and shape of the test specimens, all set serious limitations on the use of the method for production and control purposes. In addition, reproducibility from one testing centre to another is again a problem and there are difficulties in producing consistent quality of abrasive wheels.[96] Once again humidity variations can play a significant part, as shown by Lerner[97] (see also Chapter 9). Thomas[95] also points out that a freshly exposed anodic film (particularly when unsealed) takes up water vapour readily, and this increase in weight can largely offset the decrease in weight occurring through abrasion. Thus, whilst the Taber test is clearly a useful one, the problems of reproducibility have so far made it impossible to produce an international standard on Taber testing of anodic coatings.

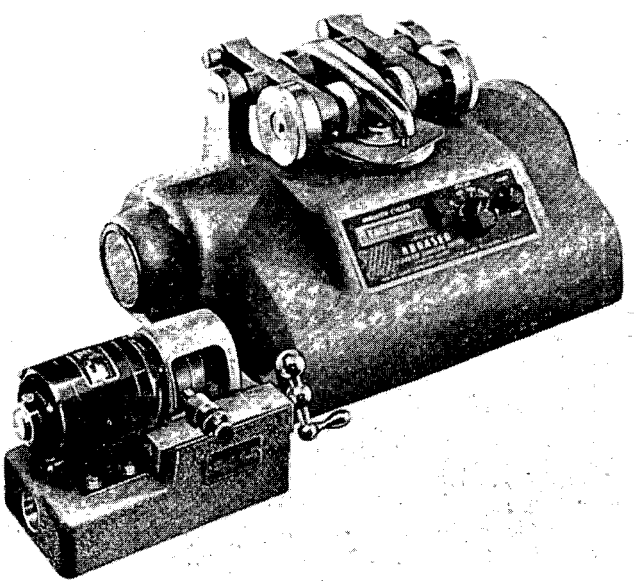


Fig. 12-18. The Taber Abraser

Abrasive wheel tests

Another abrasion test apparatus made by A.M. Erichsen in Germany uses bands of abrasive paper as the abrading medium but the method is designed so that each portion of the paper is used once only. The abrasive bands supplied with the apparatus measure 7.5 x 200 mm and these are fastened to the periphery of a metallic wheel which is then brought to rest on the surface to be tested under a constant load. By means of an electric motor the abrasive wheel can be made to slide over the surface with a reciprocating motion, but after each double stroke the wheel indexes forward by a small amount to bring a completely new abrasive surface into play. When the wheel has made a complete revolution, after 400 strokes, a new band is placed in position. The abrasion resistance is determined by fixing the number of double movements of the wheel according to the nature of the material under test and finding either the weight in mg removed or the thickness loss.

A modification of this apparatus has been designed for use with anodized aluminium and has been designated as the Type 317 abrader. Work with this was first described by Witt and Gerken.[98] They compared the abrasion resistance of sulphuric acid anodized films with those produced in sulphuric/oxalic acid electrolytes and investigated the effect of anodizing temperature. They showed that the Erichsen method offered considerable advantages over the abrasive jet method, as it allowed evaluation of the hardness of different layers of the anodic films by preselecting the number of double abrasive strokes used. They found that the oxide film is harder close to the aluminium substrate than it is at the surface, and that it is the surface layers that are most affected by changes in the anodizing electrolyte temperature. They also found that there was a linear relationship between film thickness loss and weight loss, and that use of a suitable eddy-current meter to measure thickness loss eliminated the effects of any water absorption by the film, which can affect weight loss determinations.

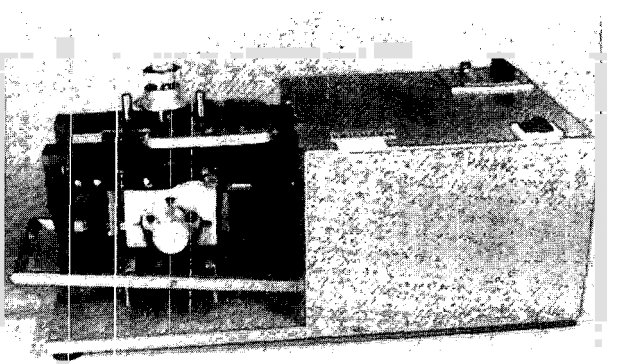


Fig. 12-19. Erichsen 317 **AI** abrasive wheel apparatus
[Courtesy Henkel KGaA]

Since then many other workers, particularly in Germany, Japan and the U.K., have examined this method of abrasion testing. Witt and Sautter[99] compared this method with other methods of abrasion testing and concluded that it had many advantages. They showed, with experiments carried out in several laboratories on the same specimens, that there was good agreement on results, but proposed modifications to the apparatus. This was developed as the Type 317-A1 abrasion tester (Fig. 12-19), and it differed from the previous apparatus in having the abrasive unit mounted on a beam which transmitted the abrading load by means of an easily interchangeable spring. This allowed the apparatus to be used on finished components such as window frames.

This apparatus has been extensively used by Göhausen,[100,101] who has studied the abrasion resistance of a wide range of anodic films. The effect of operating parameters such as the contact load on the abrasive wheel, and the number of double movements used, is shown in Fig. 12-20. In practice, for normal anodic coatings, a load of between 300 and 500 g is applied and 200-400 double movements are used.

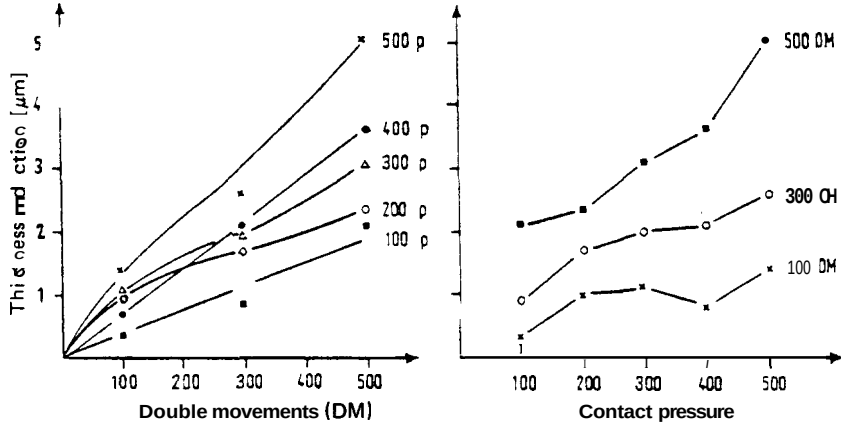


Fig. 12-20. Dependence of thickness reduction on contact pressure and number of double movements

Apparatus of the same type has been developed in Japan and described by Nakayama and Hayasaka.[102] This is known as the NUS Type Plane Abrasive Wear Tester and is shown in Fig. 12-21. It differs from the Erichsen apparatus in applying the abrasive wheel to the underside of the specimen held above the wheel on a sample stage. This allows accurate location of the specimen, so that multiple

measurements can be made in the same place on the specimen, if desired. Any oxide debris from the test also falls away from the specimen as abrasion proceeds. It is also described in work reported by Nakayama, Suga and Thomas,[89] and more recently by other workers in Japan.[103 104]

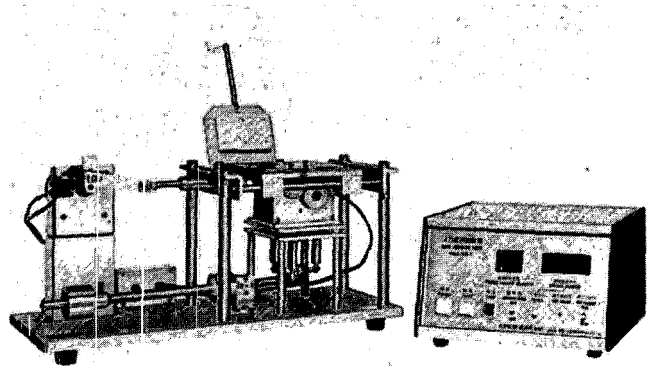


Fig. 12-21. Japanese version of the abrasive wheel testing apparatus[""]
[Courtesy of Suga Test Instruments Co. Ltd.]

The abrasive wheel test is rapidly becoming the most widely used method of evaluation of the abrasion resistance of anodic coatings, and, like the jet test, is the subject of international standards.[105] The load applied in this standard is 400 g, and 400 double strokes are normally used. The abrasive paper used is 320 grit silicon carbide. It is used only once and replaced after a complete revolution of the wheel (400 ds). As with the jet test a standard sample is used for comparative purposes and preparation is the same as already described. The only limitation of this method is that a flat sample of reasonable area (about 50 mm square) is required.

Paper abrasion tests

The tests described previously are all laboratory tests, many of which require flat specimens and are not feasible to use for production control or on-site testing. In the architectural anodizing field, problems with soft films highlighted the need for a simple method that would indicate unsatisfactory abrasion resistance. Such a test was developed in the 1980's by Michael Clarke,[106] and it used a range of abrasive papers under hand pressure to scratch the film.

The test is based on Mohs' principle[107] that a given material is scratched only by a material that is harder than itself. Mohs' hardness numbers were originally applied to minerals on a scale of 1 (talc, soft) to 10 (diamond, hard). Later workers subdivided the scale by ranking additional minerals using the same principle. Mohs' scale has no units, but it has been 'calibrated' in terms of evenly divided scales, such as that due to Knoop.[108] Relationships between Mohs' Numbers and Knoop Hardness are shown in Table 12-9 for the materials which have been used for the abrasive papers, glass, garnet and silicon carbide.

TABLE 12-9

Relationship between Mohs' number and Knoop hardness

Abrasive	*Mohs' number*	*Knoop hardness*
Glass	4.5 to 5.5	530
Garnet	6.5 to 8.0	1360
Silicon carbide	9.5 to 9.8	2480

Strips of abrasive paper, 12 mm wide, are wrapped round a 6-8mm thick rubber block, and held firmly in place as shown in Fig. 12-22. This is applied under firm pressure to the surface of the anodized aluminium, and 10 double strokes are made with an amplitude of 25-30mm, keeping to the same track over the surface. After 10 double strokes the block is lifted and the part of the abrasive paper that has been in contact with the coating is examined. A dense deposit of chalky white powder on the surface of the paper indicates that the coating is softer than the abrasive; no deposit indicates that the coating is harder than the abrasive. The amount of coating removed can also be used as a measure of abrasion resistance, but in this case 50 double strokes are usually used, moving the paper to a new area of abrasive after every 10 double strokes. A coating loss of more than 2 microns indicates that the coating is softer than the abrasive.

Clarke found that films scratched easily by glass paper were generally too soft for external architectural applications, and were likely to give chalking on outdoor exposure. On the other hand films produced under good sulphuric acid anodizing conditions were not scratched by glasspaper, but only by garnet and silicon carbide paper. Films produced by correctly operated integral anodizing processes, films produced in electrolytes containing a high concentration of oxalic acid and films produced by hard anodizing were only scratched by silicon carbide paper. These results were compared with the same abrasive papers used on an abrasive wheel tester and they are shown in Table 12-10 and indicate good discrimination.

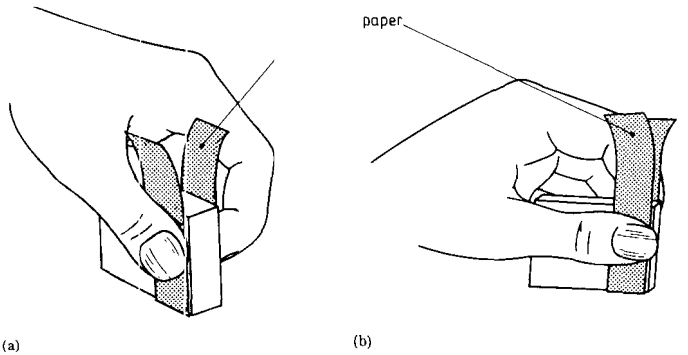


Fig. 12-22. Position of abrasive paper on block

TABLE 12-10

Loss in thickness ((microns)caused by the abrasive wheel test, 400 double-strokes, 400 gf, with silicon carbide (ISO 8251), garnet, and glass papers, compared with the results of the three paper test[106]

Rank	*Film type and colour*	*Abrasive wheel loss (microns)*			*Three paper scratched by:*
		SiC	*GARNET*	*GLASS*	
1	Oxalic acid, black	2.2	1.7	0.4	SiC
2	Integral colour, bronze	3.3	1.5	0.3	SiC
3	Integral colour, bronze	3.5	0.7	- 2.8	SiC
4	Sulphuric, unsealed, natural	4.4	1.5	0.6	SiC
5	Integral colour, bronze	5.0	2.2	- 0.6	Garnet
6	Sulphuric, electrocolour, black	6.1	–	–	Garnet
7	Sulphuric, combination, red	6.6	5.0	0.9	Garnet
8	Sulphuric, natural	7.6	7.4	0.1	Garnet
9	Sulphuric, natural	7.9	5.5	1.5	Garnet
10	Sulphuric, Prussian blue	8.9	7.0	1.8	Garnet
11	Sulphuric, natural	9.4	8.1	1.4	Garnet
12	Sulphuric, electrocolour, black	9.6	9.2	5.9	Glass
13	Sulphuric electrocolour, black	12.5	7.1	6.6	Glass
14	Sulphuric, dyed broaze	20.1	17.3	15.1	Glass

Note: negative values in the GLASS column represent thickness gain

This method was standardised in the U.K. in 1991 as BS 6161: Part 18, and it was called **up** in BS 3987: 1991 for use with architectural finishes. The latter required that a sulphuric acid anodized finish should not be abraded by glass

coated paper when using the method of BS 6161: Part 18, and integral colour anodized finishes should not be abraded by garnet coated paper. In the guidance notes in BS 3987: 1991 it is suggested that a coating produced by sulphuric acid anodizing should have a Wear Index of 1.2 or less when tested by the abrasive wheel method, and that coatings with a Wear Index of greater than 1.4 are likely to be of unsatisfactory quality for external architectural applications. Again the concern is the production of soft films leading to chalking on exposure.

So far the paper abrasion method has only been standardised in the U.K., though it is now being used much more widely.

6. FLEXIBILITY, STRESS, ELASTICITY

The brittleness of a film usually varies directly with its hardness, and conversely ductility is inversely proportional to hardness. This brittleness is manifested transverse to the direction of film growth, and coatings behave like crystals in that they are elastic within limits, though they tend to crack when bent slightly. The cracks are extremely fine, however, and unless deformation is drastic do not appreciably affect the protective value of the coating.

More elastic films are obtained by the use of higher temperatures and a.c. which for this reason are often used in the insulating of wire and strip or when anodizing must be done before plastic deformation, e.g. in the canning industry. According to Phillips[109] continuously anodized wire, which has been a.c. anodized at a fairly high temperature in 37% sulphuric acid and passed around several pulleys during the course of treatment may tolerate a bend of radius 10-15 times its thickness without visible cracking, though a certain amount of wrinkling may be noted on the underside. For electrical windings, smaller bends may be permissible as crazing will often affect the insulating properties only slightly. Particularly flexible coatings are stated to be obtained by anodizing in 23% sulphuric acid at 5-10 volts, 35-40°C,[110] and this process was used to anodize strip from which instrument hands are cut. By another process, anodizing in oxalic acid is followed by immersion in oxalic acid at 80-90°C.[111]

In general, the brittleness of anodic coatings is such that forming operations after anodizing must be very limited. Normally, cracks appear if the elongation reaches 0.5% and, as a result, elongation of anodized sheet cannot normally be carried out without the appearance of crazing. Great care is required in deep drawing and tool edges must be rounded and the depth of the draw restricted.

The elongation was determined by Hill and Mason[112] by an extensiometer which measured the elongation at which ruptures appeared and the number of ruptures per inch. In chromic acid films, Hill and Mason found a network of lines on bending as compared with the parallel lines produced on sulphuric and oxalic acid coatings when ruptured. Pullen[113] showed that the loss of apparent flexibility of the coating varied appreciably with increase in thickness and that the actual elongation of anodic films averages approximately 0.3-0.4%.

Flexibility may also be determined by bending the anodized sheet about a steel ball and measuring the angle at which the first microscopic cracks appear. The most elegant method has been to bend an anodized strip around a wooden former in the shape of an Archimedes spiral constructed so that the product of the radius of curvature at any point with the distance from another fixed point is constant. For a sheet of thickness d the surface elongation for a bend of radius R is:

$$\Delta = \frac{100\,d}{2(R + d/2)} \simeq \frac{100\,d}{2R}$$

(since d is negligible cornpared with 2R). By bending the sheet around the spiral where 1/R is proportional to the length from the fixed point, the radius of bend for crazing to appear can readily be ascertained from the position on the curve. This method has been stnndardised as ISO 321 1: 1977 and EN 12373-15, and work with the apparatus is described by Patrie.[114] The form of the spiral and clamp is shown in Fig. 12-23.

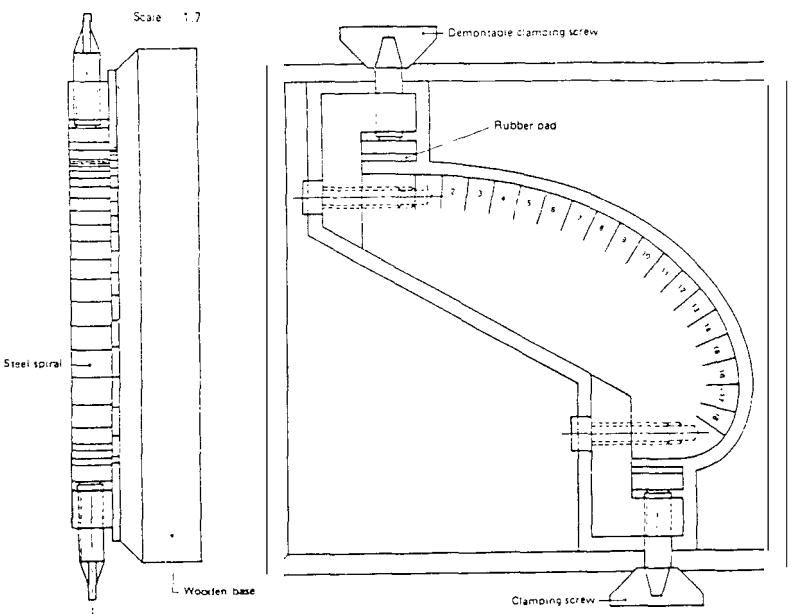


Fig. 12-23. Archimedes spiral for flexibility testing (ISO 3211)

A conversion factor has been applied to this equation by Gaynes[115] to take into account the effect of variations in film thickness. It varies as follows with the mandrel radius, for each 25 μm (1 mil) of coating:

mandrel radius R	½ inch (12.7mm)	3/8 inch (9.5mm)	¼ inch (6.35mm)	3/16 inch (4.76mm)	1/8 inch (3.18mm)	1/16 inch (1.59mm)
conversion factor	0.21	0.26	0.38	0.50	*0.73*	1.37

The elasticity of anodic oxide coatings has been measured by Tomashov, Tyukina and Blinchevskii.[116] They used a method in which 1 mm aluminium sheet was cut up into specimens measuring 15 × 60 mm and bent over a 7 mm diameter former, the angle at which cracks first appeared being measured. In this way anodic coatings on commercial aluminium anodized for 20 minutes in 4N (approximately 20% by wt) sulphuric acid at 1 A/dm^2, were found to have an elasticity of several degrees, which increased linearly with anodizing temperature between 10 and 40°C.

Internal stress

The phenomenon of film fracture has been studied frequently because it is much easier to obtain information on this readily visible or detectable aspect than on the mechanical tensile properties of coatings. However efforts have been made to study the properties of coatings both detached from the substrate and on the metal itself, and these have presented a complex picture.

Internal stresses have been measured by anodizing one side only of strips of aluminium of suitable gauge and measuring the deflection of the free end while the other is rigidly clamped.[117,118] The stress can be calculated from:

$$S = \frac{E.t^2.x}{3.l^2.d}$$

where E is Young's Modulus of the aluminium, l, t and d are the dimensions of the strip, and x is the displacement of the free end. There have been some objections to this technique,[117] and in the Hoar-Arrowsmith modification a vertical 15 cm strip carries a light iron armature at its free end, and a pair of solenoids on either side can be used to return the strip to its neutral position, the current required indicating the force, from which the tensile or compressive stress can be calculated.

Bradhurst and Leach[120] worked with barrier-type films formed in ammonium borate to thicknesses from 50-4500 Å, and found these films to be in tension to a degree that was generally independent of film thickness, but in some experiments there were compressive stresses. Current density was an important factor in determining the nature of the stress. At low current densities there is a greater

tendency for compressive stresses to develop. Values for the deflection and calculated stress in one experiment are shown in Fig. 12-24 where it will be noted that there is a voltage-dependent component of the deflection which always acts on the strip in such a way as to indicate a compressive stress, and the field must therefore be removed to obtain the true zero-field stress. Their results were much the same as those obtained by Vermilyea.[118]

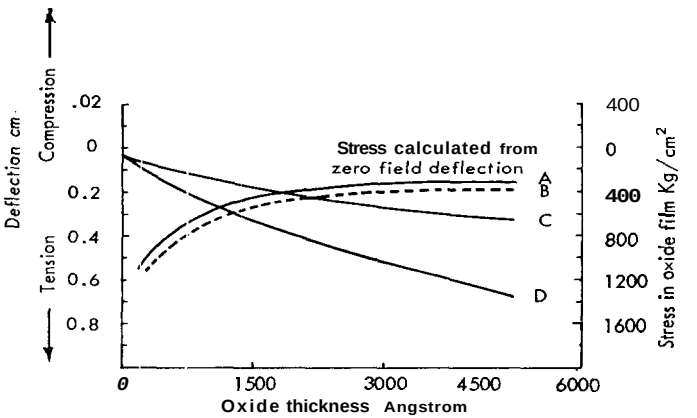


Fig. 12-24. Stress in an oxide film produced on aluminium by anodizing in ammonium borate solution (pH 9.7) at 3.3 mA/cm^2 [120]

A and B. Stress calculated (by different formulae) from zero field deflection
C. Deflection with field applied
D. 'Zero-field' deflection

Arrowsmith, Culpan and Smith[121] measured internal stresses in thicker coatings formed in sulphuric acid. They found no significant difference in deflection by switching the anodizing current off or on, and after anodizing the stress remained constant for 10-15 minutes after which there was a gradual relaxation. Their results for annealed 99.99% aluminium are shown in Fig. 12-25, and for aluminium containing 0.042% Fe in Fig. 12-26; these are very similar but were far less reproducible with the lower purity metal. They also observed the effect of altering the current density during anodizing and these results are shown in Figs. 12-27 and 12-28. These results on porous films are almost the opposite of those obtained by Bradhurst and Leach'" on barrier-type films since the stress is initially compressive and becomes less compressive at low current densities, but at current densities of about 4 A/dm^2 it can start off tensile. This confirms Vermilyea's conclusion that a final tensile stress is increased by a high oxide formation rate.[118]

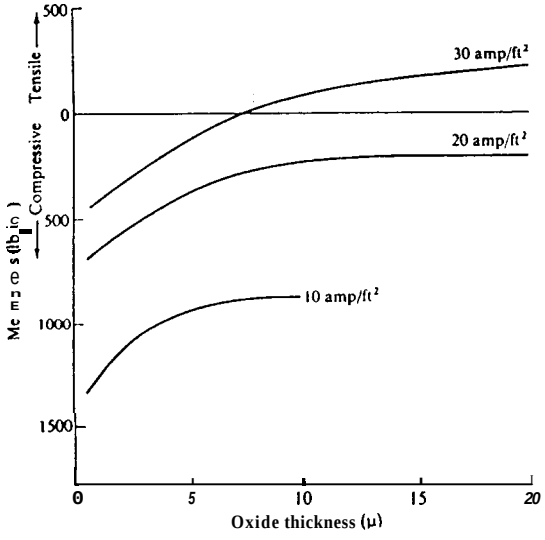


Fig. 12-25. Internal stress in anodic oxide coatings during anodizing.[121]
Super purity 99.99% AI; anodized in 15% V/V sulphuric acid at 20°C

10 amp/ft² = 1.08 A/dm² 25.4 μm = 1 mil 500 lb/in² = 3447 kN/m²

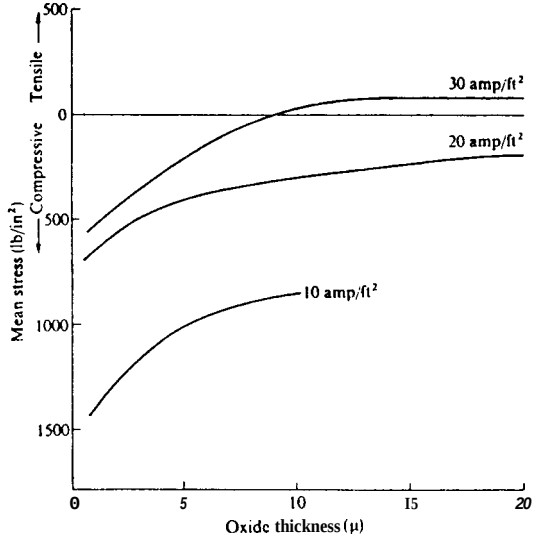
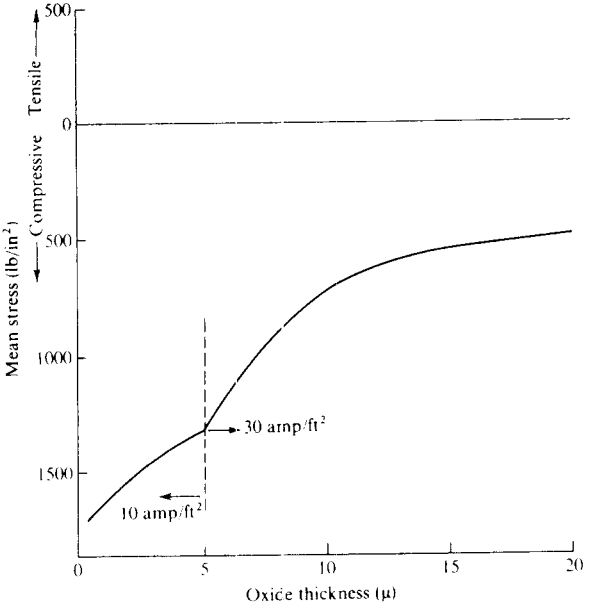


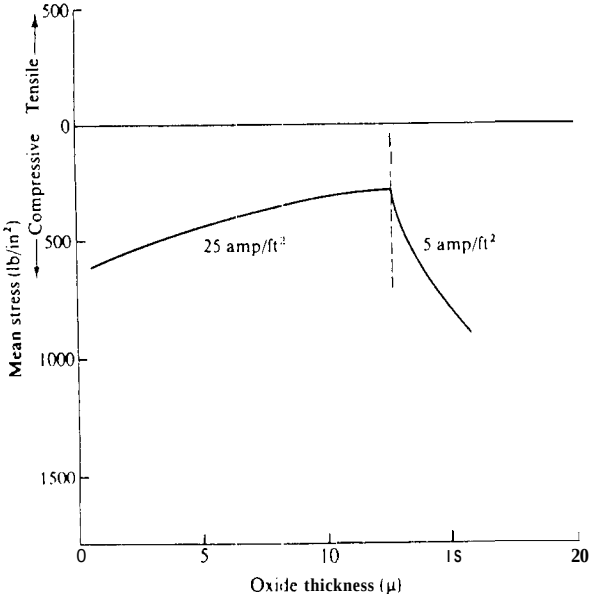
Fig. 12-26. Relation between stress and thickness of anodic coatings produced at various current densities[121]

99.99% Al base with 0.042% Fe; Anodized in 15% V/V sulphuric acid at 20°C
10 amp/ft² ≈ 1 A/dm² 500 lb/in² = 3447 kN/m²



99.99% Al anodized in 1.5% V/V H_2SO_4 at 20°C; 10 amp/ft² for 15 minutes, then 30 amp/ft² for 15 minutes. 10 amp/ft² ≈ 1 A/dm² 500 lb/in² = 3441 kN/m²

Figs. 12-27 and 12-28. Change in internal stress during anodizing on altering the current density"'



99.99% Al anodized in 1.5% V/V H_2SO_4 at 20°C; 25 amp/ft² for 15 minutes, then 5 amp/ft² for 15 minutes

Alwitt[122] measured stresses in porous anodic oxide coatings for specimens stabilised in air at different temperatures and humidities. In ambient atmosphere he found that the stress was tensile after anodizing but was compressive after sealing. However exposure to dry atmospheres caused the stress to be strongly tensile, the increase being proportional to the loss of water from the coating. These stress effects were reversible with changes of humidity, and probably explain the reversible crazing that has often been reported[123] (see also Chapter 11, p. 946).

The use of anodized aluminium for thermal control surfaces in space applications, where its high emissivity and low absorptivity, which result in efficient radiative heat transfer, are important, has raised concern over thermal cracking. The effect of thermal stress has been further studied by Alwitt and McClung[124] in order to try to predict performance in a space environment. The work confirmed the reversible coating stress depending on environment, but also detected a slow, irreversible reaction at high humidity that degrades the coating, and this thermal fatigue effect may be important in some applications.

Work by Csokan[125] with hard anodized samples confirms the Arrowsmith work, again finding that stresses in the film are initially compressive, but become tensile when the limiting coating thickness is reached. He showed that the internal stresses in hard anodic films were sufficient to cause directional dislocation effects in the film as well as cracks.

Since the stress in the oxide film depends on the point of growth, a compressive stress is to be expected in the oxide film formed at low current densities due to growth at the metal/oxide interface of an oxide with a larger lattice spacing than that of the underlying aluminium. At higher current densities the vacancies left in the metal where cations have moved into the oxide can give a tensile stress in the anodized strip. An interesting feature of the internal stress/thickness curves is the change of slope at about 5 μm. It coincides with the stage observed in electron micrographs when the initial cell colonies change to the final cell size.[121]

Elasticity and fracture of films

The modulus of elasticity can only be determined on films detached from the substrate. Early attempts had been made on wire anodized to completion;[126] this was also done by Bradhurst and Leach,'" and a study of separated films was made by Grosskreutz,[127] using 1500 Å films formed in tartaric acid. These measurements are direct and unambiguous, but difficult to perform and the success rate was about 1 in 5. Grosskreutz[128] found that the thin films were about five times stronger than bulk alumina and could be strained about ten times more prior to fracture. He also found that the humidity of the atmosphere had a big effect on the Young's Modulus as shown in Fig. 12-29; it is not possible to measure the modulus of adherent films but it has been deduced that the same applies from the behaviour of dislocations which are trapped near the metal-oxide interface under vacuum but, would not accumulate under normal atmospheric conditions.[128]

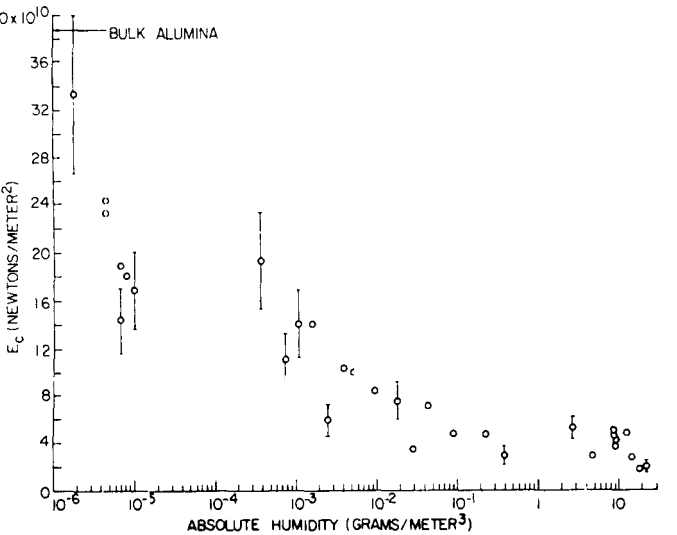


Fig. 12-29. Plot of Young's modulus E_c of aluminium oxide films versus water vapour concentration.[128] Each point represents one test. Error of ± 20% is shown for selected points

Direct measurement of fracture strains is easily obtained however, either by direct observation, or more critically by enclosing part of the sample under test by a water-tight cell filled with anodizing solution and applying a low positive potential to the sample. The micro-cracks are indicated by the sudden appearance of a measurable current. Grosskreutz finds that for films below 500 Å (0.05 μm) on 99.99% aluminium the film will fracture at slip steps when the substrate is strained, and this happens with thinner films on 99.0% aluminium, but with thicker films, and all films on stronger alloys, regularly spaced cracks appear at right angles to the tensile axis. Initially they appear at defects and are randomly spaced at wide intervals and then they acquire a uniform spacing. At this point any further stress causes additional cracks to appear exactly midway between existing ones, because the stress is highest there, so the frequency doubles. The fracture spacings are given by:

$$\log \frac{\varepsilon}{\varepsilon_0} = k\sqrt{t}\left(\frac{1}{d} - \frac{1}{d_0}\right)$$

where e, and d_0 are the substrate strain and oxide fracture spacing for which the coating begins the process of regular fracture, and t is the film thickness. When the coatings are stressed under distilled water, they fracture at a lower strain and the crack density is greater, the behaviour being different from that of detached films.

Grosskreutz examined the effect of environment in a later paper[129] where an analysis is developed to show that the fracture strength of the oxide can be derived from the minimum crack spacing observed d_s:

$$\sigma_f = \frac{\tau}{2t} \cdot d_s$$

where τ is the interfacial shear stress between oxide and substrate and t is the oxide thickness. The values obtained for fracture stress in dry air approach those reported for sapphire whiskers. The effect of other environments is to reduce the stress for fracture by 10-20% in methanol, 20-40% in sea water, and 30-40% in distilled water. These fracture stresses were of the order of 300,000-500,000 p.s.i. (2000-3500 MN/m^2). The saturation spacing of cracks is reached after the metal has begun to flow plastically and when the stress in the segments of oxide can no longer reach the fracture stress level.

The mechanical behaviour of anodic coatings attached to the aluminium substrate was examined by Cochrane and Block[130] and later by Block.[131] The first workers used aluminium monocrystals and polycrystalline wire deformed in boric acid. Film rupture was followed using a potential technique and by optical metallography. Their results suggest that the oxide-substrate interface is capable of sustaining significant shear strain. Block[131] observed buckling of the anodic coating under tensile deformation, and concluded that the buckling occurred as a result of circumferential shrinkage of the surface. Cracking of the coating occurs, and he suggested that detachment of the coating ahead of the crack permitted partial stress relaxation in the coating. More recent work in Brasil[132] has used a method which allows determination of the film stresses in situ, as well as the energy dissipated during coating formation. They concluded that plastic flow is an effective stress dissipation mechanism in anodic films, but that thicker films may store enough stressing energy to cause film failure by buckling.

An extensive study of the fracture behaviour of thick anodic oxide coatings on high strength aluminium alloys has been carried out by Forsyth.[133] In this case deliberate stresses were introduced by penetration of the coating with a tungsten carbide tipped tool, and the resultant flaking of the coating, which occurred in the vicinity of the oxide/metal interface, could be studied. This showed that, although unsealed coatings spalled at the interface between the barrier and porous layers, dichromate sealing almost totally prevented spalling in this region, but allowed cracking within the thickness of the oxide itself.

7. SEALING EFFICIENCY

In spite of the profound effects of sealing on properties and performance of anodic oxide coatings there has been a need for many years for a good infallible test to indicate when sealing has been satisfactorily performed. The most frequently

employed property has been the increased resistance to chemical attack and this can be judged visually by the appearance of the coating, or by the extent to which it absorbs a dyestuff. after attack; it can also be assessed quantitatively by a photometric measurement of the depth of this dyeing, or finally with more certainty by measuring the loss of weight in specified acid solutions. Admittance or impedance measurements also give indications of seal quality. The various methods which have been employed are given below.

In general dye absorption, admittance and impedance tests have been used for production control purposes, and the destructive weight loss tests for reference. The production control tests are intended for use on the production line soon after the sealing process has taken place, and storage and ageing effects taking place within the film may make it difficult to distinguish between poor and satisfactory sealing after some time.'''

Acid dissolution tests

Acidified sulphite test (Kape test)

In the sodium sulphite sealing test developed by Kape,[135] the specimen is immersed in a solution containing 10 g/l anhydrous sodium sulphite adjusted to pH 3.75 with glacial acetic acid and then to pH 2.5 with 5N sulphuric acid. The solution is kept at 90-98°C and the specimens are immersed for 30 minutes.

The test result was originally based on comparison with visual standards,[136] and ranged from 5 for a perfect specimen with little or no change in appearance, to a rating of 0 which represented complete removal of the coating. Intermediate values represented the degree of white bloom formed on the film surface.

In practice, however, the test is now always used as a quantitative evaluation of degree of sealing, with the weight loss measured after immersion in the acidified sulphite solution for a fixed period of time. It was the sole referee test in BS 1615: 1972, but has now been replaced by the chromic/phosphoric acid iinmersion test developed by Alcoa. It was internationally standardised as ISO 2932: 1981, and this included both the acidified sulphite solution and the sodium acetate/acetic acid solution described later. BS 6161: Part 4: 1981 describes the same test method. Both tests are also always used after a predip in nitric acid.

The reagent is a 10 g/l solution of anhydrous sodium sulphite. Acetic acid (20-40 ml) is added to this to give a pH of 3.6-3.8 followed by addition of 5N sulphuric acid (10-15 ml/l) to give a pH of 2.5 at room temperature.

The test samples, which sould be clean and wiped free from any loosely adherent bloom, are first immersed for 10 minutes in 50% nitric acid (density 1.24) at 18-22°C. After rinsing, drying and weighing they are then transferred to the acidified sulphite solution at 90-92°C for 20 minutes, taking care not to exceed 92°C since sulphur dioxide is lost rapidly at higher temperatures. After rinsing, drying and reweighing the loss of weight per unit area is calculated taking into

consideration only those parts of the surface which carry an oxide film. The solution should be freshly made up for each test. There is no significant attack on exposed edges of the samples.

The test was called up in many specifications including BS 1615: 1972 and BS 3987: 1974, and the agreed maximum weight loss in the test for satisfactory seal quality was 20 mg/dm^2 of anodized surface, but this method has been totally replaced as the referee method by the phosphoric acid/chromic acid tests discussed later. For this reason it has not been converted into a European Standard.

The preliminary nitric acid dip is based on investigations by Sheasby, Guminski and Castle[''] who found that the results were more reliable when the test was carried out in this manner. The measurement of weight loss in the nitric acid predip can also provide useful information, and high weight losses (over 10 mg/dm^2) often indicate an inadequate film quality, particularly a high anodizing electrolyte temperature. Survila and Andrews[138] have reported extensive evaluations of seal tests, and their work confirms the importance of the nitric acid predip.

The test is rapid and economical and a thorough investigation by Cooke and Spooner[136] established that the effect of sealing time, temperature and water quality is shown up well. The test correlates well with acidified salt spray and with SO, humidity tests, all of which, according to these authors,[''] gave better information on sealing efficiency than resealing weight gain and dye methods (see below).

Phosphoric acid/chromic acid test

The phosphoric acid/chromic acid test was originally proposed by Manhart and Cochran[140] and has now been adopted in most standards as the general referee weight loss test. It is covered internationally by ISO 3210: 1983 and EN 12373 Parts 6 and 7: 1999, and nationally by BS 6161: Part 3: 1984.

The solution used is the same as that used for stripping anodic coatings, namely *35* ml/l phosphoric acid and 20 g/l chromium (VI) oxide, but it is used at a temperature of 38°C ± 1°C. The solution is used in the same way as that described for the acidified sulphite test, but use of a water bath to control temperature, and continuous stirring of the solution are recommended. Rinsing and drying before weighing are also considered critical, and, after a lot of work within the Qualanod organisation,[141] very precise recommendations are included in the European Standards.

The solution is stable and can be re-used, but must be discarded after 10dm^2 of anodized surface has been treated per litre of solution. It does not attack bare aluminium significantly. It is slightly more aggressive than the sulphite or acetate solutions and a weight loss of 30 mg/dm^2 is accepted as the maximum for adequate seal quality.[141]

Originally this test was not used with a nitric acid predip, but this was first investigated by Survila and Andrews.[138] They saw benefit with this, but it was not until the revision of BS 3987 in 1991 that it was included in a recognised standard.

This standard is concerned with external architectural applications, and the new European Standard, EN 12373: Part 1: 2001, also recommends the method including a nitric acid predip (EN 12373: Part 7: 1999) as the referee method for external architectural applications, and the method without a nitric acid predip (EN 12373: Part 6: 1999) for internal architectural and decorative applications.

Acetic acid/sodium acetate test

This is an immersion test developed in France and included in ISO 2932: 1981 and BS 6161: Part 4: 1981, as an alternative to the acidified sulphite solution. The reagent contains 100 ml/l of glacial acetic acid and 0.5 g/l of sodium acetate, and it is used boiling with it specimen immersion time of 15 minutes. As with the sulphite test a nitric acid predip is used first and the weight loss in the sodium acetate/acetic acid solution measured. **A** limit of 20 mg/dm^2 is normally accepted as the maximum for acceptable seal quality. Once again, through current lack of use, it has not been covered in the new European Standards.

A general study of the changes taking place in the film during acid immersion tests has been carried out by Furneaux and Wood.[142] They looked particularly at the effect of the acidified sulphite solution and the phosphoric acid/chromic acid solution, and examined the effect by transmission electron microscopy, gravimetric measurements and admittance measurement. They found that the phosphoric/chromic acid solution attacks the coating relatively uniformly. The nitric acid predip, used with the sulphite test. undermines and rapidly removes the surface layer of sealing product, and presumably this is the **reason** that **it** makes the sulphite test itself more sensitive. They also point out that, whilst the acid dissolution tests are good for evaluation of conventionally scaled films, they may be less suitable for evaluating finishes produced, for example, by 'cold sealing.'

Sulphur dioxide tests

When testing with a chamber containing sulphur dioxide in the gaseous state the rate of attack is much slower than with the above solution methods, which were in fact devised to replace it. and the method requires an exposure of 24 hours, when a white surface bloom shows up on badly sealed anodic films.

The test used moist air at 95-100% relative humidity containing 0.5-2% (vol) sulphur dioxide, and this was contained in a special cabinet described in BS 1615: 1972, Appendix H. The cabinet temperature was controlled at 25 ± 2°C and specimens were hung in the cabinet for the required test period. After removal from the cabinet they were rubbed with a soft cloth and checked for residual bloom formation. The method was originally developed by the British Non Ferrous Metals Research Association,[143] and was investigated for testing anodized aluminium by Brace and Pocock,[144] but, owing to the development of simple alternative methods, it is no longer used.

Other chemical tests

Other solutions that can and have been suggested for use in weight loss tests to indicate the degree of sealing include nitric acid,[145] hydrochloric acid,[146] sulphuric acid,[146] caustic soda, and phosphoric acid as well as mixtures of these. The nature of the sealed anodic coating is such that almost any chemical reagent which attacks it can be adjusted to an appropriate strength and temperature, so that it will attack considerably the unsealed coating during a period in which there is no appreciable attack or loss of weight on an adequately sealed surface. The principal requirement is that the solution does not deposit solution products into or onto the coating.

In Russia one routine test for the control of anodizing was carried out by noting the time taken for a spot of the following test solution to penetrate the coating and turn green; potassium dichromate 3 g, hydrochloric acid 25 ml, water 75 ml.[147] This test combined film thickness, film quality and sealing since all of these influence the time indicated.

In a rather similar approach, Britnell and Ward[148] proposed the use of a hydrofluoric acid-potassium permanganate solution, which lost its colour when the film was penetrated. Again this method depended on both thickness and seal quality, and slightly different solution compositions were suggested with films of different thickness. Typically the solutions contained 2 g/l of $KMnO_4$ and 5-20% (vol) of HF.

Kape[149] suggested a simple test for 1-2 min at room temperature in dilute solutions of monofluorophosphoric, fluoboric or fluorosilicic acid. The weight loss in these solutions was measured and was found to give a good guide to seal quality with a wide range of different anodic finishes, but the tests were relatively insensitive to silicate and phosphate contamination in the sealing solution.

Dye absorption tests

There are a number of tests in current use which depend on the extent to which the anodized surface absorbs dyestuff after it has been exposed to a suitable chemical reagent.

Much work was carried out on the development of dye spot tests, and the currently used tests have evolved over a period of several years. Early tests mainly used methyl violet as the dyestuff, but a green dye, Aluminium Green GLW, was also used.

Such tests were first put forward by Sacchi and Paolini[150] and described independently by Neunzig and Röhrig.[151] The method proposed by the latter authors used a spot of 50% nitric acid solution on the surface before the application of the dye, and use of this sort of initial sensitising treatment has become the accepted method with dye spot testing. The Aluminium Green GLW dye was used at a concentration of 10 g/l at a pH of 5.2 ± 0.5, whilst methyl violet, which could

also be used after nitric acid treatment, was used at a concentration of 20 g/l. The 50%(vol) nitric acid solution was left in contact with the surface for 10 min at 18-22°C, and after rinsing arid drying the dye was put on the surface in the same area and left for 5 min.

In all of these tests no colour at all is observed with perfect sealing; a very pale colour denotes good sealing and the depth of colour progressively increases as sealing gets worse.

Scott[152] then described a spot test in which the sensitising treatment was carried out with a 46 g/l (2.5% v/v) sulphuric acid- 10 g/l potassium fluoride solution. This was used for exactly one minute, and, after rinsing, a drop of a 10 g/l solution of Aluminium .Fast Red B3LW dye was used. The discrimination of this test was good and it was a quicker and more reproducible test than those proposed earlier and it became the preferred dye spot test in British Standards.

Speiser[153] then showed that a 5 g/l solution of Aluminium Blue 2LW dye was a suitable dyestuff for the spot test, and that sensitisation could usefully be carried out with a 25 ml/l solution of fluorosilicic acid (1 min at 23°C).

These latter two tests became internationally accepted and have been standardised as ISO 2143: 1981, EN 12373-4 and BS 6151: Part 5: 1982. These methods require the surface of the anodized specimens to be cleaned and one drop of the acid solution applied to the horizontal surface for exactly one minute. After rinsing and drying one drop of the dye solution (Red B3LW or Blue 2LW) is applied to the same spot and left for 1 minute. The drop of dye is washed off and the surface cleaned ;thoroughly with a light abrasive such as pumice powder. The residual stain is compared with a colour chart, which has ratings of 0-5, 0 being no residual stain and 5 a very heavy residual stain. Most specifications accept a residual stain level of 0, 1 or 2 as indicating acceptable seal quality.

Clearly this is a very simple type of test, which is non-destructive and is ideal for production control, but one of the problems is the subjective nature of the evaluation. Colour printed spot charts are now issued with the international standards and this helps (considerably,but earlier work looked at immersion rather than dye spot methods,[154] and the possibility of evaluation of colour retention with a spectrophotometer.[155]

Limitations of the dye spot method are that it cannot be used with dark coloured anodic finishes, that it is less sensitive to seal quality with nickel or cobalt sealed work, and that it can give misleading results when some antismutting additives at-e used in the sealing baths.

Impedance and admittance tests

Measurements of impedance, or the resistance of the anodized surface to the passage of alternating current under precisely specified conditions, is another useful method for the measurement of sealing efficiency. The principles on which this is based and an account of the work leading up to it has been given in

considerable detail in Chapter 11. This method is now generally accepted and is covered in ISO 2931:1983 and BS 6161:Part 6: 1984 (admittance and impedance), in EN 12373-5: 1999 (admittance only) and in **ASTM** B457-67 (1998) (impedance only). Commercially constructed test apparatus for either admittance or impedance measurement is generally available.

The area to be tested is cleaned and defined by an adhesive rubber ring of internal area 133 μm^2 which is applied to the surface and can hold a small amount of aqueous potassium sulphate (3.5 g/l) in contact with it. This constitutes the small cell to be tested, and by connecting the basis metal and a small metal electrode whose end is immersed in the liquid to a suitable meter, the effective resistance of the coating at a frequency of 1000 Hz can be measured. In accurate electrical work this sort of measurement is normally carried out by a.c. bridge techniques using null point or balancing methods, which impose only a very small voltage on the component to be measured. The bridge (see page 937) has fixed ratio arms which may be either resistances or capacitors of ratio ***k***, the unknown in a third arm, and the fourth made up of a variable resistance R_s and a variable capacitance C_s which are connected in series, but the bridge may equally be operated if the variable resistance and capacitance are connected in parallel, in which case we call them R_p and C_p. Either method gives the same result, because at a particular frequency a series combination can be made to have the same impedance as a parallel combination; when the bridge is in the balanced condition, the impedance of the variable arm is:

$$Z_4 = \sqrt{R_s^2 + 1/4\pi^2 f^2 C_s^2} = \sqrt{R_p^2 / (1 + 4\pi^2 f^2 R_p^2 C_p^2)}$$

where f is the frequency of operation, i.e. 1000.

It should be noted that the individual values of R and C are not specifically related to any physical feature of the anodic film and no supposition is made concerning any electrical analogue. The only identity is in the impedance which the cell and the balancing arm of the bridge have at that particular frequency, and it is a matter of experience that this value relates to both the film thickness and the effectiveness of sealing.

It is also a matter of experience that the 'admittance' or the reciprocal of the impedance $1/Z$ (or conductivity of the film) is a better term to use. This is measured in microsiemens and BS 1615: 1987 and BS 3987: 1991 require a value of less than 500/t microsiemens, where t is the coating thickness in microns, i.e. as sealing improves the admittance value falls. Some other standards, such as EN 12373-1: 2000 and the Qualanod specification,[141] require a value of below 400/t (expressed as 20 μs for a 20 μm coating).

These relationships are satisfactory in the range of 5-30 μm, so that, in the case of the B.S. values, a 5 μm coating must have an admittance of less than 100 μs, and a 25 μm coating must have an admittance of less than 20 μs. In practice the values obtained have to be corrected for temperature, and, if the area tested is different

from the stipulated 133 mm^2, it must also be corrected for area. The international standards EN 12373-5: 1999 and ISO 2931 : 1983, also correct all values to that for a 20 μm coating. and the corrections needed are shown below for both admittance and impedance values:

	Admittance		*Impedance*
1)	$Y_1 = Y'' \times \frac{133}{A}$	1)	$Z_1 = Z_m \times \frac{A}{133}$
2)	$Y_2 = Y_1 \times f_1$	2)	$Z_2 = Z_1 \times f_2$
3)	$Y_3 = \frac{Y_2 \times e}{20}$	3)	$Z_3 = \frac{Z_2 \times 20}{e}$

where

Y_m is the measured admittance value, in microsiemens;
Z_m is the measured impedance value, in kilohms;
A_m is the actual measuring area, in square millimetres;
Y_3 is the corrected admittance value, in microsiemens;
Z_3 is the corrected impedance value, in kilohms;
e is the thickness of the anodic oxide coating, in micrometres;
f_1 and f_2 are coefficients given as a function of the temperature (t °C) in the table.

TABLE 12-11

Coefficient f_1 and f_2 as a function of the temperature t

t°C	10	12.5	15	17.5	20	22.5	25	27.5	30	32.5	35
f_1	1.30	1.25	1.20	1.15	1.10	1.05	1.00	0.95	0.90	0.85	0.8
f_2	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.05	1.10	1.15	1.20

It will be noted that the admittance has two parameters R and C from which Y is to be calculated. The commercial instruments indicate Y directly on a meter, and no balancing adjustments of the type encountered in bridge circuits need to be made. This means that the method of measurement is not exactly the same as in the technical literature describing the impedance techniques but measures the degree of 'off-balance' .

It has been argued[156] that the dielectric loss factor, also known as the loss angle, is a better indication of sealing since it is independent of film thickness:

$$\text{Loss factor } D = \tan \delta = 2\pi f R.C.$$

According to Birtel and Leute[157] values of 0.7 are poor, just below 0.6 is normal and good, while *0.5* is very good, and for very prolonged sealing the loss

factor may fall to 0.2. An unsealed coating may also give a value of 0.2 but this rises very rapidly at the beginning of sealing (Fig. 12-30). Sheasby and Bradshaw[158] have found the loss factor unreliable and misleading when applied to sealing conditions normally used in Britain. and its measurement is not usually carried out other than in Germany.

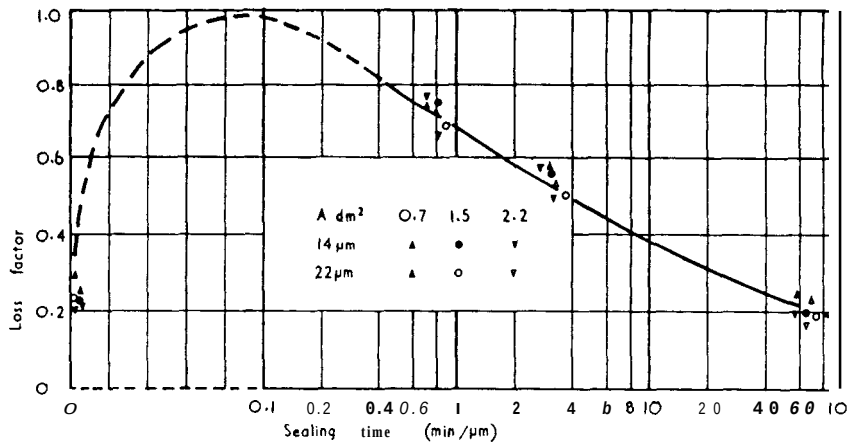


Fig. 12-30. Change of dielectric loss factor with time of sealing."' Anodized in sulphuric acid, d.c., 20°C; sealed in water at 98°C

A limitation on admittance and impedance testing is that the values obtained are dependent on many factors other than just thickness and seal quality, and they can give misleading information with electrolytically coloured finishes and when sealing additives are present in the seal solution (see p. 942). They are also not very sensitive to the presence of silicate and phosphate contamination in the seal water.[158] Admittance or impedance measurement is a useful production control for seal quality, but it should never be used as the only control, and dye spot, or preferably acid dissolution tests, should also be carried out on a routine basis.

Commercial instruments have been the Z-Scope made by Alcoa to carry out the AZTAC impedance test; the Testa14 and the Anotest made in Germany, the former measuring impedance and the latter both admittance and dielectric loss factor; and the 'S' Tester (Anospec S) made in Britain which also measures admittance and dielectric loss factor. A fuller account of this method with bibliography is given in Chapter 11 on sealing.

Marron and Wood[159] suggested that the best frequency for measurement was 100 Hz and that the measurements should be obtained as the equivalent series resistance and capacitance, both of which give information on the sealing process at this frequency. Fig. 12-31 shows that the spread of impedance values is much

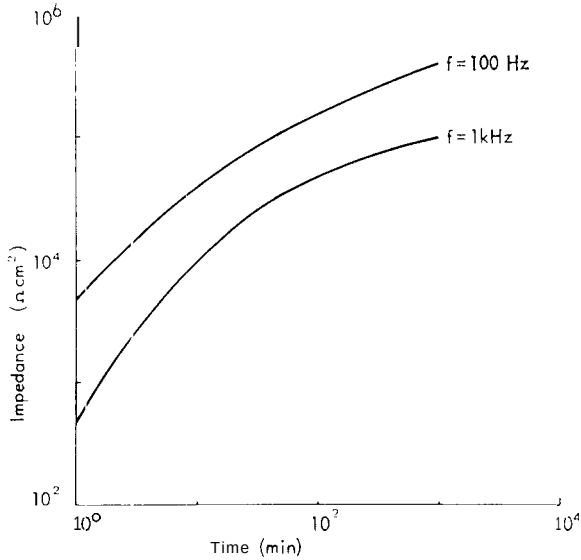


Fig. 12-31. Variation of total impedance Z with sealing time for a 15 μm film.[159] (15 μm films sealed in water at 100°C; measured at 25°C in dilute KNO_3)

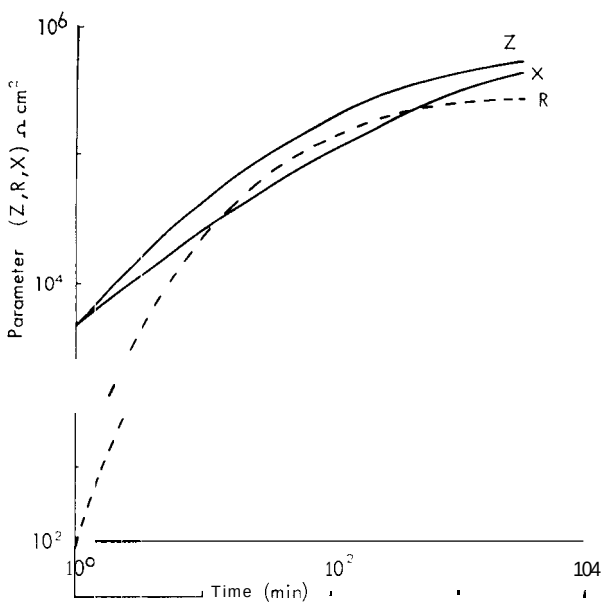
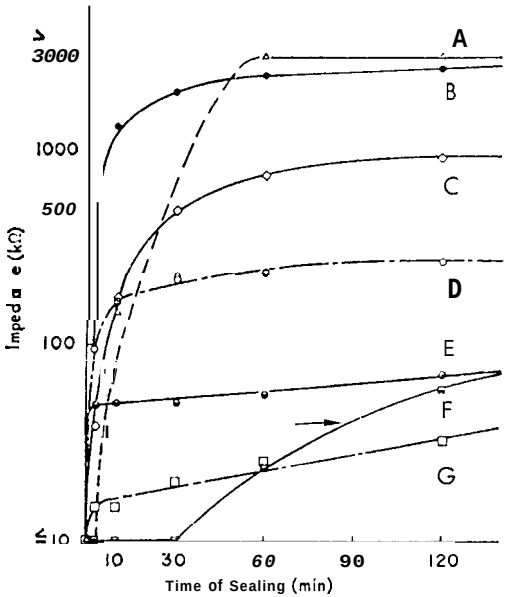
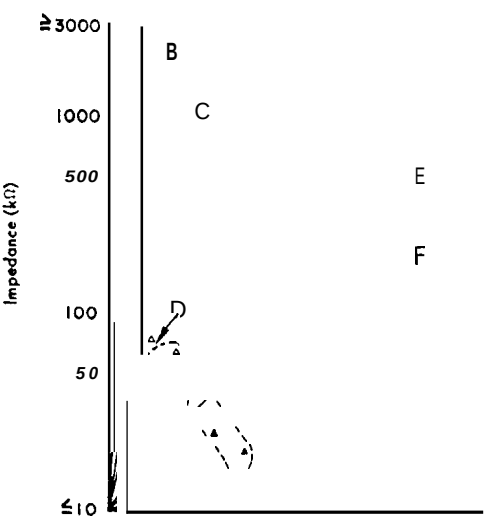


Fig. 12-32. Relationship between Z, X and R and sealing time.[159] (15 μm films sealed in water at 100°C; measured at 25°C in dilute KNO,; $Z = (R^2 + X^2)^{1/2}$



A. Anodized in sulphophthalic acid, sealed in water
B. Anodized in oxalic acid, sealed in water
C. Anodized in sulphuric acid, sealed in water
D. Anodized in phosphoric acid, sealed in water
E. Anodized in chromic acid, sealed in nickel acetate solution
F. Anodized in chromic acid, sealed in water
G. Anodized in phosphoric acid, sealed in nickel acetate solution

Fig. 12-33. Effect of sealing time on impedance of porous anodic films[160]



A. Anodized in oxalic acid, sealed in water
B. Anodized in sulphophthalic acid, sealed in water
C. Anodized in sulphuric acid, sealed in water
D. Anodized in chromic acid, sealed in nickel acetate solution
F. Anodized in phosphoric acid, sealed in water
G. Anodized in phosphoric

Fig. 12-34. Variation in impedance with weight gain (per cent) in sealing of porous anodic films[""]

greater at 100 Hz than at 1000 Hz, and Fig. 12-32 shows that while impedance, resistance and reactance are equivalent over most of the range, during the critical early stages of sealing the resistance is giving more information about the progress of sealing. The function of current instruments has been to serve as a pass-or-fail test and less attention has been given to getting meaningful numerical measurements of partial sealing.

Spooner[160] has examined the use of impedance techniques when applied to specimens anodized in a variety of commonly used electrolytes and sealed in either water or nickel acetate for various times (Fig. 12-33), and he has also made a correlation of the impedance measurements with gain of weight on sealing (Fig. 12-34), and also with results obtained by X-ray emission spectroscopy.

Electrochemical impedance spectroscopy is increasingly being used by research workers to follow the progress of sealing and the natural ageing process that continues under some circumstances. This method measures the impedance over a range of frequencies and is said to be very sensitive to changes occurring during sealing. It has been discussed in Chapter 11, and, so far, has not been used to develop a practical test method, but workers at UMIST[161] suggest that it could form the basis of an on-line test for monitoring seal quality.

Gravimetric tests

The most direct method of estimating sealing efficiency is by measuring the increase of weight that takes place, but it is only applicable in laboratory work because it is destructive, and the unsealed coating must be thoroughly dried and its weight known in order to get maximum information from the test. The weight gain on sealing is expressed as a fraction of the unsealed coating weight. Spooner[160] has defined the term:

$$\text{Unit sealing} = \frac{\textit{weight gain on sealing}}{\textit{unsealed coating weight}} \times 1000$$

which he has used in investigations. Its theoretical maximum value for a completely hydrated layer of alumina is 176 and actual values are considerably below this, but their magnitude is related to the degree of sealing and figures can be compared regardless of film thickness. Apart from the practical difficulties of such a test there is the problem that a very soft powdery film can appear to seal more effectively than a normal film, which it might well do, but this does not say much in favour of either the film or the sealing.

In the case of an unknown film it is possible to boil it in distilled water to see whether it will gain further in weight, and Bury and Godard[163] have proposed a test along these lines. However weight-gain measurements of specimens of unknown history tend to be subject to more uncertainties than some of the other assessments that can be made.

Gravimetric measurements are best employed when the whole procedure is carried out in the laboratory.

Emissivity measurement

The emissivity of anodized aluminium is affected by the presence of hydroxyl radicals and since these increase with sealing it should be possible to monitor the progress of sealing, provided that a sensitive enough apparatus were available for detecting infra-red radiation. Research in this field has made such apparatus available with an incredible sensitivity but there is only one reported instance of the use of the property for measuring sealing, and that is by Lawler and Pirzadeh[164] who measured coating weight and sealing simultaneously (see page 945).

8. COLD IMPREGNATION TESTS

There are no specific tests that have been developed to establish the quality of cold impregnation (cold sealing) processes. In general the normal seal quality tests, phosphoric acid/chromic acid weight loss, dye absorption and admittance measurement, have been used with cold impregnation processes. Of these the most suitable is the weight loss test, particularly with the inclusion of the nitric acid predip (EN 12373-7: 1999). Of the production control tests, cold impregnated samples readily pass the dye spot test, but there is more difficulty in using admittance measurements. As discussed in detail in Chapter 11, admittance values measured on freshly produced work are high with cold impregnated material, but they drop with time to reach acceptable levels. However, the use of double sealing treatments, with a hydrothermal process added after cold impregnation, allows the use of admittance measurements in the normal way at the end of the production line.

9. CORROSION RESISTANCE

Accelerated tests

Conventional salt spray tests

Conventional neutral salt spray tests have become largely discredited for use with anodized aluminium as correlation, even with outdoor exposures in marine conditions, is doubtful. This is illustrated in Table 12-12 which gives loss of weight figures obtained by Harper[165] on untreated and anodized aluminium casting

alloys in marine exposures over 10 years and in 1500 hours salt spray test. It is seen that on untreated LM 1, LM4 and LMS in the as-cast condition, loss of weight in marine atmosphere was about half that under salt spray, while very different results were obtained on LM6M, LM14WP and LM23P. Nor did the results on anodized coatings correlate well, though it appears that anodizing gives somewhat better resistance to salt spray than to marine exposure.

British Standard Tests

There are now two test methods included in the British Standard 1615: 1987, which recognises that the CASS test bears more relation to the results of outdoor exposure in various environments than any other accelerated test. Accordingly it is the recommended test for Grades AA25, AA20, AA15, AA10 and AAS coatings, which are exposed for 8 hours. After testing, the procedure described in BS 3745 (Method for the Evaluation of Results of Accelerated Corrosion Tests on Metallic Coatings) is used to assign to the coating a rating that represents the relative freedom from spots at which the coating is penetrated. The rating must be at least 8 for Grades AA25 to AA15 inclusive, and at least 6 for Grades less than AA15 down to and including AA5.

The acetic acid-salt spray test is applicable to Grade AA3 which must withstand 24 hours without exhibiting pitting. It is considered that corrosion tests are not normally required for Grade AA1.

TABLE 12-12

Comparison between salt spray tests and marine atrnosphere exposure results[165]

Alloy	*Untreated*		*Anodized (30min in 15% H_2SO_4, 15 V, 13-17°C and sealed in boiling water)*	
	Salt spray (g/1500 h)	*Marine atm. (g/10 pears)*	*Salt spray (g/1500 h)*	*Marine atm. (g/10 years)*
LM1M	0.87	0.43	0.06	0.09
LM4M	0.34	0.18	0.02	0.09
LM5M	0.19	0.06	Nil	0.10
LM6M	0.05	0.12	Nil	0.04
LM14WP	0.14	0.25	Nil	0.06
LM23P	0.26	0.23	0.02	0.07

M as cast, W solution heat treated, P precipitation heat treated.

CASS test

This test is described in BS 5466: Part 3, 1977, and the letters CASS stand for 'copper accelerated acetic acid-salt spray test' which is operated at a higher

temperature than the acetic acid-salt spray test and includes a proportion of cupric chloride which is perhaps the best additive for promoting rapid attack of exposed aluminium. The test is also described in EN ISO 9327 and in ASTM B368-97 (1998).

The solution used for spraying is made by dissolving 50 ± 5 g of sodium chloride (NaCl) and 0.26 ± 0.02 g of cupric chloride ($CuCl_2.2H_2O$) in water containing less than 100 ppm of total solids or having a conductivity of less than 0.002 S/m, and diluting to 1 litre. Glacial acetic acid (CH_3COOH) is added to adjust the pH to 3.2 ± 0.1.

The cabinet in which the test is carried out is frequently made from transparent Perspex but may be constructed from, or lined with, any material resistant to corrosion, and containing supports to hold the specimens so that the significant surfaces are at an angle of 15-30° to the vertical and facing upwards. The operating temperature inside the cabinet is 50 ± 2°C and the test solution is sprayed through nozzles at such a rate that the spray collected over a horizontal area of 800 mm^2 during 8 hours averages 1.5 ± 0.5 ml per hour, taking care that no liquid falling from the specimens or parts of the cabinet is collected. Direct impingement of the spray onto the specimens is prevented by baffles. The air used to provide the spray is humidified by passing through a saturator tower containing water at a slightly higher temperature than the enclosure so that the latter is maintained, about 57°C usually being about the required level.

The test requires 8 hours to complete with anodized aluminium, after which the specimens are rinsed in clean running water to remove any deposits of salts, and dried. The frequency of corrosion spots is determined by counting the number of spots where there is evidence of basis metal corrosion and a rating is allocated from 0 to 10 according to the frequency of pitting, where 10 is the best result completely free from corrosion and 0 is the worst. The method of counting is prescribed in British Standard 3745: 1970. The 5000 mm' significant area is divided into 5 mm squares and the corrosion frequency is the ratio of squares with corrosion pits expressed as a percentage of the total number of squares. The size of a corrosion spot is defined as the area of penetration, and discolourations without penetration are not counted. Spots on more than 1 square are counted once only, but cracks are counted in all squares entered. The 'initial ratings' are then assigned according to Table 12-13.

If a specimen with a significant surface area equal to or greater than 10.000 mm^2 is being examined, in addition the 50×50 mm area with the greatest number is chosen, the number of 5 mm squares with spots in it is counted, and the initial rating is reduced by 1 for each 10 squares. Samples are unsuitable if more than 10 spots can be included in any two 5 mm squares, if any spots present are greater in area than 2.5 mm^2, or in the case of cracks traversing more than one square, if the area affected in any one square exceeds 2.5 mm^2.

TABLE 12-13

Assigning initial ratings

$$\text{Frequency \%} = \frac{100n}{N}$$

where n = no. of squares containing one or more corrosion spots
N = total no. of squares

Corrosion rating number	*over*	*up to*
10*	0 (no corrosion spots)	
9*	0	0.25
8*	0.25	0.5
7	0.5	1
6	1	2
5	2	4
4	4	8
3	8	16
2	16	32
1	32	64
0	64	

* If the rating number required is 8 or greater, the total significant area of the sample shall exceed 10,000mm^2.

The conditions of CASS testing have been investigated by Nakayama *et al.*[166] and they stressed the importance of consistent spraying conditions. Angle of exposure is also very important and the rate of pitting decreased as the specimens became more horizontal. Within the specified range of 15-30', very small changes can have significant effects and EN ISO 9227 now recommends that the angle should be as close to 20' as possible. In a later paper[167] the same authors investigated the effect of pH of the CASS solution, and as a result recommended that the pH should be 2 rather than 3. Their results for a pH of 2, 2.5 and 3 are shown in Fig. 12-35, RN refers to the rating number for the degree of pitting which is based on a chart system (JIS H8681). Clearly the lower pH leads to greater pitting attack, but pH 2 has not so far been accepted on an international basis.

Matsushita and Togawa[168] have suggested a combination test, which involves exposure of the specimens to SO, gas, spraying with the CASS solution and then a period of drying. They called this the Accelerated Atmospheric Corrosion Test (AAC), and claim that it gives better correlation with the types of pitting seen on atmospheric exposure. The level of SO_2 in the test chamber was 3,000 ppm and the CASS solution used was identical to that in EN ISO 9227. The cabinet temperature was kept at 50°C, and the first 30 minutes of the cycle was used to get the specimens and the cabinet to this temperature. SO, was then passed into the cabinet for 12 minutes and allowed to remain for 60 minutes. The CASS solution was then sprayed for 18 minutes so that the cabinet was filled with salt fog. At this

point the refrigeration cycle is started so that condensation occurs, and the time of wetness of the specimens is recorded. After about 2½ hours the specimens are dry and remain so for the rest of the 3 hour cycle; the whole process is then started again. The authors claim that the AAC method gives an equal or higher rate of corrosion than the CASS test, and relates better to atmospheric corrosion, but it does not appear to have been used outside Japan.

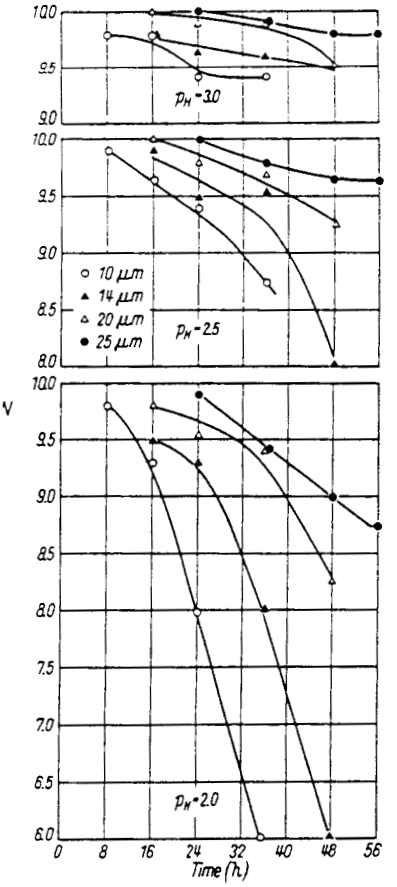


Fig. 12-35. Relationship between the testing times and RN for different pH values[167]

Investigations by Carter[169] at the British Non-Ferrous Metals Research Association have shown that the CASS test correlates better with exterior exposure

in marine and industrial environments, and Skerrey and King[170] who conducted similar tests in collaboration with BNFMRA also came to the same conclusion, but considered 18 hours a better exposure time than 8 hours for the thicker coatings.

Corrosion is a notoriously variable phenomenon but on the basis of *ad hoc* experience such a test would correspond to 15-20 years in neutral salt spray or a severe marine environment, about 15 years in an average industrial environment, and considerably less in severe industrial environments where there can be gross contamination of an acid *or* alkaline nature with a very variable incidence from point to point. Some aspects of the CASS test have been discussed in Chapter 11, particularly the fact that it does not discriminate between well-sealed and poorly-sealed surfaces, and the incidental sealing effect during testing, as noted by Thomas and Jackman, is referred to (p. 950). The sealing effect that can occur during salt spray testing has also been reported by workers in Spain,[171] though they were using a neutral salt spray test. They found that this effect masked the difference between sealed and unsealed coatings.

Workers in Italy[172] also encountered the sealing effect in the CASS test, but believed that the test gave useful information on the general quality of the anodic coating. They suggested the addition of a salt capable of releasing sulphur dioxide in the solution. so the test could provide information on seal quality as well as overall corrosion performance. However they indicated that more work would be needed to establish the optimum parameters to be used.

Acetic acid-salt spray test

This test is described in **BS** 5466: Part 2: 1977, EN IS0 9227 and **ASTM** G85-98. It is specified in BS 1615: 1987 for grades below **AA5** in cases where corrosion resistance is required. It is carried out in much the same manner as the CASS test and uses very similar apparatus, but the test solution comprises 50 ± 5 g of sodium chloride in one litre of demineralised water which is adjusted to a pH of 3.2 ± 0.1 with glacial acetic acid.

The solution is sprayed into the cabinet with clean air of controlled pressure and humidity, taking care to see that it does not impinge directly onto the specimens under test, so that the collected spray rate, averaged over a period of at least 8 hours on 8000 mm^2 of horizontal surface, is 1.5 ± 0.5 ml per hour measured with at least two collector vessels. The solution must not be recirculated. The temperature inside the cabinet is maintained at $35 \pm 2°C$, and the specimens are supported on inert supports, as far as possible with the significant surfaces at an angle of 15-30° to the vertical.

After an exposure period of 24 hours the specimens are rinsed in clean running water and dried for inspection. The present requirement is that there shall be no pitting to comply with the test. The acetic acid-salt spray test is quick to reveal defects in the continuity of the coating but is a quite mild test for the coating itself, and its use on thicker coatings has been largely superseded by the CASS test described above.

Sheasby, however, has shown that the test can be useful in evaluating the corrosion performance of dark electrolytically coloured architectural finishes,[173] and it is sensitive *to* the way that the deposited metal is distributed through the film (see also p. 716). Patrie[174] used the **CASS** test with similar finishes and showed a good correlation with pitting performance in industrial atmospheres. Ellard and Morita[175] showed that the acetic acid salt spray test gave differences between the pitting resistance of cold impregnated and conventionally sealed work, the former generally showing significantly more pitting. Work with thick films, however, requires much longer periods of testing, often exceeding 1000 hours, so it is only suitable for research studies.

Hydrogen peroxide test

One modification of the cabinet-type spray tests which was said to have given good results involved the addition of 1% of hydrogen peroxide to the acetic acid-salt solution.[83] The recommended composition was:

hydrogen peroxide (100 vol)	1.0% (vol)
sodium chloride	2.5% (wt)
acetic acid (glacial)	1.5%(vol)

In testing 1100 aluminium with sealed 0.56-0.68 mil (14-17 μm) sulphuric acid coatings produced in 15% sulphuric acid at 21°C and 15 amp/sq ft (1.61 A/dm^2), the acetic acid-hydrogen peroxide solution, used at 21°C and 80% humidity, produced pitting attack within six days and yielded good reproducibility. This test showed that the relationship between time to breakdown and coating thickness was nearly linear up to a coating thickness of 0.4 mil (10 μm), above which the corrosion resistance improved markedly. **As** well as pitting attack, badly-sealed anodic coatings were shown up by the formation of a white bloom.

MLD corrosion test

An accelerated weathering corrosion test intended for the testing of anodic finishes which were to be subjected to atmospheric exposure was reported in Japan in 1962 by Fukushima and Suzuki.[176] Designed at the Tokyo Metropolitan Industrial Research Institute and known as the MLD test, it involved spraying onto the work to be tested one of the following mixtures at 25°C for 20 to 40 minutes during a 20 to 70 hour test cycle.

a) 1% sulphuric acid containing 60 g/l of carbon black;
b) 1% sulphuric acid containing 20 g/l carbon black and 100 g/l of kaolin.

Kesternich test[177]

The Kesternich test was used in the past in Germany, but was very little used in Britain. It was a lengthy vapour phase test conducted in a 300 litre enclosure

containing 2 litres each of water, carbon dioxide gas and sulphur dioxide gas. The temperature was held at SO-55°C for 8 hours after which the samples were held in air for 16 hours, and this cycle was repeated six times.

Acetic acid-salt-peroxide test

Liquid immersion tests have never been considered particularly indicative of atmospheric exposure behaviour. One simple test that has sometimes been used is an immersion for a period of six days in:

Sodium chloride	25 g
acetic acid	15 ml
hydrogen peroxide (30%)	3.3 ml

Other methods depend on rotation of the samples in salt solutions and subsequent loss in weight per unit area per day.[178]

Corrodkote test[179]

In this accelerated corrosion test devised by the Chrysler Corporation, a slurry is prepared of kaolin mixed with cupric nitrate, ferric chloride and ammonium chloride. It is brushed onto the surface to be tested, dried for 1 hour and then exposed at 38°C for 20 hours in a humidity cabinet at 90- 100% relative humidity with no condensation. The slurry is prepared from:

kaolin	30 g
cupric nitrate (5 g/l)	7 nil
ferric chloride (5 g/l)	33 ml
ammonium chloride (100 g/l)	10 ml

It was designed for use with automotive finishes.

F.A.C.T. test

The F.A.C.T. test[115,180,181] for sealing efficiency was again designed for automotive finishes and was intended to be an electrolytic version of the CASS test operating at very high speed to give a result in minutes instead of hours. It is in effect a doubly accelerated corrosion test and purports to give in one numerical measurement an overall assessment of film thickness, continuity, porosity, sealing and quality generally. The F.A.C.T. test (Ford Anodized Aluminium Corrosion Test) was developed in the quality control laboratories of Ford, U.S.A., and employs the same electrolyte as the CASS test, namely sodium chloride 50 g/l, cupric chloride 0.26 g/l, adjusted to pH 2.8-3.0 with acetic acid. This solution is brought into contact with the surface by means of a glass cylinder of 9 mm diameter fitted with a neoprene gasket, in much the same manner as for the impedance test for sealing. Using a platinum anode the

aluminium is made cathodic from a 200 volt source through a high resistance, which limits the current, even in the case of short circuit, to 0.85 mA.

At the beginning of the test there is a high voltage across the area under test, and there should be very little current, but under the influence of the current the anodic film environment becomes alkaline and the film is subjected to attack at a rate which is dependent on the film thickness, quality of sealing and any other defects or weaknesses which may be present in the coating. This causes the cell resistance to fall, which fact is registered by a drop in the voltage across the cell, because of the ohmic drop increasing across the series resistance. The test operates for 3 minutes, and there are several ways in which the performance could be assessed, but in the Ford method the variable voltage across the cell is connected to a voltage-to-frequency converter with the gate selector set to 1 second, and a frequency counter. This then provides an integration of the area under the voltage-time curve, which is related to the total current that passes during the period of test. This arrangement then provides a high count when the cell resistance or film quality is good, and a low count if it is poor. Other things being equal the F.A.C.T. rating will depend principally on the quality of sealing, but any mechanical damage or film weaknesses will strongly influence the result, particularly with thin anodic coatings.

The test is repeated from 2-5 times according to the consistency of results and for automotive anodized trim a minimum rating of 750 is required. Fig. 12-36, which gives F.A.C.T. ratings, shows a linear relationship between the temperature of the sealing water and sealing efficiency.[115] The F.A.C.T. number of 600 obtained by sealing at 71°C is only very slightly better than that obtained with an unsealed sulphuric acid anodized coating.

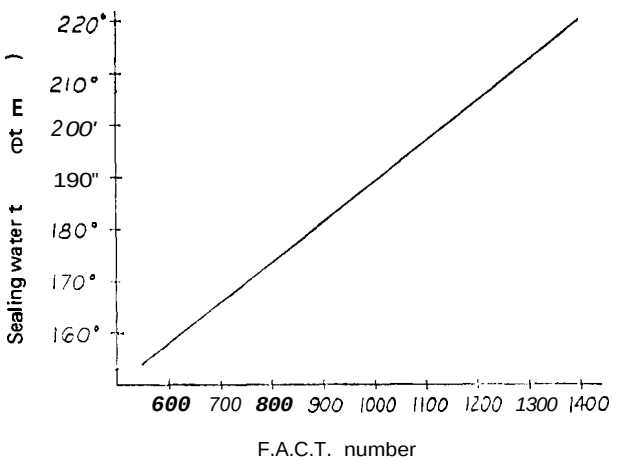


Fig. 12-36. Effect of temperature of sealing water on sealing efficiency as measured by the F.A.C.T. test[115]

Stone, Tuttle and Bogart[182] have discussed the theoretical basis of the F.A.C.T. test and presented a large number of results which go into the questions of ageing, significance of the basis metal quality and the susceptibility to mechanical damage.

Bolmer and Graue[183] compared results in the F.A.C.T. test with those for sealing tests such as impedance and acid dissolution, and with corrosion tests such as CASS. They found that the F.A.C.T. results correlated with the acid dissolution and impedance tests, but not with the CASS test, which was sensitive only to anodic film thickness. Anodic film thicknesses from 2.5 to 17.5 microns were used on alloys 5252 and 5005.

EQT test (Electrolytic quality test)

A slightly different British-made version of the electrolytic quality test dispensed with the expensive voltage-to-frequency converter in favour of a simpler current-time integration which provided a numerical estimate of the film quality at a fraction of the price. It was marketed commercially as the 'Anodization Comparator',* but it is no longer available.

The British EQT test was investigated by Carter and Edwards[185] and Carter[186] who found a remarkably good correlation between the amount of pitting on outdoor exposure at various sites and the EQT rating. They concluded that the test provided a rapid and simple means of differentiating between coating thickness on well sealed articles, and distinguishing variations in the quality of sealing on articles of the same coating thickness. It was particularly suitable for anodic coatings in the lower ranges but results became very scattered with coatings greater than 15 microns.

Neither of the above two tests has in fact achieved a wide popularity and they have attracted less interest than the impedance tests for sealing.

Electrolytic nitric acid test

Bogoyavlenskii and Belov[187,188] have also suggested methods for the rapid evaluation of the protective properties of anodic coatings, and one of these used an electrolyte of 2% nitric acid with an applied current, noting the time taken for the layer to be destroyed.

A further test which they proposed was to apply a small quantity of potassium permanganate + hyclrochloric acid to the surface to be tested; by making a cell with the basis metal and a piece of platinum wire immersed in the electrolyte, the time was noted for a predetermined potential to appear.

Electrolytic sulphuric acid test

D.A. Jones[189] devised a test whereby the anodized aluminium was polarized in contact with an electrolyte containing sulphuric acid and sodium sulphate in order to obtain a measurement which parallels the performance in atmospheric exposure. It was sensitive to both coating thickness and the efficiency of sealing and was claimed to have advantage:, over the acidified sulphite test (quantitative) and also over the F.A.C.T. test, in which the specimen is made cathodic for an essentially anodic

process. The test area was 1 cm^2 and the electrolyte in contact with it for test purposes was 1N Na_2SO_4 adjusted to pH 1 with sulphuric acid. The electrode potential was measured with a Luggin-Haber probe with a solution bridge saturated calomel electrode (SCE), and it was necessary to control the temperature to ± 0.1°C. After initially exposing the specimen to the electrolyte for two hours, the anodic polarization was performed in 50 mV increments with current recorded after 1 minute at each potential, but the curves could also be plotted automatically by potentio-dynamic methods. Figs. 12-37 and 12-38 indicate the effects of coating thickness and sealing time on the polarization curves.

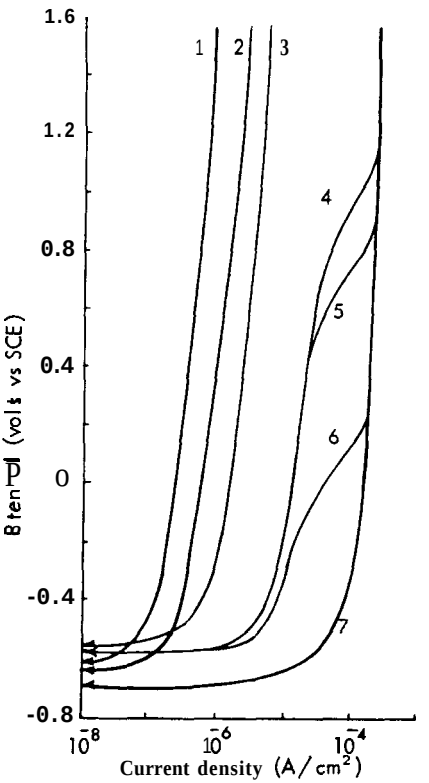


Fig. 12-37. Effect of coating thickness on the anodic polarization of anodized 5052 alloy. (30°C, 1N Na_2SO_4 .pH 1) Current increasing with time at potentials indicated by the arrows[189]

6	3	2.5 μm (0.1 mil)
5	2	10 ym (0.4 mil)
4	1	17.5 μm (0.7 mil)
7		bare metal

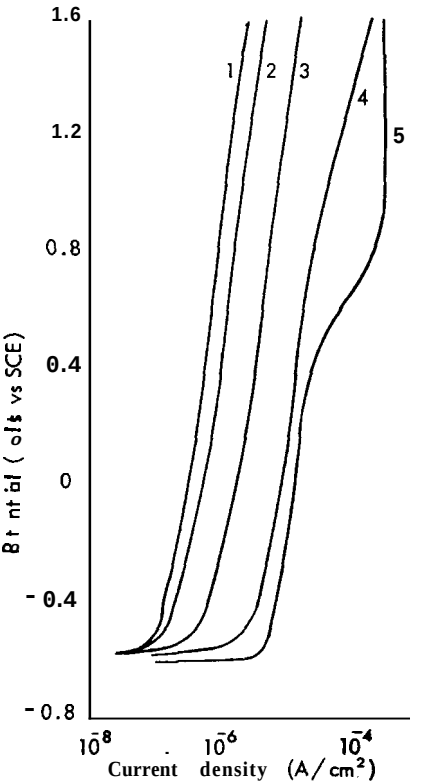


Fig. 12-38. Effect of sealing time on anodic polarization of anodized 5052 alloy. (0.4 mil (10 μm), 30°C, 1 N Na_2SO_4 , pH 1. Coatings sealed in boiling water (pH 5.5)[189]

1	30 min
2	15 min
3	10 min
4	5 min
5	0 min

Other electrolytic tests

Workers in Greece[190] have used weight loss measurements in salt and sea water solutions, under imposed anodic current of 1 mA/cm^2, to measure the corrosion resistance of anodized aluminium specimens. A test period of 23 hours was used and corrosion rates calculated. They found that the presence of corrosion products in the sea water accelerated the corrosion process, and that sea water caused more corrosion than salt solution alone.

An interesting study on the evaluation of anodic coatings on small decorative parts[191] also used an electrochemical method. In this case the anodized frame of the part (an aluminium buckle) was made the cathode in an electrochemical cell, and a voltage of 1.6 V applied in a sodium chloride solution (5 wt.%) at 60°C. The time necessary to reach a current density of 3.1 mA/cm^2 was defined as the necessary criterion for coating quality. The effect of coating thickness and sealing quality were detected in this test.

Canadian researchers[192] used an anodic activation procedure to evaluate the corrosion resistance of anodized aluminium and compared the results with those obtained in salt spray tests. This method produced a partial breakdown of the coating, which could be correlated with long-term salt spray performance.

Exposure tests

The published work on long term outdoor exposure tests of anodized aluminium is limited and not always useful. This is *not* because a great deal has not been done but because as new insight is gathered into the process, methods modified and standards changed, then each generation must start a new series of corrosion tests which take many years to perform. Some of the factors which are known to affect the corrosion performance of anodized aluminium are the alloy used, the anodizing conditions, the anodic film thickness, the quality of sealing, post sealing treatments used (if any), the maintenance procedures employed and the exposure environment.

Sheasby[193] has examined the effects of many of these factors and, in an extensive programme of testing covering sites in the U.K., Canada, Sweden and Germany, concluded that major factors determining the long-term pitting resistance of anodic coatings are the alloy, anodic film thickness, environment and degree of maintenance. Sealing has more effect on short term effects such as bloom formation and iridescence.

In all exposure testing, the type of environment has a particularly pronounced effect. The results in Table 12-14 demonstrate the corrosion resistance of anodized and sealed 1200 and 4043 alloy panels after 6 years exposure at sites around the U.K.[193] The time periods in the Table indicate the time to reach a defined degree of pitting, and P indicates that pitting has occurred, but not to this level; NP indicates no significant pitting. Letters from A-F indicate the coarseness of the pitting. A the coarsest and F the finest. The Table shows that industrial exposure is a great deal

TABLE 12-14

Effect of exposure site and anodic film thickness on pitting produced on 1200 and 4043A panels (Unless otherwise stated panels have been exposed for 5-6 years)[193]

Alloy	Anodic film thickness	Exposure site: Manchester		Leeds		Euston		Bristol		Southampton		Hayling Island		Banbury
SiC (1200)	5	8-10 months	E	10-12 months	E-F	1 year	E-F	2%-3years	E-F	2%-3years	D-E	5-6years	D-E	5-6 years
	10	1½-2 years	D	2-2½ years	C-D	2%-3years	C	5-6 years	D-E	5-6 years	D-E	NP		NP
	15	P		P		P		NP		NP		NP		NP
	20	P		NP		NP		NP		NP		NP		NP
	25	NP		NP		NP		NP		NP		NP		NP
	30	NP		NP		NP		NP		NP		NP		NP
	35	NP		NP		NP		NP		NP		NP		NP
	40	P*		P*		NP		NP		NP		NP		NP
Al-5%Si (4043)	5	6-8 months	E-F	6-8 months	F	8-10 months	F	2%-3years	F	2-2½ years	E	5 years	E-F	5-6years
	10	1-1½ years	D-E	1-1½ years	E	1%-2½years	E	5-6 years	E	5-6 years	D-E	P		NP
	15	3 years	C-D	3-4 years	C-D	4-5 years	C-D	NP		P		NP		NP
	20	4-5 years	B-C	5-6 years	B-C	P		NP		NP		NP		NP
	25	P		P		NP		NP		NP		NP		NP
	30	NP		NP		NP		NP		NP		NP		NP
	35	NP		NP		NP		NP		NP		NP		NP
	40	NP		NP		NP		NP		NP		NP		NP

* Pitting has occurred owing to crazing of the film.

more severe on anodized aluminium than is exposure in marine environments, and it is a general experience that the resistance of well-anodized and sealed aluminium to marine conditions is particularly high. In any particular environment, alloy and anodic film thickness are the major factors controlling the pitting resistance of the anodic coating. These tests have continued over a period of 25 years or more at some sites, and in general the recommended 25 micron films on the SIC (1200) alloy are still in excellent condition. Equally exposure for more than 30 years at the Banbury site shows no pitting on any of a wide range of alloys anodized to 25 micron thickness.

Carter[194] reported 9 years exposure of super purity aluminium and 1050, 3003, 6063 and 6082 alloys at industrial and marine sites in the U.K. and related the results to CASS, ASS, Corrodkote, SO_2 and F.A.C.T. tests. He confirmed that anodic film thickness was a major factor controlling pitting performance and concluded that the CASS test results most closely related to those on outdoor exposure. Later he reported results of a cooperative exposure programme at sites in Belgium, France, Germany, Italy and the U.K.[195] These were with 6063 alloy only, but were anodized to 20 and 30 microns and sealed in water, nickel sulphate or steam. Within the period reported little deterioration had occurred and panels were generally in good condition.

Ten year exposure tests in a severe industrial atmosphere in the U.K. were reported by Liddiard *et al.*,[196] who concluded that increasing purity of the aluminium improved performance. Oelsner[197] reported exposure in Germany for a similar period and again concluded that marine atmospheres were much less aggressive than industrial ones, and they measured a film thickness reduction of 0.4-0.6 μm/yr in the former and 0.7-0.9 μm/yr in the latter atmosphere, with unmaintained specimens. Experience in Italy has been reported by Attini and Di Russo,[198] and they found that the quantity and nature of the iron bearing phases in the 6063 alloy affected the performance, but they only observed this with thin anodic coatings (6 and 12 μm) in the 9 year exposure period covered. From a different area, Fahy[199] has reported 12 year exposure results in New Zealand.

Spooner[200] made a comprehensive review of all published work on long term tests, and reported on tests carried out by himself over periods of up to 10 years, at previous exposure sites. This subject is intimately bound up with the sealing process and this has been discussed in the appropriate pages of Chapter 11 where some of Spooner's results have been quoted (pp. 868 *et seq.*).

Spooner[200] found that the extent of pitting was proportional to the accumulation of dirt, and generally large dirt particles were associated with large pits. Pitting decreased as the quality of sealing was improved. The pitting on upper surfaces was almost always less than on those facing downwards. The frequency of pitting was inversely proportional to the film thickness up to 60 minutes anodizing time in sulphuric acid. The pitting attack decreased as the temperature was raised in the range 15 to 25°C – a surprising conclusion whose practical application must be viewed with some caution. Pitting decreased with increasing sealing time up to 30 minutes, but was worse for a sealing time of 60 minutes, indicating that laboratory

sealing assessments are not the last word. There was less pitting by sealing at pH 4 than by sealing at pH 5-9, another result which is contrary to what most accelerated testing would indicate. Sealing in dichromates and molybdates or any other additives were no improvement on water. Pressure steam sealing was more effective than open steam sealing in reducing pitting attack, but this only became evident after 5 years exposure and the difference was less than noted in an earlier investigation. On the whole this valuable catalogue of results indicates how little is known about the conditions which affect corrosion resistance.

In a later paper Spooner[201] investigated weathering and bloom formation over a period of 15 months on sets of bright anodized panels, where exposure was commenced at four weekly intervals. He discovered that the initial conditions were of great importance in governing the subsequent behaviour, particularly when unsealed panels were exposed, since bloom formation varied markedly with the time of exposure due to the variations in the type and specific exposure period. Under beneficial conditions air sealing or ageing would occur during exposure when partial sealing would be as effective as normal sealing in minimizing bloom formation.

However many different exposure tests are being reported, particularly in Germany. Faller and Sautter[202] describe the changes in film thickness of anodized material during outdoor exposure for periods up to 17 years. They measured a significant film thickness loss at industrial and marine sites of up to 0.6 microns per year, and their results are shown in Table 12-15. Similar film thickness losses have been reported by Sheasby[203] for sulphuric acid anodized samples exposed at industrial sites in the U.K. (Fig. 12-39). However Faller and Sautter[202] point out that the test panels are exposed at an angle of 45° to the horizontal, and that those high erosion rates are not representative of film thickness loss on actual buildings. They looked at a wide range of buildings in Germany, from 17 to 32 years old, and found film thickness losses of 0 to 0.03 microns per year, with even some slight film gain on building components exposed for 4-8 years. **A** film thickness gain in the first few years of exposure has also been reported by Witt and Jahnke.[204] They found an average gain of 2 microns in the first 5 years of exposure of a range of anodized finishes, but subsequently detected the normal erosion effects.

Later work by Faller[205] describes a 10 year exposure programme at sites in Germany of 10, 15, 20 and 25 micron films anodized using the sulphuric acid (GS), Duranodic and Colorox processes. He found that the alloy and anodizing conditions, within the range chosen, had little effect on performance, and corrosion behaviour was mainly controlled by anodic film thickness and exposure site. Hamburg was found to be the most aggressive site, closely followed by Dusseldorf. He indicated that the requirements of the German Standard, DIN 17611, for a minimum oxide thickness of 20 microns were fully justified, and that in very aggressive environments it is advisable to increase the minimum to 25 microns.

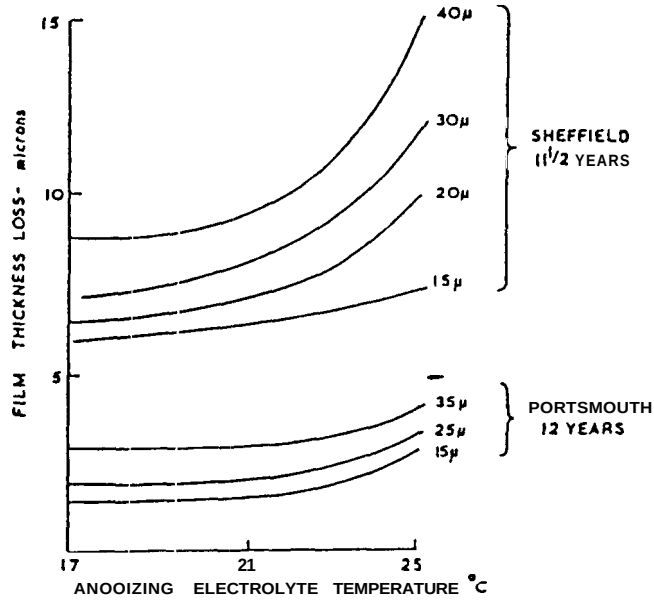


Fig. 12-39. Anodic film thickness loss during exposure

Workers in Spain[206] have reported 17 years exposure of anodized samples in Madrid, but they were mainly concerned with changes in apparent sealing quality with time. They exposed both sealed and unsealed samples and found that the unsealed samples were slowly self-sealed, but in aggressive situations this could be too slow to prevent corrosion. However, in the case of Madrid, self-sealing masked any differences between the two sets of panels. Workers in Italy[207] have compared the performance of hydrothermally sealed and cold impregnated panels exposed at Genoa for up to 4 years, as part of the Qualanod exposure programme. 'They found rather variable results on the cold impregnated samples, with some giving a poorer appearance than the hydrothermally sealed samples. In addition samples electrolytically coloured black in a tin-based electrolyte were already showing some fine pits. This reduced pitting resistance of electrolytic black tin finishes has also been reported by Sheasby.[203]

TABLE 12-15

Measurements of thickness reductions of anodic oxide films after free weathering on test racks[202]

Position	Exposure site climate	Semiproduct B = sheet P = profile	Alloy, after DIN 1712 or DIN 1725	Surface r = rough g = smooth	Anodizing process*)	Initial oxide film thickness in µm	Exposure time in years	Film thickness reduction in µm (mean) total front	total rear	per year front	per year rear
1	Bonn	B	AlMgl	r	GS	19 to 25	8	2.0	1.5	0.25	0.19
2	(mild		AlMn0.5Mg0.5	r	DA	19 to 29	8	1.5	1.2	0.19	0.15
3	industrial		AlMgl	g	GS	5 to 10	17	3.5	0.2	0.21	0.01
4	climate)		A199.9	g	GS	20 to 30	17	4.0	1.5	0.24	0.09
5			AlMg3	g	GS	5 to 10	17	1.0	0	0.06	0
6			AlMg3	g	GS	20 to 30	17	1.0	0	0.06	0
7		P	AlMgSi0.5	r	GS	18 to 25	8	2.3	1.3	0.29	0.16
8			AlMgSiMn*)	r	DA	18 to 30	8	1.5	1.0	0.19	0.13
9			AlMgSi0.5	g	GS	5 to 10	17	2.0	1.0	0.12	0.06
10			AlMgSi0.5	g	GS	20 to 30	17	1.0	0	0.06	0
11	Duisburg	B	AlMgl	r	GS	19 to 25	8	3.3	2.7	0.41	0.34
12	(severe		AlMn0.5Mg0.5	r	DA	19 to 29	8	3.5	2.5	0.44	0.31
13	industrial	P	AlMgSi0.5	r	GS	16 to 25	8	4.0	3.0	0.50	0.38
14	climate)		AlMgSiMn*)	r	DA	18 to 30	8	3.3	2.7	0.41	0.34
15	Westerland/	B	AlMgl	r	GS	19 to 25	8	4.7	2.5	0.59	0.31
16	Sylt		AlMn0.5Mg0.5	r	DA	19 to 29	8	3.5	2.0	0.44	0.25
17	(marine		AlMgl	g	GS	5 to 10	15	2.0	3.0	0.13	0.20
18	climate)		A199.5	g	GS	20 to 30	15	6.5	6.0	0.43	0.40
19			AlMg3	g	GS	5 to 10	15	1.0	1.0	0.07	0.07
20			AlMg3	g	GS	20 to 30	15	2.0	3.5	0.13	0.23
21		P	AlMgSi0.5	r	GS	16 to 25	8	3.5	2.7	0.44	0.34
22			AlMgSiMn*)	r	DA	18 to 30	8	3.3	2.3	0.41	0.29
23			AlMgSi0.5	r	GA	8 to 9	15	1.5	2.5	0.10	0.17
24			AlMgSi0.5	r	GS	20 to 30	15	5.3	4.8	0.35	0.32

*) non-standard; **) GS DC sulphuric acid process (natural colour). **DA** Duranodic process (colour anodizing, grey)

The effect of sealing is more associated with short term weathering effects. Friedemann *et al.*[208] have looked at short term weathering effects on anodic coatings in architectural applications, and these are more related to sealing quality and anodizing conditions than to other factors. Their work emphasised the need for regular maintenance, particularly of coloured anodic finishes, and indicated that an initial abrasive clean, when a building was first completed, was very desirable. Short term weathering effects have also been described by Furneaux *et al.*[209] and are referred to on page 929. Extensive studies of short term weathering effects have been reported by Schulz *et al.*[210] and by Paatsch.[211] Both groups agree that there is a difference in performance of coatings sealed with and without seal additives (usually anti-smutting additives). In the case of conventional sealing the surface has a fine honeycomb structure which deteriorates progressively with increasing free weathering time. On the other hand weathering effects on films sealed in the presence of additives are characterised by rounded and flaky particles, with a diameter of less than 1 micron, on the surface. This is the effect known as 'iridescence', and it is caused by light scattering effects. The weathering effects, however, are not just a function of sealing conditions, but are also affected by anodizing parameters. Higher anodizing bath temperatures as well as very high sealing additive concentrations increase the effect. Attempts to predict the formation of iridescence in an accelerated test were reported by Liotard."' He used the QUV test, with 6 hour periods under condensing conditions at 45°C followed by 6 hour periods of intense UV at 65°C. However it was not found that this test could predict the formation of iridescence. The subject of iridescence has also been studied by Paulet *et al.*[213]

In the case of coloured anodic finishes Faller[202,214] has reported good performance of integral colour and electrolytically coloured finishes after up to 8 years exposure in Germany, and Knutsson and Dahlberg[215] have found good results with similar finishes in Sweden. Sheasby has described up to 12 years exposure of nickel and cobalt based electrolytic finishes[173] in the U.K., and Patrie and Colombier 8 years experience with similar finishes in France.[216] For dyed finishes Speiser and Schenkel[217] have carried out extensive exposure tests with the more lightfast dyestuff's.Exposure of coloured finishes in a much drier atmosphere, in Kuwait, has also been reported, but so far for a 1 year exposure period only.[218] These results with colour anodized finishes have been described in more detail in Chapter 8.

Many workers have shown that the maintenance of anodized aluminium is an important influence on performance, particularly in polluted atmospheres. The extensive efforts in Germany to develop suitable cleaning formulations have been described in Chapter 8 (p. 625), and these have become the basis of an organisation for the control and approval of cleaning contractors (Gutegemeinschaft fur die Reinigung von Metallfassaden eV, Nurenberg). The actual cleaner used, as well as the cleaning practices, is very important, and cleaners that are too aggressive to anodized aluminium have been used on some occasions. Pfeiffer[219] describes the evaluation of a range of acid cleaners, of which only one, an inhibited nitric acid

cleaner, was considered suitable. Another study in Germany[220] describes actual experience of cleaning anodized aluminium facades.

In mobile tests,[221] electropolished and anodized commercial purity aluminium extrusions were fitted into the radiators of Birmingham buses, where they were exposed both to atmospheric corrosion and to damage from road slush and gravel. After 4 years, no corrosion was seen on 12 μm (0.5 ml) sulphuric acid coatings, although some mechanical damage was evident. Thinner anodic coatings (5-10 μm; 0.2-0.4 mil) showed no corrosion within 12 to 18 months. Porter reported a series of tests to determine the effect of coating thickness on the life of bright anodized aluminium.[222]

A quite different study examined the behaviour of anodized aluminium when immersed in sea and brackish water.[223] Immersion was only for a 6 month period, but anodized 3003 and 5083 alloys maintained their initial appearance without corrosion, regardless of whether they were sealed or not.

In some instances, e.g. anodized aluminium kitchenware, resistance to pitting corrosion depends on water impurities, particularly heavy metals such as copper, nickel, lead and tin, or chloride and bicarbonate, as well as impurities such as iron or silicon in the basis metal.[224] As in outdoor exposure, regular cleaning of anodized aluminium reduces the incidence of pitting corrosion.

10. ELECTRICAL PROPERTIES

Dielectric constant

The dielectric constant of aluminium oxide is a property of most significance in electrolytic capacitors made from foil anodized with a thin and highly insulating barrier type coating. The capacitance of a parallel plate capacitor is $\varepsilon A/4\pi d$ where A is the area, d the plate separation and ε the dielectric constant of the insulating material. Electrolytic capacitors are highly rated because the very thin anodic film constitutes the separation distance and a further bonus is conferred by a dielectric constant of about 8 which increases the capacitance by this factor (see also page 539). Alternative terms are permittivity and specific inductive capacity.

Corundum and precipitated alumina have a dielectric constant of 12-12.3,[225] and a value of 8.00 has been quoted for γ-Al_2O_3.[226] The presence of water with a dielectric constant of 80 is liable to have a quite substantial effect. It is to be expected therefore that barrier type films would have a fairly consistent dielectric constant, that porous unsealed coatings would be lower, but that these would also tend to be variable. A dielectric constant of 9.3 has been quoted for Al_2O_3 in the range 8-9 giga cycles."'

Values quoted for barrier films formed in ammonium borate at high voltage have been 7.64 by Okada;[228] 8.5 by Nagase[229] who used ammonium borate up to

150 V and measured thicknesses by multiple beam interferometry; 8.7 ± 0.3 by van Geel and Schelen[230] with a density of 3.1; 8.4 ± 0.2 by Bernard and Cook[231] who formed coatings at up to 150 V in ammonium pentaborate in ethylene glycol; and 9.8 ± 0.5 by Harkness and Young[232] in aqueous borate solutions employing interference techniques for film thickness and using a refractive index of 1.57-1.58 obtained by the Becke immersion method. An error on the high side would be obtained if there were a porous layer on top of the barrier layer because the capacity measurement would depend only on the latter. The most probable value would appear to be 8.5.

Values quoted for porous films are understandably more varied. Gunterschulze *et al.*[226] found by various methods that the dielectric constant of the unsealed anodic coating was about 7.45; Zauscher[233] obtained values of 7.4-7.6 and showed that by carefully preventing any disturbing effects of moisture, e increased by approximately 0.6% per °C over the range 20 to 100°C; above 100°C it increased rapidly and did not return to the same value on cooling, and there was no further increase after 300°C. Using dry d.c. oxalic films, ε increased with film thickness almost independently of voltage up to approximately 55 μm (ε = 7.0). The dielectric constant of oxalic films is somewhat higher than that of sulphuric films; the resistance of the film decreases with voltage and humidity of the ambient air, and is higher in the case of polished than unpolished metal. Herrmann[234] has given a value of approximately 8 for the dielectric constant, which varies with film thickness and anodizing process. Dielectric constants of 5.0 to 5.9 have also been reported for sulphuric films.

Electrical resistance

Moisture in oxide coatings does not increase the conductance of the coatings to the extent experienced with other materials, e.g. porcelain. The conductance of unsealed oxalic acid films has been found to decrease with the use of higher voltages, while it is lower in d.c. than in a.c. coatings and increases with the time the film is allowed to dry.[235] With rising temperature it passes through a maximum at 40°C, a minimum between 80 and 200°C, and rises again up to 320°C.

Table 12-16 shows the specific resistance of the dry anodic film compared with other materials at various temperatures.[236] Anodic coatings are good insulators. Though they tend to craze at high temperatures, the breakdown voltage is not seriously affected by this as cracks are filled with air. Most of this work was done in Germany and the results are mostly concerned with oxalic acid coatings.

Workers in Japan[237] have shown that the electrical insulation properties of sulphuric acid anodized films can be improved by a subsequent pore-filling treatment in a barrier anodizing electrolyte such as a boric acid/ammonium borate solution. However, although there was some increase in specific resistance with unsealed films treated in this way, the specific resistance of sealed films was shown to be dependent on their thickness and not on the influence of the pore-filling process.

TABLE 12-16

Specific resistance of various insulating materials[236]

	Specific resistance (ohms per cm)		
Slate	1×10^8	at	20-22°C
Hard fibre	2×10^{10}		20-22°C
Glass	5×11^{11} to 5×10^{13}		20-22°C
Porcelain	3×10^{14}		20°C
	4×10^{13}		97.5°C
	1.7×10^{11}		160°C
	2×10^7		400°C
Dry anodic film (50 μm; 2 mil thick)	4×10^{15}		20°C
	8×10^{14}		100°C
	1.1×10^{14}		200°C
	9×10^{12}		300°C
Hard rubber	2×10^{15}		20°C

Breakdown voltage

The phenomenon of breakdown after the electrical stress across an insulator exceeds a certain value is essentially an unstable condition and can be preceded by an immensely complicated train of events. In the case of very thin films there may be a rapid transition from almost complete insulation to conduction with the sudden physical rupture of the medium and formation of an arc. Much more frequently there is a substantial pre-breakdown leakage current, which may be ionic, and which can lead in turn to a chain reaction of ionising collisions, or purely thermal escalation. Breakdown with arc formation will depend greatly on how quickly the voltage is raised. The ability to sustain an arc will also depend on the voltage reached and the impedance of the external circuitry, the latter also influencing the voltage across the medium as soon as any current begins to flow. These considerations all apply to homogeneous insulating media. In the case of anodic coatings the behaviour is more complex still and it must be said that most investigators have confined themselves to describing the results obtained without accounting for them.

There have been two reasons for investigating breakdown voltage. The primary one was to obtain a method for measuring the thickness of anodic films, and far less importance has been attached to measuring the dielectric strength. The best methods for achieving these two objectives are not necessarily the same. If

sufficient pressure is applied to a test probe to deform and fracture the coating the results may well be more consistent and reproducible but they impart less real information about the coaling itself.

The use of breakdown voltage measurements for film thickness estimation has been discussed on page 970, but it is rarely used as a method today. The relationship between breakdown voltage and thickness has been quoted by Nachtigall[238] and is shown in Fig. 12-40.

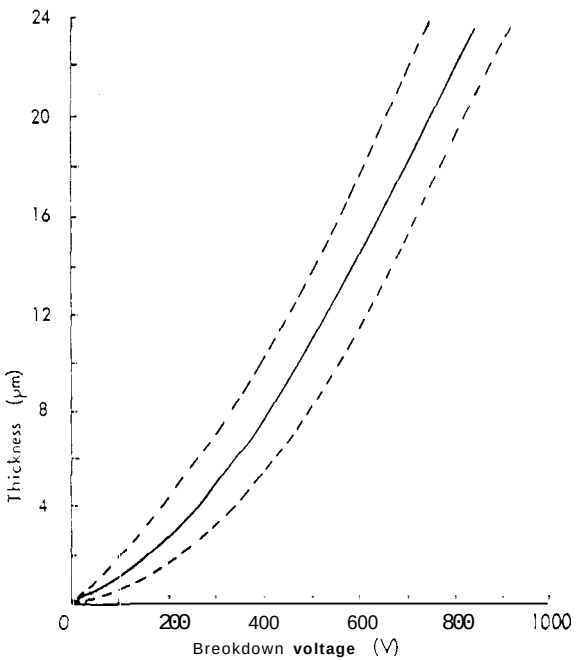


Fig. 12-40. Breakdown voltage-thickness relationship lor coatings formed in sulphuric acid at 20°C and 1.5 A/dm²[238]

Values quoted for breakdown voltage in recent times vary between about 25 and 10 volts per micron, but these differences only indicate that it is a complex situation and in practice one either needs to know the precise conditions of service, or to specify a thickness well above any likely requirement. The one certain feature however is that alloys high in copper will have a lower breakdown voltage than pure metal, and to a lesser extent this is true of silicon. Table 12-17[239] gives recommended thicknesses for withstanding various voltages in the case of copper and silicon alloys and for alloys where these are relatively low. If there is

considerable segregation of the $CuAl_2$ constituent it may be difficult to obtain any reasonable electrical insulation at all. Campbell[79] has stated that while a hard coating of 100 μm on pure aluminium will have a breakdown voltage of the order of 10,000 V, this may be reduced to as low as 500 V in alloys containing about 4% copper.

Pullen[240] found that the breakdown voltage could be described by the equation:

$$V = A\ e^{-1/x} + Bx$$

where the first term expresses values obtained for very small values of the thickness x, while this becomes practically constant at about 5 μm to give a linear relationship between V and x up to 20 μm. This work was done with a 250 g pressure on a flat brass electrode, in contrast to Compton and Mendizza[16] who used 1-2 kg on a 3 μm chromium-plated steel ball.

TABLE 12-17

Effect of composition of aluminium or alloy on breakdown voltage[239]

	Film thickness (in μm)	
Approx. breakdown voltage (V)	***Aluminium or alloy without Cu or Si***	***Alloy containing Cu or Si in quantity sufficient to exceed solid solution***
100	2	2-3
200	3-4	5-8
300	5-8	10-14
400	8-12	16-22
500	11-17	
600	16-22	
800	26-38	

Factors affecting breakdown voltage

The most consistent and reproducible results for breakdown voltage tend to be obtained for coating thicknesses between 3 and 10 microns, where the normal scatter with pure aluminium will be about ± 10%. For thinner films it is often difficult not to fracture the coating with the counter electrode, especially when the surface is rough. At higher thicknesses the results become increasingly scattered; in this region too the arcing can cause rapid deterioration of the electrodes. Thomas[241] noted that at more than 300 volts the air ionized beneath the electrode, transferring a greater stress to the film over a greater area, and that arcing would frequently be outside the contact area; by reducing the air pressure to values where it became more readily conducting the arcing could select weak spots 1 or 2 cm away, and as the pressure

was further reduced these would become extinguished because of the increasing mean free path of the molecules to be replaced by other arcs further away.

Breakdown voltages using direct current were rather higher than with a.c., the relation being linear when aluminium was negative, and non-linear and higher when aluminium was positive.[241] Results were more consistent and reproducible over long periods when the electrode material was graphite, which did not appear to be subject to anything like the same deterioration experienced with all other metallic electrodes. The breakdown voltage dropped with increasing temperature, and above 300-350°C there was a very rapid decline. Up to this point log V was approximately proportional to the reciprocal of the absolute temperature, which is a fair indication of ionic conduction with an avalanching mechanism for breakdown.[241]

For thin coatings up to about 3 microns there is fairly sudden failure of the coating almost as soon as any current is detected and this seems to be a disruptive breakdown determined by the breaking of the electron bonds in the atoms. With thicker films an appreciable current can be measured before breakdown and this can be sustained for long periods; in the case of alternating current it is seen to be a very high frequency pulse which occurs at each voltage peak. With d.c. there is a small continuous high frequency oscillation superimposed on the steady voltage, and as the latter is further increased there appear very short transient current pulses of considerable magnitude and these become more frequent until a continuous arc is established, which can also be a high frequency arc. The events at this stage, however, are greatly influenced by the external circuit; if this contains a series resistance which is too high, then a true breakdown is never reached with films over 15 μm, and the apparent breakdown voltage in any case will relate to what energy is required to operate the visual indicator.?" These considerations affect the design of test apparatus (rather more than has usually been taken into account), but Ruff[23] as indicated earlier, also made a study of the pre-breakdown behaviour and decided on a current of 100 μA as the criterion for 'breakdown'. The practice of applying the voltage to two neighbouring probes would appear to introduce greater complication still.

Thomas[241] found that the pre-breakdown current was frequently proportional to V^3 and considered that an upset of the ionisation balance by ionising collisions led to the avalanching that formed an arc. At the higher thicknesses the thermal effects also play an increasingly important part.

The effect of sealing on breakdown voltage is also complicated. Initially the sealed coating has a lower breakdown voltage than the unsealed coating, but in the course of a month or so it slowly rises until it reaches a higher value than the unsealed coating originally had. The effect of sealing and subsequent ageing was observed by Ruff,[23] and Weeks[242] had also noted the same effect with coatings anodized in chromic acid (see also p. 944).

Electrical breakdown voltage has become more important with the application of coil anodized aluminium strip and wire in capacitors and electrical transformers, and work in this field has been reported by Dima and Anicai.[243] They studied the

effect of a wide range of anodizing electrolytes, and the results are shown in Tables 12-18 and 12-19. The voltage was applied at a rate of 50 V/sec and they concluded that highest breakdown voltages were obtained using an oxalic acid, citric acid, boric acid and iso-propyl alcohol electrolyte. Using such an electrolyte, films of 5 ± 1 microns gave a minimum breakdown voltage of 150-200 V, and had a very good thermal resistance up to 500°C. They measured the effect of thermal shock with strip and wire conductors deformed to different bending radii, and these results are shown in Tables 12-20 and 12-21. The thermal shock treatment involved rapid heating at 500°C for 30 minutes, followed by cooling at room temperature for 30 minutes. Again the 5 micron films gave good results.

TABLE 12-18

Anodizing electrolytes based on organic and inorganic acids (monocomponent solutions)[243]

Elecirolyte type	*Current density (A/dm^2)*	*Electrolyte temperature (°C)*	*Anodic film thickness (μm)*	*Breakdown voltage (V)*
Oxalic acid, 5%	2	25	4.0	200
		45	3.1	190
		60	3.3	160
	5	25	10.5	360
		45	8.2	330
		60	4.4	180
Oxalic acid, 10%	2	25	6.0	220
		45	4.4	200
		60	2.8	180
	5	25	12.0	380
		45	8.7	270
		60	4.5	220
Chromic acid, 20%	2	45	3.3	170
		60	3.1	160
	5	45	5.0	240
		60	4.5	230
Tartaric acid. 5%	2	25	3.9	I90
		45	3.5	160
		60	3.0	150
	5	25	8.5	300
		45	8.0	280
		60	4.3	220
Tartaric acid, 10%	2	25	4.5	200
		45	4.0	180
		60	3.0	I60
	5	25	8.4	260
		45	7.8	240
		60	4.0	200

TABLE 12-18 *(continued)*

Electrolyte type	*Current density (A/dm^2)*	*Electrolyte temperature (°C)*	*Anodic film thickness (μm)*	*Breakdown voltage (V)*
Lactic acid, 10%	2	25	4.0	200
		45	3.6	I80
		60	3.5	I60
	5	25	3.5	300
		45	7.9	280
		60	4.0	200

TABLE 12-19

Anodizing electrolytes based on organic and inorganic acid mixtures[243]

Electrolyte Type	*Current density (A/dm^2)*	*Electrolyte temperature (°C)*	*Anodic film thickness (μm)*	*Breakdown voltage (V)*
Oxalic acid, 5%	2	25	4.0	200
Tartaric acid, 10%		45	3.5	180
		60	3.2	I60
	5	25	8.9	290
		45	8.5	270
		60	5.0	210
Oxalic acid, 5%	2	25	4.5	230
Citric acid, 10%		45	4.0	200
		60	3.8	180
	5	25	9.0	340
		45	8.5	260
		60	6.0	230
Oxalic acid, 5%	2	25	3.9	200
Lactic acid, 10%		45	3.7	180
		60	3.3	160
	5	25	7.0	280
		45	6.5	270
		60	4.0	190
Oxalic acid, 5%	2	25	5.0	250
Citric acid, 10%		45	4.5	230
Boric acid, 5%		60	4.0	200
	5	26	9.0	340
		45	8.8	330
		60	7.1	250
Oxalic acid, 5%	2	25	6.0	230
Citric acid, 10%		45	5.0	210
Boric acid, 5%		60	4.2	200
Isopropyl alcohol, 50 ml/L	5	25	12.3	360
		45	10.5	340
		60	8.2	300

TABLE 12-19 *(continued)*

Electrolyte Type	*Current density (A/dm^2)*	*Electrolyte temperature (°C)*	*Anodic film thickness (μm)*	*Breakdown voltage (V)*
Oxalic acid, 5%	2	25	6.0	230
Citric acid, 10%		45	5.0	210
Boric acid, 5%		60	4.2	200
Isopropyl alcohol, 50 ml/L	5	25	12.3	360
		45	10.5	340
		60	8.2	300

TABLE 12-20

Breakdown voltage for different anodic oxide film thicknesses at different values of curvature radius for aluminum strip conductor[243]

Oxide layer thickness (μm)	*Bending curvature radius (mm)*	*Breakdown voltage (V)* *Initial*	*One cycle of thermal shock*	*Five cycles of thermal shock*
5 ± 1	50	330-380	300-360	340-360
	25	320-380	300-360	280-340
	12.5	3 10-360	260-340	270-320
10 ± 1	50	340-400	340-380	350-380
	25	300-380	320-360	340-360
	12.5	280-300	300-320	280-320

TABLE 12-21

Breakdown voltage for different anodic oxide layer thicknesses at different values of curvature radius for aluminum wire conductor[243]

Oxide layer thickness (μm)	*Bending curvature radius (mm)*	*Breakdown voltage (V)* *Initial*	*One cycle of thermal shock*	*Five cycles of thermal shock*
5 ± 1	50	340-380	340-360	340-360
	25	300-380	280-340	240-260
	12.5	280-340	210-300	230-250
10 ± 1	50	350-400	320-380	320-380
	25	300-340	240-320	300-370
	12.5	280-300	240-280	320-330
15 ± 1	50	600		
	25	300-380		–
	12.5	250-300		–

In transformer applications the anodized strip or wire is frequently coated with lacquer or other organic coating, and Olin Corporation[244] in the U.S.A. claim benefit for a film sealed in an epoxy cresol novolac material with a low room temperature viscosity. but which cures to a highly crosslinked polymer.

The effect of humidity on electrical properties has been studied in Japan,[245] and the effect of incorporation of electrodeposited metals, such as copper or silver, within the pores has been studied by workers at the University of Keele.[246 247]

Tests for breakdown voltage

In the EN 12373-17: 2001 and BS 6161: Part 15: 1987 tests for breakdown voltage, the alternating voltage from an a.c. source is applied to the contact electrode of smooth hard metal having a contact surface of 3-8 mm diameter resting on the test surface with a force of 0.5-1.0 N (50-100 g). The 50 Hz source has a sinusoidal wave-form with a peak voltage within the limits $\sqrt{2} \pm 5\%$ of the r.m.s. voltage (1.34-1.49). There is a current limiting resistor of 0.5 MΩ in series with the test piece.

The test pieces must be dry. The voltage is increased from zero at a uniform rate not exceeding 25 V/second until the specified test voltage is reached, or a sudden voltage drop on the meter indicates breakdown of the film. Not less than five tests shall be carried out. A similar test is specified in ISO 2376: 1972.

In the case of anodized wire the test apparatus is the same but the voltage is applied to a pair of test wires which are twisted together. This is a more severe test in view of the deformation of the wire, but it is also an application where this particular test is of relevance to the final application. The wire is twisted in a machine having jaws 400 mm (15.75 inches) apart, the number of twists per 50 mm being related to the wire diameter as in Table 12-22. A length of 50 mm is untwisted at each end and the specified voltage which a pair of wires must withstand in contact with each other is then applied.

TABLE 12-22

Breakdown voltage test for round wire

Diameter in mm			*No. of twists per 50 mm*
0.2	**up** *to* **and** including	0.3	5
over 0.3		0.5	4
over 0.5		0.75	3
over 0.75		1.25	2
over 1.25		3.25	1
over 3.25		6.5	0.5

1 mm = 0.03937 inches

A mercury pool method for determining the dielectric breakdown voltage of hard anodic oxide coatings has been reported by Hafer.[248] The arrangement for this test is shown in Fig. 12-41 and the advantage of this method is that it gives a breakdown voltage value over an area of approximately 32 cm^2 (5 sq inch) and is thus more likely to include local areas of low dielectric strength than methods which rely on the use of a probe. Thus the mercury pool method tends to give rather lower values than the probe tests on specimens on which the continuity of the coatings is poor. As an example, while the ASTM B-110 probe test gave results of up to 1800 volts on 100-125 μm (4-5 mil) coatings on both 2024-T3 and 6061-T6 alloy specimens, the mercury pool method gave values of less than 600 volts on 2024-T3 and of 1500 volts on 6061-T6 on which it is markedly easier to obtain a continuous coating.

Properties of anodized aluminium strip and foil for electrical windings are also discussed in Chapter 7.

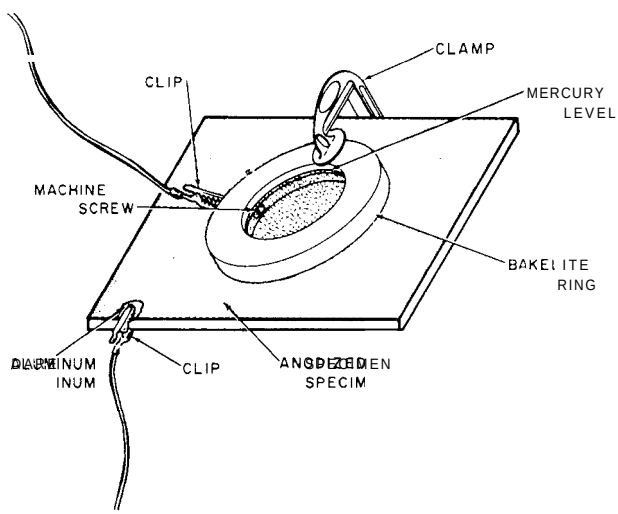


Fig. 12-41. Mercury pool method of determining the dielectric breakdown voltage of hard anodic oxide coatings[248]

11. OPTICAL PROPERTIES

The terms and measurements used in connection with the appearance or the optical properties of metal surfaces can be a source of great confusion, not assisted by the fact that several descriptive terms are used by various people to describe

different things. Metallic surfaces are more problematical than other surfaces because their visual attributes are more difficult to define and measure than is the case with the products of the paint and paper industries.

Broadly one distinguishes between colour attributes and geometric attributes. The colour of a surface is due to selective absorption in precisely the same manner as for any other surface. except perhaps that one is more concerned with subtle differences of shade and might not go about measuring it in exactly the same manner. The geometrical attributes refer to the manner in which the incident light is distributed in various directions, and it is the high mirror finishes with sudden changes in highlights that lead to the peculiar metallic properties which often defy verbal description.

Total reflectivity

Total reflectivity is one of the basic physical properties which has a more or less fixed meaning. If we suppose a beam of white light to fall on a surface, a certain proportion of the energy will be absorbed and the rest will be reflected back. Assuming the incident light to represent 100 units if measured by some means then this divides into reflected light T and absorbed light A, and $T + A = 100$. Then $T\%$ is the total reflectivity, and $A\%$ the absorptivity, and Tis generally fairly high for metallic surfaces, e.g.:

	Total reflectivity (%)
electrodeposited silver	98
electrodeposited chromium	65
stainless steel	60
99.99% aluminium	90
99.8% aluininium	88
99.5% aluininium	85

Total reflectivity is intimately bound up with colour but in the case of pure aluminium it is uniform through the visible spectrum and one is generally not concerned with colour unless it is added. Also, the concept of total reflectivity does not take into consideration the direction of the reflected light. Thus a piece of white paper can have exactly the same total reflectivity as polished aluminium, the only difference being in the distribution of reflected light; also, polished or etched aluminium will tend to have much the same values.

Specular reflectivity (specular gloss)

It is usual to distinguish between mirror-type reflection, where a narrow incident beam becomes an equally narrow reflected beam at the same angle according to the laws of reflection, and the light which is scattered in other

directions. The specular reflectivity is the proportion of the light in an incident beam which is reflected within a narrowly defined cone about the angle of reflection, and if this contains S units out of the original 100, then the specular reflectivity is S%. It is important to note that whereas total reflectivity is an absolute property of the material except insofar as it is affected by the angle of incidence, the concept of specular reflectivity is an arbitrary one which depends on how wide an angle of acceptance is considered to define the specular beam, and this tends to vary with different instruments and for different purposes.

Diffuse reflectivity

This is defined with reference to the specular reflectivity as the balance of light which is reflected at all other angles. Thus the diffuse component D and specular components S together constitute the total reflected light, so that $S + D = T$. Occasionally one talks of S/T and D/T ratios and the former is sometimes also called specular reflectivity. This would be appropriate in comparing aluminium with chromium plate where S is relatively low because T is only 65%, whereas the S/T values would indicate better how close to a mirror finish each was.

Geometric attributes

The basic instrument for measuring the geometrical pattern for light reflection which determines appearance is the goniophotometer, which for a beam of light incident at a specified angle is able to measure the intensity of reflected light at every angle to obtain a complete polar curve, or goniophotometric curve. R.S. Hunter[249] found in 1937 that the term gloss was employed for a variety of attributes and he was able to define six 'types of gloss':

(a) freedom from haze
(b) distinctness of image gloss
(c) contrast gloss or lustre
(d) directionality
(e) surface uniformity
(f) specular gloss.

Hunter[250] has more recently summarised the various terms that have been used for metallic surfaces (Table 12-23) and has found little cause to modify his original categories of some 33 years previously.

Haze is distinguished on an otherwise specular surface as a cloudy grey background by small amounts of light reflected at angles far from the specular beam. The word 'brightness' is often used to describe freedom from haze; it has also been used as synonymous with specular reflectivity, and for total reflectivity. Brightness is in short a very much overworked word.

TABLE 12-23

Intercomparison of terms from different sources to describe the geometric appearance of metals[250]

Source	Metals Industry Terms					
		Brightness of bright finishes		Lustre of diffuse finishes	Uniformity of both types of finishes	
Hunter 1937 'six types of gloss'	freedom from haze	distinctness-of-image gloss	specular gloss	contrast gloss	absence of surface texture	absence of directionality
Tingle and George (between haze and distinctness of image. Tingle and George identify an attribute they call bloom)	freedom from haze	freedom from image blur		diffuseness or mattness		
Robinson	whiteness	image clarity			microlinearity	macrolinearity
Glubish		distinctness-of-image gloss	specular gloss as indication of glare	lustre		directionality
Hunter 1970 metals proposal	freedom from haze	distinctness-of-image gloss	specular gloss	contrast gloss	absence of surface texture	directionality

Distinctness of image, or *image clarity,* refers to the sharpness with which the outlines of a reflected image are seen. Two surfaces of equal specular reflectivity may differ appreciably in this respect because one may spread light over a slightly wider angle to give a confused image but still within the specular cone as arbitrarily defined.

Lustre, or *contrast gloss,* is a property which distinguishes two diffuse surfaces one of which will show a large change in brightness of reflected light as the viewing angle is altered but with no visible reflected images. It is generally appropriate to metallic surfaces.

Directionality is a very frequent attribute of aluminium surfaces and can be due to rolling lines which are impressions of the roll profile, die lines on extruded sections, finishing or polishing lines, metal structure, etc. It is one of the dominant visual effects and any other measured optical property may be influenced by the direction in which a measurement is made.

Surface uniformity, or *texture,* relates to variations of the optical properties from point to point which can relate to impressed patterns, coarse grain in the form of 'orange peel', etch patterns, etc.

Specular gloss has been defined above.

It is possible to make some sort of measurement of most optical properties but the visual appearance is largely a subjective appraisal in which all of the various attributes take part as the observer alters his angle of viewing and quickly integrates the whole complex into one, often irrational, assessment. What is required is to define, in any particular context or for any specific purpose, which attributes are appropriate, and to see whether a measurement is relevant.

Total reflectivity

The Guild Meter[251]

Consideration of the mechanics or optics of total reflectivity measurement indicate that this requires some form of integrating sphere or enclosure with a completely reflective interior in which a relatively small aperture is open to the test surface, and another small aperture holds the photoelectric cell for measurement. Such an instrument is the Guild Photometer designed at the National Physical Laboratory on rigorous physical principles and with accompanying formulae to take the various correction factors into account. It is essentially a laboratory instrument, rather tedious to use and hardly ever encountered now, but it should be observed that this provides an exact measurement of the physical property of reflectivity. The incident light, through a third aperture, is at 36° and the photometer is equipped with a light trap that can when required intercept the specular beam

and measure only diffuse reflectivity, and the specular component by difference. It should be noted equally however that in this mode of operation the instrument is no longer an absolute one because the geometry of the specular cone is an arbitrary selection, and in point of fact the Guild Photometer has largely been demoted from measurement on aluminium because the specular beam does not accord closely enough with the visual requirements for bright anodized aluminium.

The Guild meter is shown in Fig. 12-42. **A** is a hollow sphere of spun copper 152 mm (5.98 inch) in diameter, made in two halves and with peripheral flanges which are butted together and held by screws. Its inner surface is covered with magnesium oxide. **A** 13 mm diameter aperture B is cut into the sphere and a flat sole plate C, 100 mm in diameter, is attached. The axis of the tube D, which is lined with black paper, is set at 36° to the vertical and carries the lens F (focal length 50 mm) and an elliptical diaphragm which reduces strong light from the 12-14 volt, 48 watt clear gas-filled lamp E. This lamp has a 9 mm filament and is mounted in the cylindrical lamp house so that the filament is parallel to the major axis of the diaphragm. **A** separate tube slides on the tube D to hold the lens for the initial adjustment. The shutter J is attached to a lever K and is operated by a handle L.

The instrument is placed on the test piece G which covers the aperture B. The illuminated part of the specimen acts as the light source shining into the whitened sphere. The illumination in the sphere is then indicated by a rectifier photo-cell H connected to a galvanometer.

In the case of a perfect mirror, the whole of the incident light is specularly reflected and the beam will be that indicated by the dotted lines. If the shutter is turned so that the blackened cavity interrupts the beam, none of the light will reach the walls of the sphere. If the shutter is turned so that the beam strikes the white surface next to the aperture, all the light is reflected into the galvanometer. If, on the other hand, all the reflectivity is diffuse, turning the shutter from one position to another will not affect the illumination. The total reflectivity T is given quantitatively by the following equation:

$$T = \frac{D+S}{D_m} = \frac{\tau}{\tau_m} \times \frac{\beta - \alpha - (\beta - 1)\delta/\tau}{1-\alpha}$$

and S/T by $\dfrac{S}{D+S} = 1 - \dfrac{D}{D+S} = 1 - \dfrac{\delta}{\tau} - \tau$

where D is the light diffusely reflected at B, S the light specularly reflected at B, D_m the total light reflected by a MgO surface, α is the fraction of S still operative when the shutter is set to absorb the specular cone, β is the ratio of the effectiveness on the photo-cell of a unit of light from the aperture B to that of a unit of light from the surface of shutter J, δ and τ are the galvanometer deflections when the shutter cavity and the white surface of the shutter respectively intercept the specular cone, and τ_m is the galvanometer deflection of an MgO surface.

In practice. approximate values can be obtained by using only the terms $1 - \delta/\tau$ and τ/τ_m.

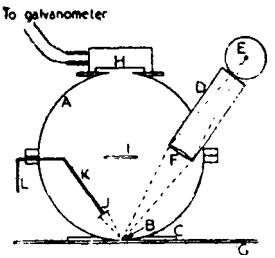


Fig. 12-42. Diagram of Guild meter

The limitations of the Guild Photometer for specular reflectivity were discussed by B.A. Scott[252] who indicated that the relatively large acceptance angle of 0.2 steradians for the specular beam gave insufficient distrimination and proposed a different method whereby this angle was reduced to a cone of 0.001 15 steradians of solid angle. The more rapid method for measuring total reflectivity noted below was also introduced at the same time.

Mark III Reflectometer

Total reflectivity can also be measured with the P.R.S. Head described in BS 6161: Part 11: 198.5. The apparatus was originally designed, in cooperation with the Paint Research Station, for the measurement of brightness or paint opacity.

This instrument (seen in Fig. 12-43) has a circular photo-cell, about 4.5 mm (1% inches) in diameter, with a central hole about 8 mm ($^5/_{16}$ inch) in diameter, which is mounted parallel to the test surface and a short distance away, about 5 mm (0.2 inch). The circular aperture is illuminated by a 3 W lamp, and a diffusing screen. The contacts of the photo-cell are connected to a galvanometer fitted with a variable shunt.

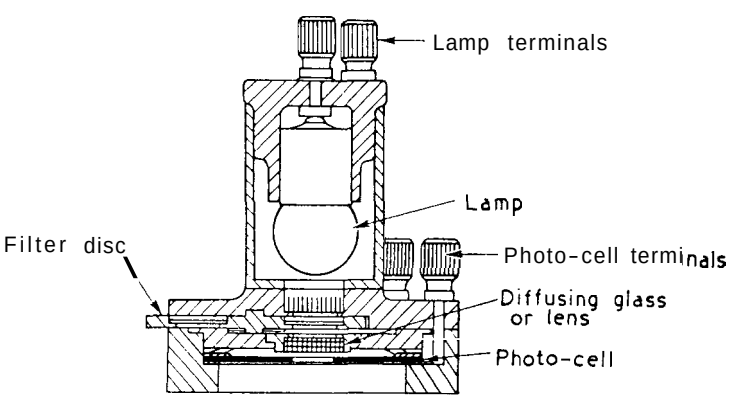


Fig. 12-43. E.E.L. Mark III Reflectometer

In the original instrument, various filters could be interposed into the beam by means of a rotating wheel. For this measurement, a neutral filter could be employed to avoid overloading the galvanometer.

To calibrate the instrument, it is placed with its base in contact with a freshly-scraped plane-surfaced block of pure magnesium carbonate, and the galvanometer sensitivity is adjusted to 100 units on the scale. Alternatively, a plane surface of white vitreous enamel or opal glass of known total reflectivity may be employed as a sub-standard which should be checked periodically against the magnesium carbonate surface.

The instrument is then placed on the flat test surface, when the galvanometer reading gives the total reflectivity as a percentage of that of magnesium carbonate. Four readings are taken at different points on the surface, and the mean value recorded. Repeated mean readings on the same surface should not differ by more than 1%.

The total reflectivity of bright anodized aluminium measured by this method will be about 85%, while lower values of 70-80% will be obtained on diffuse finishes or etched and anodized surfaces. The whole range of brightness down to about 5% is obtainable depending on the anodizing electrolyte, alloying constituents, metallurgical state and surface preparation. The lowest values can be obtained with certain silicon alloys, with hard anodizing or integral colour anodizing of alloys containing copper and manganese where the colour is almost black. The Mark III reflectometer has been used most successfully in fact with the medium or dark grey finishes, and also with bronze colour finishes where the results are meaningful for depth of colour control because only variations in shade of one basic hue are involved. It has also been used in conjunction with dye absorption tests for sealing in the same manner, and Sautter[154] has found it useful here to set the instrument to read 100% on the surface before testing.

It is one of the limitations of the Reflectometer that it requires a test area of about 45 mm^2 which is reasonably flat, and no external light must be allowed to fall on the photo-cell. The instrument is in fact supplied with a metal mask with a smaller aperture that allows it to be placed on a smaller area, but the readings obtained in this manner are not the same and are not total reflectivities according to the British Standard. It is better in this case to use the Head to compare two samples of similar texture and reflectivity.

Values shown in Table 12-24 for the total reflectivity of anodized aluminium as measured with the Guild Reflectometer have been given by Pearson and Phillips.[253]

TABLE 12-24

Total reflectivities obtained with Guild Reflectometer

Film thickness	2 μm	5 μm	10 μm
99 99% aluminium	84	84	84
99 8% aluminium	82	83	–
99 5% aluminium	80	79	77

Using the Mark III reflectometer Scott[254] obtained the values shown in Table 12-25, with material anodized to a range of thicknesses.

TABLE 12-25

Total reflectivities obtained with Mark III Head

	2	5	10	15	20 μm
99.99% aluminium	90	90	89	88	88
99.8% aluminium	89	88	87	86	84
99.5% aluminium	86	84	81	77	73

No correlation between these methods of measurement has been attempted. The above measurements are separated in time by a good many years, the precise composition of the lower purities is not recorded, and whereas the Guild instrument employs an angle of incidence of 36°, the light is normal to the surface in the case of the Mark III Head.

Gardner Hazemeter

A further apparatus which has been used to a considerable extent in the U.S.A. for measurement of reflectivity is the Gardner Pivotable Sphere Hazemeter which was modified by Barkman[255] to be particularly applicable to aluminium surfaces. It has much in common with the Guild Photometer in that a totally white coated sphere is used for integrating the reflected light, but in this case the incident light is projected through an aperture (Fig. 12-44) to fall normally on the surface.

In one position of the sphere the specular light is returned back through the aperture of entry, whose geometry is such that any light within ± 4" of the normal is defined as specular, and the sphere with photo-cell picks up only the balance or the diffused light. Then by rotating the sphere through an angle of 8°, the specular light is also caught within the sphere and the total reflectivity is then measured. Certain correction factors are applied as in the case of the Guild Photometer.

The light source is a filament lamp with combined blue and amber conversion filters designed to give a transmittance curve closely approximating to the visual response of equal energy light at various wave lengths. The optical principles are relatively simple, but the instrument also has provision for splitting the light source into two components and using two balanced photo-cells whose output is automatically compared, thus taking into account any variations in the power output of the source, and the percentage reflectivity is recorded on automatically controlled dials. These auxiliary attachments for dispensing with an operator add considerably to the cost of this instrument.

Use of this type of integrating sphere instrument for measuring total and diffuse reflectivity has been standardised internationally as ISO 6719: 1984, and EN 12373-12: 2000 (formerly also ASTM E429 in the U.S.A., but discontinued in 1996).

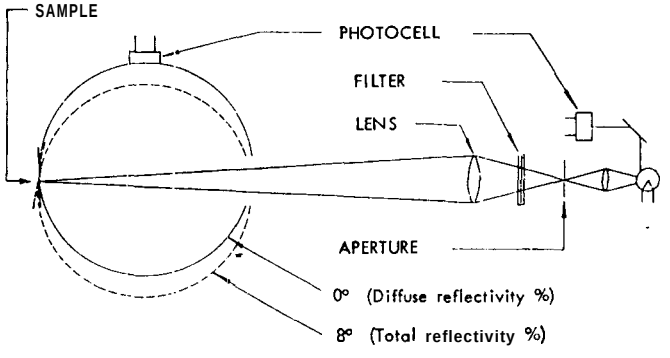


Fig. 12-44. Gardner Hazemeter

Specular reflectivity

This term has been discussed above and it has been indicated that it may be measured with the Guild Reflectometer and with the Gardner Hazemeter. Barkman defines it, in the same way as Guild, as $(R_t - R_d)/R_t$ or R_s/R_t, but R_s can equally define it in the case of bright aluminium surfaces for which variations in R, will be very small.

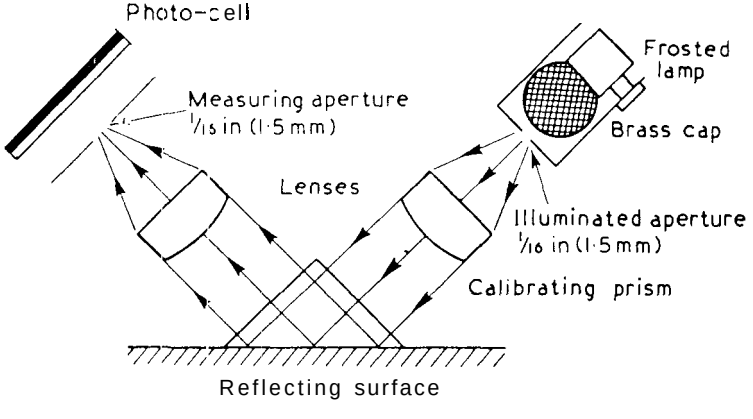


Fig. 12-45. Modified Gloss Head

Modified Gloss Head

As will be discussed later the Modified Gloss Head method has now been incorporated in more complex specular reflectivity standards, but it originated in the U.K. and is still widely used there. It was described in BS 1615: 1972, Appendix Q, where the specular reflectivity was measured by the Modified Gloss Head shown in section in Fig. 12-45. It was also known as the Metspec Head and was a modification proposed by Scott[252] of a gloss head specified in Defence Specification DEF 1053 to render it more sensitive to small departures from a mirror finish.

The light from a frosted 3 watt bulb is used to illuminate the 1.5 mm ($^1/_{16}$ inch) aperture at the focus of the lens. The resulting parallel beam of light **is** reflected from the surface of the specimen held flat against the base of the instrument. Angles of incidence and reflection are 45° and the beam is turned through 90". The reflected light is brought to a focus by a second lens, forming an image of the illuminated aperture which just fills the hole in an orifice plate. The intensity of the light emerging is measured by a photo-cell with galvanometer indication and a variable shunt to adjust sensitivity. The lenses should be cemented achromatic doublets working at a relative aperture not exceeding f/3 while the photo-cell should be mounted sufficiently far from the orifice plate for the illuminated area to be about 20 mm (¾ inch) in diameter. The position of the illuminated aperture is adjustable for focusing and alignment by means of three screws in the base of the lampholder.

In the test, the illuminating system is adjusted to provide an evenly illuminated sharply focused circular spot of light at 3 m (10 feet) distance. **A** sheet of plain glass through which the orifice plate can be observed is held against the base of the instrument, and the aperture is aligned so that its image exactly coincides with the hole in the orifice plate. The aperture is then adjusted for maximum indication with each screw in turn.

The reference surface as proposed by Thomas is the hypotenuse face of a 45° right-angle prism with total internal reflection of the incident light. The absolute specular reflectivity must be known (e.g. 90%). To calibrate, the hypotenuse face is placed in contact with a plane sheet of anodized aluminium, and the gloss head is placed over the prism (without fouling it) with its base on the sheet. The galvanometer sensitivity is adjusted to give an indication of n units on the scale, where n will normally be 90.

The reflectivity of the sample, which must be flat, is then measured by placing the gloss head with its base firmly in contact with the surface under test, and noting the galvanometer reading. At least four readings, two each in two directions at right angles, should be taken on each specimen, and the mean value recorded. Repeated mean readings should not differ by more than 1%.

Discussion on results obtained with Gloss Head

Specular reflectivities, as measured with this instrument, of 75-99% will only normally be achieved with super-purity aluminium (99.99% Al). 1080A

(99.8% **Al)** can provide values up to 85% when polished and brightened but these will drop on anodizing to 50-75% depending on anodic film thickness and method of anodizing. It will be found that surfaces with values above 60% possess good image clarity and can be called mirror finishes (with perhaps a little liberty in the use of the term) while below 60% there is a very noticeable deterioration in image clarity, so that in practice minima of about either 60% or *55%* are set according to application. Below 50% the Modified Gloss Head no longer gives visually meaningful results, and specular gloss in these regions is better determined by the original Gloss Head as specified in DEF 1053.

Scott[254] has reported the values, obtained with the Modified Gloss Head on super purity aluminium and two lower purities, shown in Table 12-26. These sheets were rolled to a reflector grade so there would be no intluence of surface texture, mechanical distortion or other artefacts, and the values represent the best values obtainable with good anodizing practice, but this does not mean that variations of composition within the allowable composition tolerances, or changes in metallurgical history. could not influence these figures upwards or downwards.

TABLE 12-26

Specular reflectivity of anodized aluminium[254]

anodic film **thickness** *(μm)*	*0*	*2*	**5**	*10*	*15*	*20*
99.9% Al	90	87	87	86	85	84
99.8% Al	88	68	63	58	53	47
99.5% **Al**	75	50	36	26	21	15

Using the above noted criteria for good image clarity, it will readily be seen that in the case of 99.8% metal, and this will also apply to bright anodizing alloys containing magnesium and based on this purity, one needs to stop anodizing at a thickness below 10 μm, which is the usual practice with automotive trim for instance. With 99.5% purity, although a good minor finish can be obtained on polished or brightened sheet, the mirror finish is lost before 2 μm of anodic film are applied.

It has been indicated above that the concept of specular reflectivity is one that is arbitrarily defined. In the case of the Gloss Head, Scott set about defining suitable parameters by preparing a series of surfaces which started with the best mirror finishes on Brytal treated 99.99% aluminium that could be prepared, and declining gradually with variations in grain, ripple and haze to semi-diffuse surfaces. These were ordered by a visual assessment made by several observers to correspond with specific requirements, i.e., bright trim for decorative applications.

Measurements were then made using a series of acceptance apertures in the Gloss Head, the incident beam having been made parallel light from a source of small area focused at the plane of the aperture. When using large apertures the bright finishes tended to have values close to each other with poor discrimination, and these spread out more as the aperture was decreased while the diffuse finishes then congregated together, but the bright finishes did not have the same order of merit for each aperture. Scott selected 3 mm as the one which best correlated with visual assessment; the smaller ones were evidently picking out features which were too insignificant. This indicates the essentially subjective nature of the specular attribute. Fig. 12-46 shows results on five surfaces for various aperture diameters. A correlation was made with both the Guild Meter and the Gardner Hazemeter[255] and the sensitivity in the bright range of the Gloss Head was found to be greater, while it also sorted out degrees of image clarity as variations in specular brightness, which neither of the other instruments did with certainty.

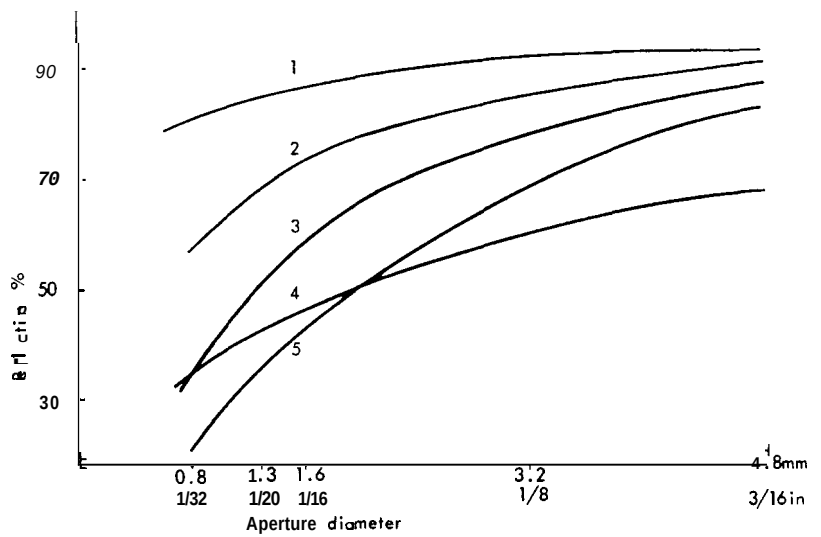


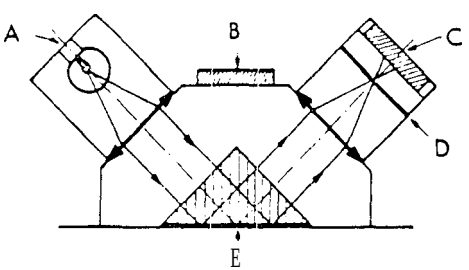
Fig. 12-46. Variation of specular reflectivity with aperture of measuring instrument?"

One penalty to be paid for this sensitivity, however, is that the sample must be perfectly flat and correctly positioned or very large errors can result. This is the largest source of error because a great many surfaces in which one may be interested do not have the requisite flatness, and no amount of pressure on the head will rectify it. An approach to the correct value can sometimes be made by carefully tilting or positioning the head, because the maximum reading obtainable is the most nearly correct one; it is not possible to obtain too high a reading.

Measurement of specular reflectivity was originally standardised in ISO 2767: 1973, but this was later divided to cover specular and total reflectivity separately. In the case of specular reflectivity the 45° measuring head was combined with the 20°, 60" and 85° angles used for measuring gloss on paint finishes and previously described in ISO 2813: 1978. This new specular reflectivity standard became ISO 7668: 1984. Inevitably it has become a much more complicated standard, but the details and use of the 45" gloss head are essentially the same as previously. This method was later standardised in the U.K. as BS 6161: F'art 12: 1987 and replaced now in Europe as EN 12373-11: 2000.

Dr. Lange optical head

Drapier and Lelong[256] have considered that two measurements are necessary to describe the optical attributes of aluminium surfaces, particularly those that are employed in general architectural work. This involves specular gloss, but measured with a 45° head of the type employed in DEF 1053 rather than the High Gloss head as modified by Scott, and also a measurement of diffused or scattered light which can be incorporated into the same measuring device according to the system devised by Lange and illustrated in Fig. 12-47.

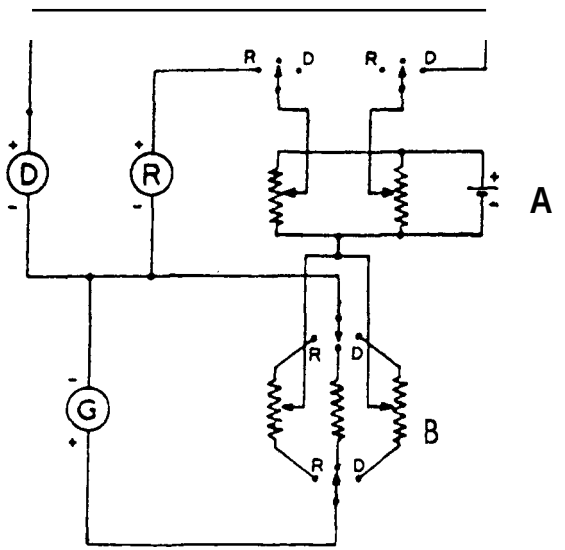


A Lamp
B Diffusing cell
C Reflecting cell
D Diaphragm
E Right angle prism

Fig. 12-47. Schematic drawing showing the optical head of the reflecto-diffusometer (Dr. Lange optical head).[256] **A** total reflectivity prism is also shown in position for reflectivity calibration

The lamp housing can in fact be demounted and fixed to the base so that the incident beam falls directly into the photoelectric cell to measure its intensity, but it is simpler to follow the practice of the British Standard in using a prism of known reflectivity as a standard. **A** magnesium carbonate block is also employed as a standard for the diffuse reflection.

An area of 1-2 cm^2 is illuminated. The principles of the circuit used are shown in Fig. 12-48.[256] Lelong and Segond[257] have described in considerable detail the use of this instrument to control the appearance of anodized aluminium at large plants in France.



A Zero shift
B Sensitivity range

Fig. 12-48. Schematic drawing of the measuring circuits in the reflecto-diffusometer[256]

Robinson Photovolt meter

The simple Photovolt 45 deg 0 min reflectometer designed by Robinson is shown in Fig. 12-49.[258] It is similar in principle to the P.R.S. Head but uses a beam of light so that only diffuse reflectivity is measured by the cell. Robinson used it to measure what he termed 'whiteness', which has also been called 'greyness' and would correspond to 'haze' on a bright surface if using the terminology defined above.

It has been used in France for measuring reflectivity of etched surfaces used in architectural applications, and was internationally standardised as ISO 5 190: 1983. Like the P.R.S. Head, it has not been converted into a European Standard, and ISO 5 190 was withdrawn in 1991.

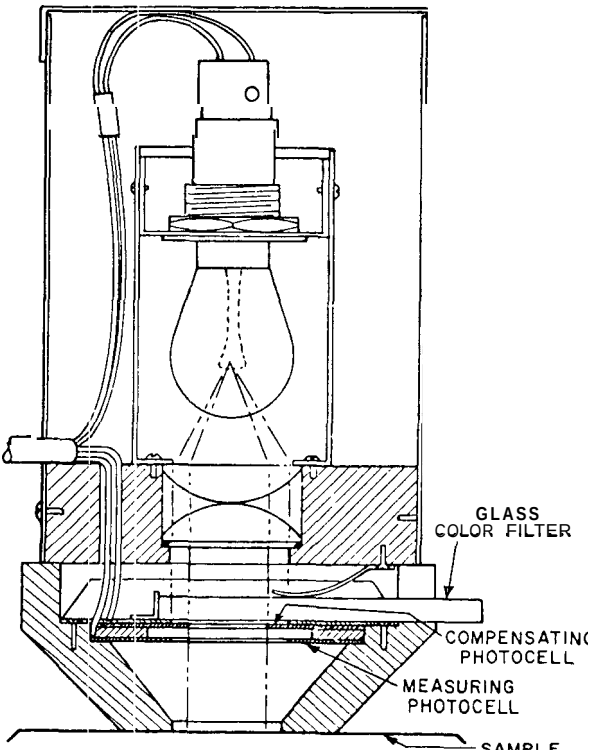


Fig. 12-49. Optical head of the Photovolt reflectometer[258]

Distinctness of image (Image clarity)

illuminated grid method

A simple direct test of the clarity of a reflected image in a bright surface is to view the reflected image of an illuminated grid or some other pattern of parallel lines in the surface, which is held in the hand by the operator who increases his distance from the grid until the pattern can no longer be resolved. The distance from the grid is then proportional to the image clarity.

Methods of this type were widely used for many years, and the method specified in BS 6161: Part 13: 1987, is attributed to the late Dr. Gardam. It consisted of an oblong box open at one side which could be filled in with a glazed screen suitably marked out with black stripes as shown in Fig. 12-50. This was illuminated from behind with a strip light covered by frosted or pearl glass. Two

grids were available, a coarse grid to BS 1669 of 9 mm pitch and a fine grid of 4 mm close pitch. The latter was preferable for specimens of good image clarity, and the former for those where the image clarity was not good. It was important of course for the operator to have normal eyesight (with glasses if worn) and normal optical accommodation.

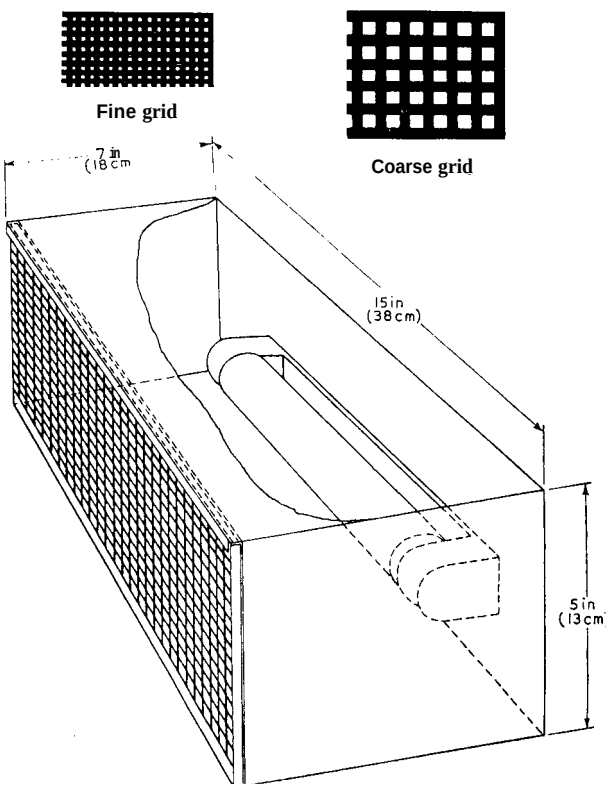


Fig. 12-50. Gardam Grid

The outstanding advantage of this test was that it could be applied to curved specimens up to a point, which is a facility that even the most sophisticated instrumentation cannot achieve. Scott once constructed a 'vest-pocket' test consisting of the gapped circles used by opticians, photographed at seven reductions and these were held at a fixed distance from the surface and the number of the smallest one noted which could just be resolved (Fig. 12-51).

Most recently Suga in Japan[259] has described a system of parallel lines of different thickness and spacing, which can be reflected in an anodized surface, and his method is shown in Fig. 12-52. Lines of Grade 7-11 would be used for evaluating surfaces of good image clarity, and Grades 1-6 for less clear surfaces. This method has been standardised as ISO 10215: 1992, EN 12373-14: 2000 and BS 6161: Part 13: 1093, replacing the Gardam Grid in the latter standard.

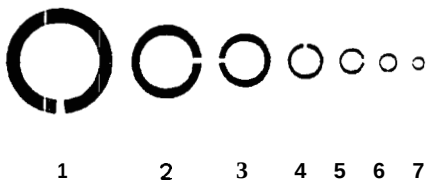


Fig. 12-51. Gapped circles for assessment of image clarity (B.A. Scott)

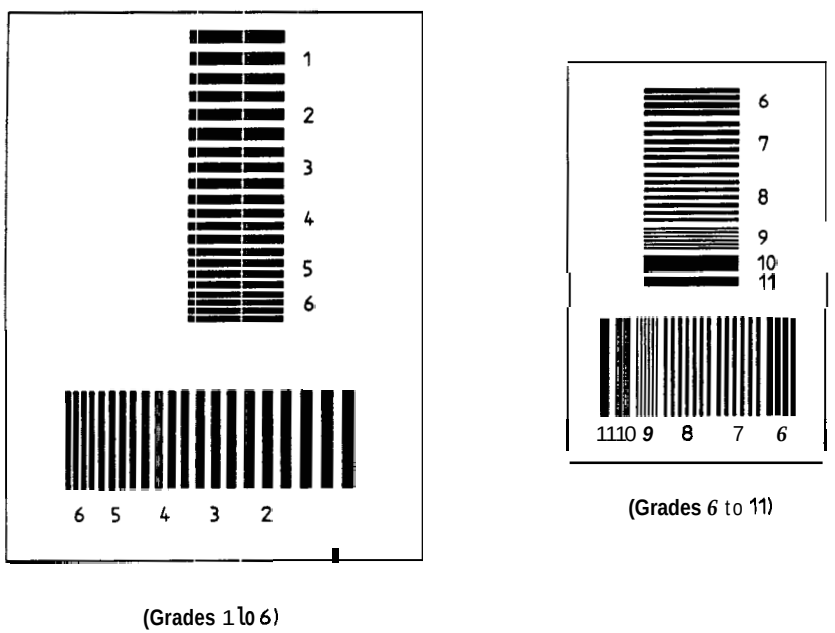


Fig. 12-52. Chart scale proposed by Suga[259]

The DORI meter

The most difficult instruments to make are in fact those for measuring the sharpness of a reflected image, because of the high angular resolution needed. Tingle and Potter[260,261] of Alcoa have described an instrument for doing this which they called the DORI meter, the letters standing for Distinctness Of Reflected Image. A diagram of the optical arrangement is shown in Fig. 12-53, the light source consisting of a pair of closely spaced illuminated slits whose image is reflected by a flat portion of the sample under test onto a single receiver slit located midway between the two bright mirror images. The centres of the bright images are only 0.3° apart and of course the amount of light which reaches the dark spot between them is proportional to the image clarity, being zero for a perfect mirror surface. Measurements are made by scanning the image and expressing the result as the ratio between the brightness of the slit and the darkest spot between the two.

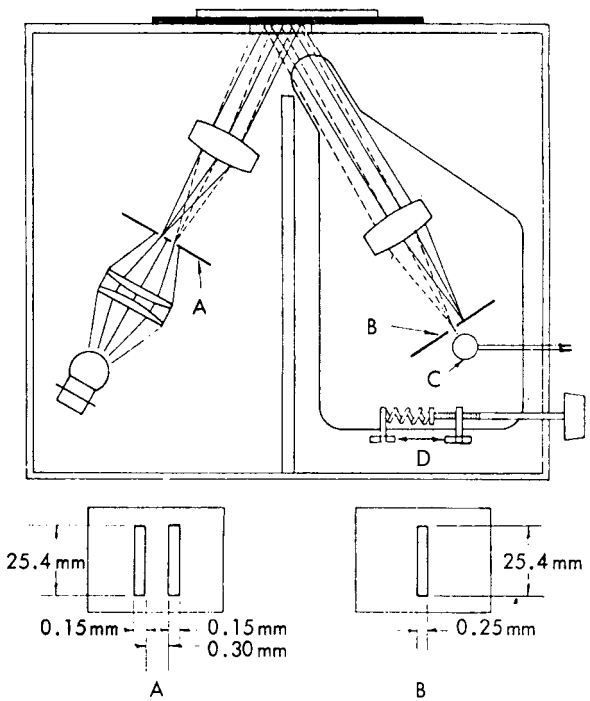


Fig. 12-53. DORI meter for measuring image resolution[260]

A. Primary slits
B. Scanning slit
C. Photocell
D. Scanning

Abridged goniophotometer

Some time later Tingle and George[262] constructed what they called an abridged goniophotometer for measuring the attributes of metallic surfaces. A goniophotometer is of course a versatile instrument with which complete polar curves can be constructed for any angle of incidence, and such a meter is the Hunterlab D10. In the Tingle and George model the light from a narrow slit is incident at a fixed angle of 30" and arrangements are made to measure the light reflected at the specular angle, and also at angular distances from it of 2, 5, 10, 15 and 20°, comparing the latter measurements with the flux intensity of the mirror image itself. They called the ratio for the 2" angle bloom; for the 5° angle haze; and for the 15" angle diffuseness or mattness. The use of the abridged goniophotometer for anodized aluminium is described in ISO 7759: 1983, EN 12373-13: 2000 and ASTM E430-97.

Hunterlab D36 meter

Both the brightness and image clarity can be measured by the Hunterlab D36 meter, which is based on a design by Middleton and Mungall[263] and is illustrated in principle in Fig. 12-54. The light from a very narrow slit C illuminated by a source A through a lens B forms an image in the plane F by projection through the lens D. A rotating slit wheel F in the receptor assembly carries 130 slits per second past the reflected image and is arranged so that each slit scans the reflected image repetitively. The photoelectric signal is therefore a small segment of the goniophotometric curve of the specimen, approximately 3" to each side of the specular centreline. The electronic circuitry is designed to measure the signal peak, and the slope of maximum rate of change of the signal with angle. As with other instruments a great deal depends on holding the sample flat and in the correct position. The dimensions of the slits are chosen to simulate the angular resolution of the human eye, and good correlation has been obtained between the results given by the instrument and visual inspection of bright anodized aluminium specimens.

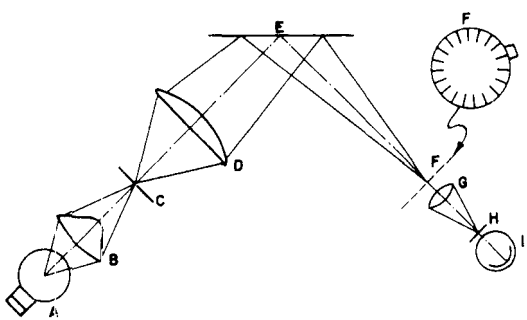
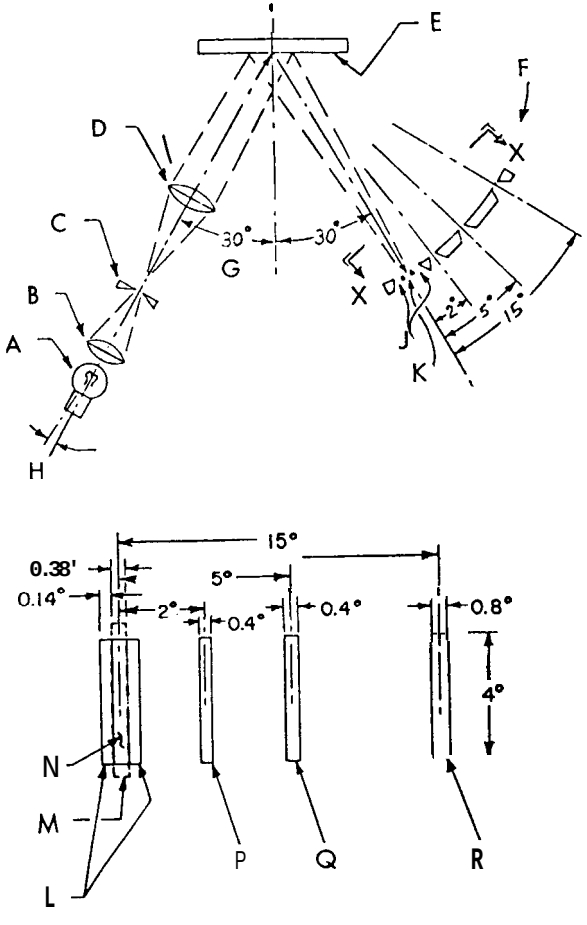


Fig. 12-54. Optical diagram of the Hunterlab D36 Distinctness-of-Image Glossmeter

A. Lamp	D. Source objective lens	G. Collector lens
B. Condenser lens	E. Specimen	H. Diffuser
C. Source slit	F. Slit wheel	I. Phototube

The Dori-Gon glossmeter (Hunterlab D47)

Another addition to the catalogue of instruments for assessing metal surfaces has combined the functions of both the distinctness-of-image meter and the abridged goniophotometer into a single versatile machine which Hunterlab have called the Dori-Gon glossmeter (D47).[264,265] The optical system is illustrated in Fig. 12-55, where it will be seen that the DORI principle is inverted in that there is now a single illuminated source slit and two closely spaced receptor slits (D of I slits) which performed the image clarity-determining function. The R_s slit for specular reflectivity determination is critically positioned on the source image, and the adjacent distinctness-of-image **slits** cover an angle of ± 0.27". In addition there are three off-specular apertures at a greater angle, spaced at 2,5 and 15°, for the measurement of narrow-angle haze (bloom), wide angle haze and diffuse reflectance (see also ISO 7759: 1983 and EN 12373-13: 2000).



A. Lamp
B. Condenser lens
C. Source slit
D. Source obiect lens
E. Specimen plane
F. Image plane
G. Incident angle
H. Source arm centre line adjustment for maximum peak
J. D/I (± 0.27")
K. R_s (peak)
L. D/I slits
M. Source image
N. R_s slit
P. 2" slit
Q. 5" slit
R. 15" slit

Fig. 12-55. Optical diagram of the Hunterlab D47 DORI-GON glossmeter[264]

The Dori-Gon meter takes the advantage of fibre optics to collect the signal from each aperture by means of fibre bundles which convey it to a position on the arc of a disc where each one can readily be selected by means of a mask rotating concentrically with the disc. This allows a simple d.c. measuring system with precision and stability; the specular reflectivity is indicated directly and the other properties as percentages of R_s. One of the important features of this instrument is considered to be the specimen clamping turret designed by Robinson of Alcan to hold the specimen flat and rigid, and also permit a rotation through 90" for measuring directional properties.

The Suga Image Cllarity Meter

The optical arrangement for the Suga apparatus is shown in Fig. 12-56. Light comes through a first slit, which serves as a light source, and it is converted to parallel light through a first lens (collimator), is reflected at the surface of the test piece, which is set at 45" to the light beam, and is then focussed at a combed shutter through a second lens (condensing lens). If the test piece has a completely flat and smooth surface, the reflected light beam is concentrated as a sharp image of the first slit at the combed shutter when the shutter is slid laterally. When the centre of the comb space coincides with the image, the beam passes completely through the space of the comb and generates a signal maximum on the photo-receiver. Otherwise the beam cannot pass through the comb completely and generates a lower signal, depending on the degree of dispersion of the light. This signal corresponds to the image clarity. (Opticalevenness is shown by the ratio of the longitudinal and transverse values.

This is a sophisticated method of measuring image clarity which is used in Japan, and it has been standardised as ISO 10216: 1992 and in the U.K. as BS 6161: Part 19: 1993. The method was examined in comparison with specular gloss and glossiness measurements in a study by Czepluch, Suga and Sheasby.[266] In this work the concept of glossiness was a new one in relation to anodized aluminium, and was defined as the light reflected in an annular region around the chosen angle that was measured, an opaque diaphragm eliminating the light in the central region. It was felt that this method could give closer correlation with visual evaluation of bright anodized aluminium, and the ,apparatus for the measurement was proposed and tested. This was very similar to the specular gloss measuring apparatus of ISO 7668, but modified to give the annular measurement as described above. Such equipment has been manufactured in Japan, but so far has not been used elsewhere.

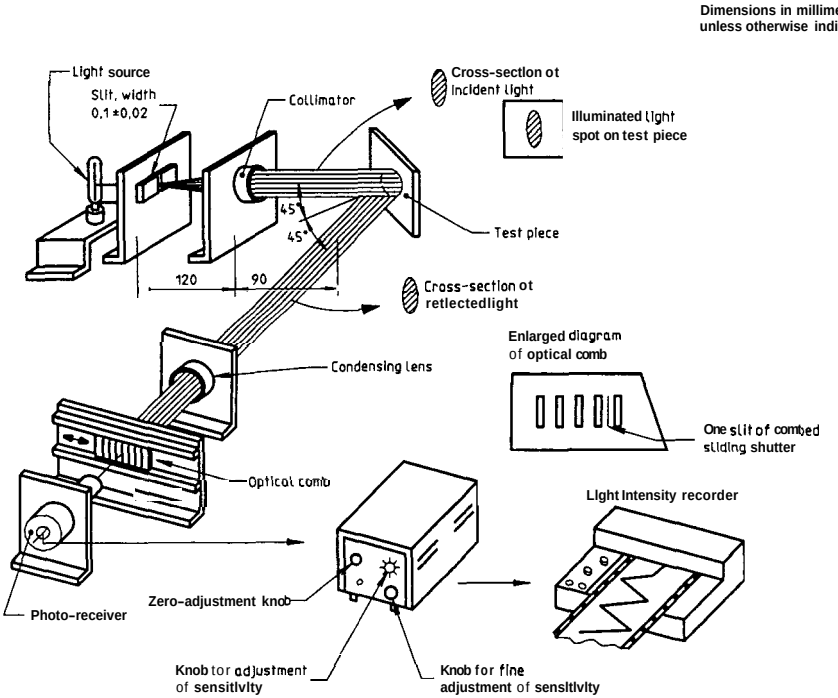


Fig. 12-56. Testing apparatus for image clarity measurement (Suga)

Colour measurement

From the foregoing discussion on reflectivity it can be seen that this is a complex subject with anodic coatings, and the introduction of colour into the film makes it even more so. In practice this has made colour measurements in production plants largely impractical, and most coloured work is still matched by eye to agreed colour limit samples. **A** major factor in this is that the visual colour seen is dependent both on the actual colour of the work, and on the surface texture. Thus samples produced to the same colour on polished and etched surfaces will look completely different, and control of etch texture is a very important factor in ensuring a consistent appearance with colour anodized work.

Gardam[267] measured the colour of dyed anodic finishes using a reflectance attachment on a Unicam SP 500 spectrophotometer, and showed that satisfactory colour measurements could be made. His results for 1200 aluminium (2S) and 4043 alloy (33S) are shown in terms of the CIE colour triangle in Fig. 12-57. He concluded that the numerical results which could be calculated from the spectral reflectivity curves provided objective and permanent records of the colours, but the method used was not easily adapted to process control.

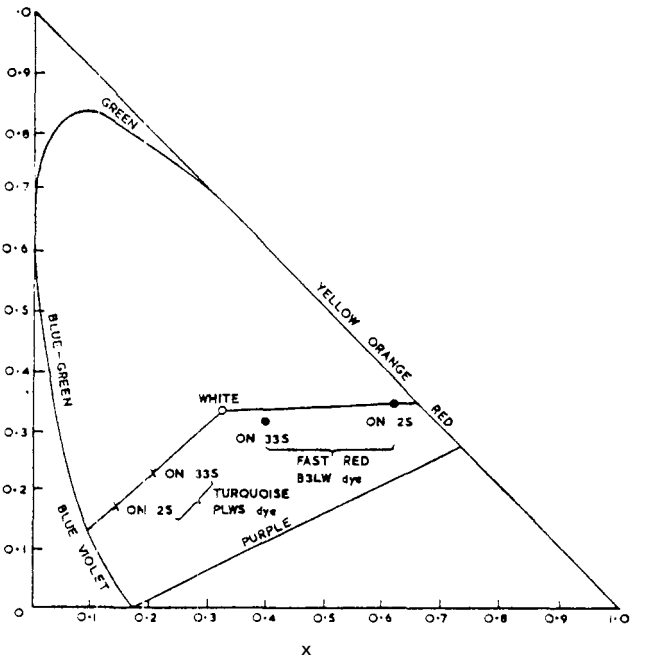


Fig. 12-57. Colour triangle showing position of colours of aluminium (2S) and aluminium-5% silicon (33S) anodized and dyed with turquoise PLWS or fast red B3LW dye[267]

In recent times electrolytic and integral colour bronze finishes have become dominant in architectural applications, and colour measurement with these finishes causes many problems. Work in Germany, however, appears to have been successful in devising a relatively simple instrument for colour control. The instrument concerned has been developed by Dr. Lange and described by Moller and Brücker.[268] They recognised the effect of surface roughness on colour evaluation and set out to eliminate this from the measuring process. This they did by making the measurements on a surface which was oiled or kept wet. A glass cover on the base of the measuring head minimises the liquid layer, and prevents the surface drying out. The measuring head is shown in Fig. 12-58 and has a source of light directed vertically onto the surface being examined, the light diffusely reflected, which is directly related to the colour density, being collected on an annular photo cell. The resulting photoelectric current is conducted through an amplifier to an analog or digital indicator, from which the determined values can be read directly. The instrument can be used at the colouring tank or on processed work and is

sensitive to very small colour changes. It is calibrated against a standard surface, or on samples indicating the colour limits which have been agreed, and it gives a comparative measure of colour rather than absolute values. The instrument is known as the Dr. Lange LFE 1 photometer

This instrument has been further developed to produce a device called the 'Color Pen', which is designed to be used on-line in conjunction with the control colour limit samples. As a result it comes with a removable plastic cover to protect it from process solutions (Fig. 12-59). The principle is the same as that for the LFE 1 Photometer, and the glass on the base of the protective cover compresses the wet film on the sample surface, again eliminating the effect of surface texture. Colour measurement is in the standard L, a, b units and colour difference in E units is also calculated. This is a practical colour measuring device which is quite widely used.

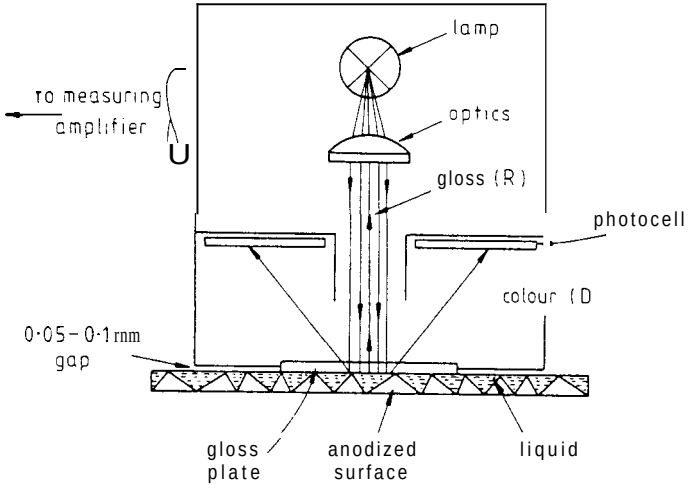


Fig. 12-58. Principle of Dr. Lange LFE 1 photometer[268]

Brace[269] has reported colour measurements on electrolytically coloured bronze finishes with three different colour measuring devices, the Lovibond Flexible Optic Tintometer Mk. 3, the Sheen Miniature Colorimeter and the Diffusion Systems Mk. III Reflectometer with C.E.E. filters. Of these the Mk. III Reflectometer, which has been described in the section on total reflectivity measurement, was considered the most suitable. The instrument for this purpose includes a rotatable filter wheel containing the three primary C.I.E. filters. Measurements are made with each of the filters in place, so that the X, Y and Z

C.I.E. values are obtained. Brace found that this instrument was least affected by directionality, for example on extrusions, but, as expected, colour measurements were affected by surface texture. He concluded, however, that for control purposes the instrument gave adequate differentiation with bronze finishes.

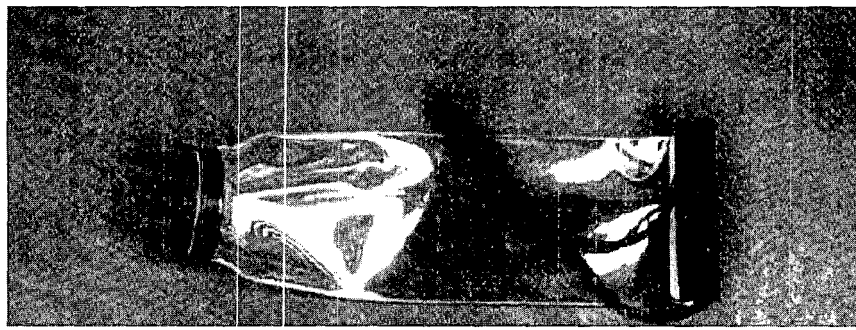


Fig. 12-59. Color pen with splash protection for use with colour anodizing

In recent times several anodizers have used the Minolta CM-2002 Spectrophotometer for practical colour measurement (Fig. 12-60). This is an integrating sphere instrument, the principle of which is shown in Fig. 12-61. It is possible to use it for measuring a variety of retlectivity attributes, but for colour anodized aluminium it is the standard L, a, b units that are normally used. As with the Lange head, it is essentially measuring total reflectivity.

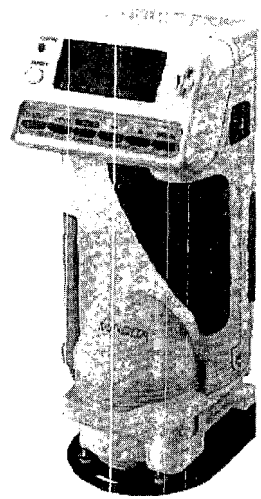


Fig. 12-60. Minolta CM-2002 photometer

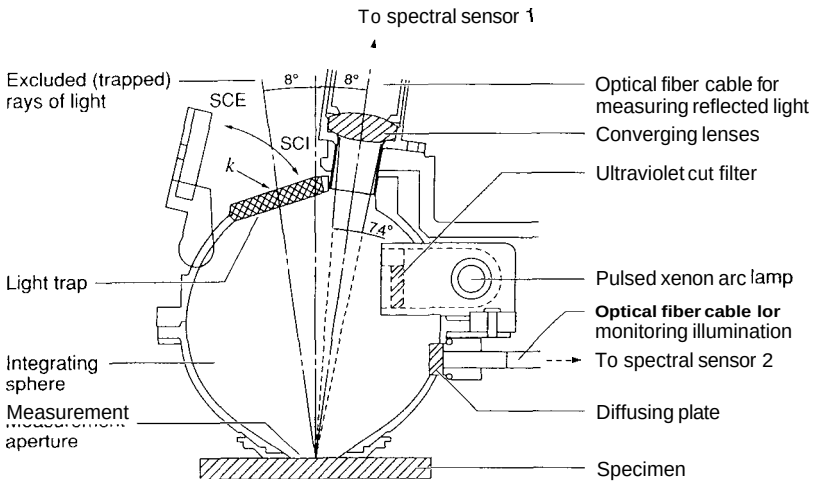


Fig. 12-61. Geometry of Minolta CM-2002 and specular component included (SCI)/specular component excluded (SCE) switching system

Many very sophisticated instruments exist for absolute colour measurement, but they are usually only suitable for laboratory use and suffer from the same problem as the simpler instruments in differentiating colour and texture. These sort of problems have prevented any international standardisation of colour measuring techniques so far, and ISO have produced a technical report (ISO TR 8125) indicating the difficulties involved.

Factors affecting reflectivity and image clarity

Image clarity is more important than reflectivity in determining the visual appearance of a bright anodized surface. The way in which image clarity, and incidentally some other properties, varies with anodizing conditions has been investigated by Cochran and Keller,[270] Scott,[271] Cooke[272] and Spooner.[273]

The effect of anodic coating thickness and anodizing voltage on the image clarity of 5557-H25 (strain-hardened) and 5557-0 (annealed) alloys is shown in Fig. 12-62. Of particular interest is the effect of anodizing voltage. Figs. 12-63 and 12-64 show how the image clarity, abrasion resistance and anodizing coating weight and ratio vary with voltage on 5357 alloy (0.8-1.2% Mg) and on 5557 alloy (0.4-0.8% Mg). The improvement in image clarity which is derived from anodizing at lower voltage and higher temperature is much more pronounced in the fully

annealed than in the hard condition. Other properties, such as coating weight and abrasion resistance on the other hand, are little if at all affected by the condition of the alloys.

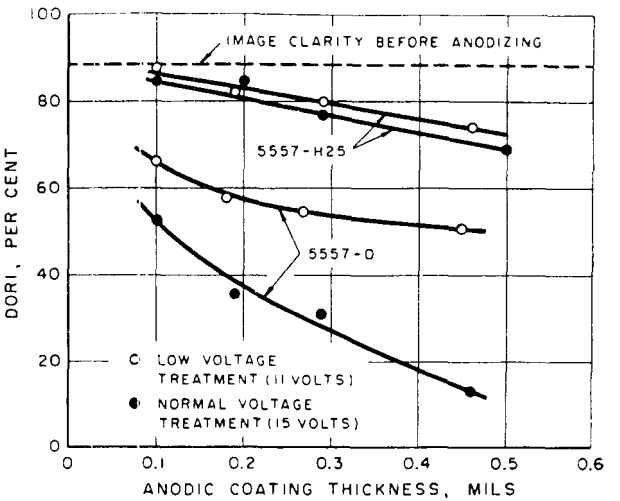


Fig. 12-62. Effect of anodic coating thickness and anodizing voltage on image clarity of 5557-H25 and 5557-O alloys.[270]

In these experiments, the voltage was decreased by increasing the operating temperature at constant current density, but similar curves are obtained when the current density is changed while keeping the temperature constant. Cooke[272] has shown that the change in properties is associated primarily with anodizing voltage rather than factors such as temperature, current density or acid concentration and his work has been described in Chapter 7 (page 473). Nevertheless Fig. 12-65, which combines results obtained by Cochran and Keller, shows that the curves are broadly of similar shape, but it is clear that the effect of high acid concentration at least is not to be explained solely by the reduction in voltage.

This effect of the anodizing voltage is ascribed by Cochran and Keller to the effect on the cell size and number of pores, and they suggest that when the best brightness and image clarity are required, a sulphuric acid concentration of 15-18% (vol) should be used at 29.5°C and 12 amp/sq ft (1.29 A/dm^2) with a voltage of 10-12 V.

Unfortunately, high image clarity and good abrasion resistance are to some extent incompatible and the low voltage method, in which the abrasion resistance drops by some 12-20%, should not be used where coatings of more than 10 μm (0.4 mil) are applied.

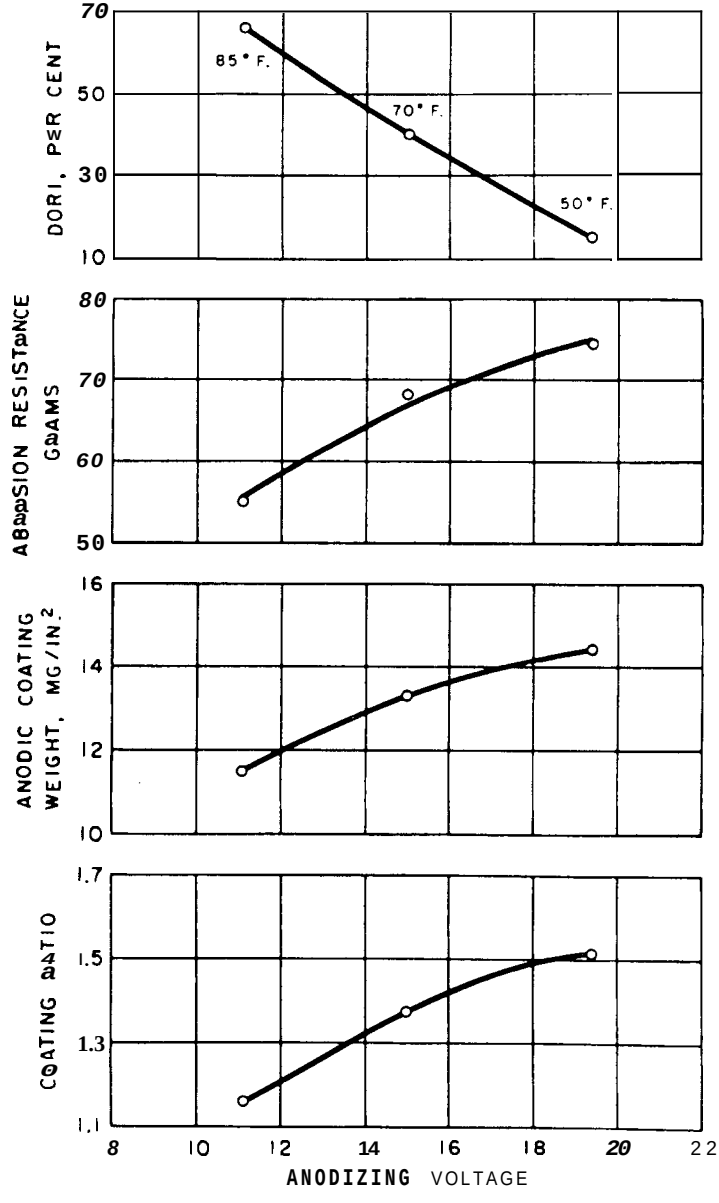


Fig. 12-63. Effect of anodizing voltage on image clarity (DORI meter), abrasion resistance, coating weight and coating ratio on a 0.3 mil (7.6 μm) sulphuric acid coating on strain hardened (5357-H25) Al-1.0% Mg bright anodizing alloy.[270]

50°F = 10°C 70°F = 21°C 85°F = 29°C 6.45 mg/in² = 1 mg/cm²

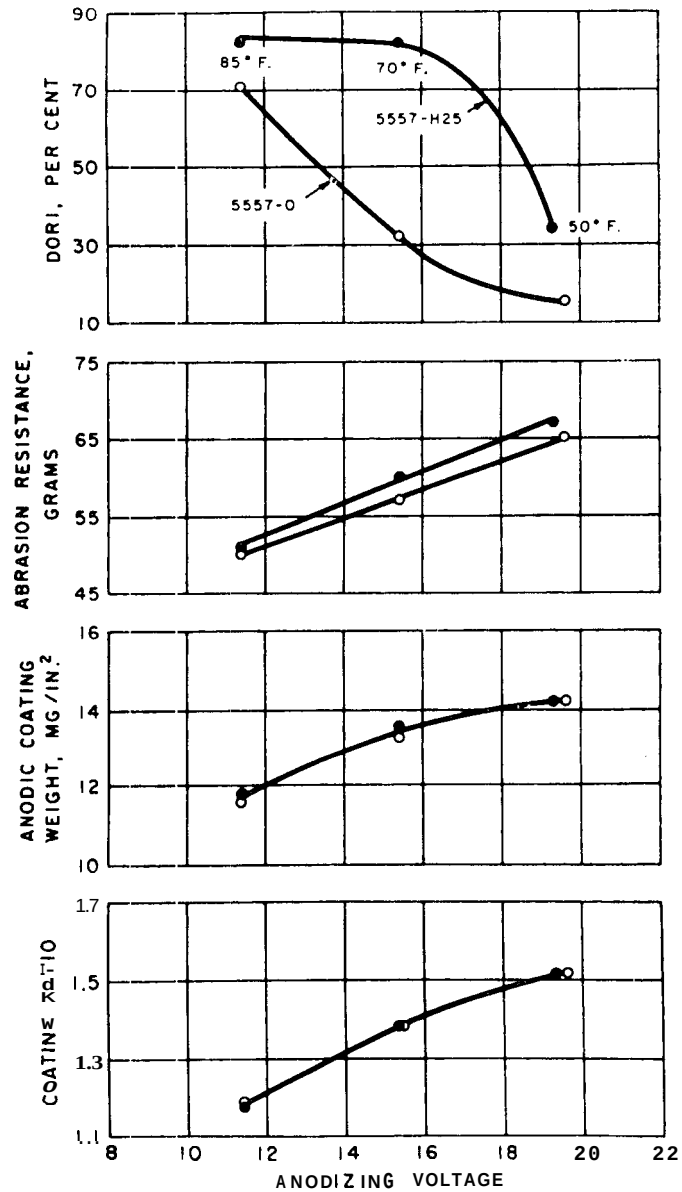


Fig. 12-64. Effect of anodizing voltage on image clarity (DORI meter), abrasion resistance, coating weight and coating ratio on a 0.3 mil (7.6 pin) sulphuric acid coating on annealed (5557-O) and strain-hardened

(5557-H25) Al-0.6% Mg bright anodizing alloys[270]

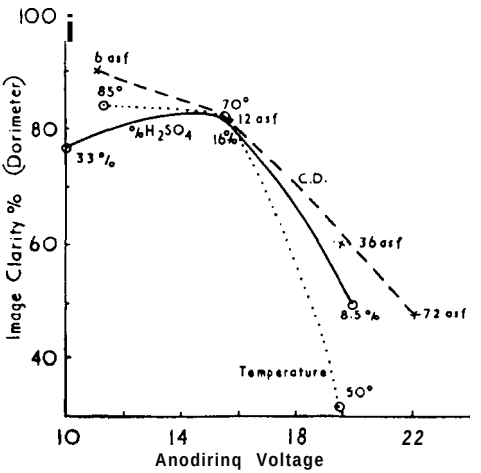


Fig. 12-65. Effect of voltage on image clarity. Voltage changed by varying (a) temperature (in °F), (b) current density (amp/sq ft) and (c) sulphuric acid concentration. 6 amp/sq ft = 0.64 A/dm^2

Effect of defects

The way in which defects affect the optical properties was also investigated by Cooke[272] who suggests that, because inert impurities or second phase constituents have better electrical conductance than the barrier layer, current is concentrated at the impurity particle and results in the formation of a critical asperity below the particle, which may grow to a hundred times its original size (see Fig. 3-30). As the coating grows, the distance of the particle from the metal-oxide interface grows and the cone is gradually undercut, leaving a thread of aluminium between the particle and the metal which is finally consumed leaving the impurity embedded in the coating. A contributory factor is that pits around the particle are caused by the concentration of current towards the latter during growth and also by the increased dissolution of oxide around the particle due to the heat resulting from the higher current flowing through the impurity.

Apart from giving a picture of the growth of defects, this hypothesis also explains why a decrease in anodizing voltage, which decreases the barrier layer thickness and thus reduces the difference in conductance between barrier oxide and impurity, improves the specular reflectivity, and why the loss in brightness of an anodized surface is highest during the first few moments of anodizing, after which the slower linear loss in specular reflectivity with increasing coating thickness is a function of the number of occluded particles embedded in the film (see Fig. 12-66).

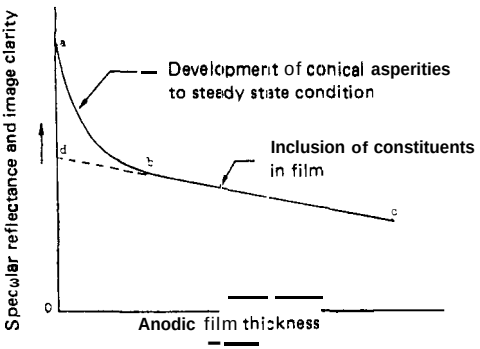


Fig. 12-66. Loss of specular reflectivity with increasing film thickness.[271] Extrapolation predicts the brightness after stripping the anodic film, leaving the critical asperities

It is interesting to note that Spooner[273] found a distinct increase in corrosion resistance of anodic coatings produced in sulphuric acid on raising the anodizing temperature from 15°C to 25°C, which results in a decrease in voltage. He associated this improvement with the increased water uptake and hydration during sealing, shown by the loss of water on heating (Fig. 12-67), but it is more likely the effect of the conical .asperities described by Cooke.[272]

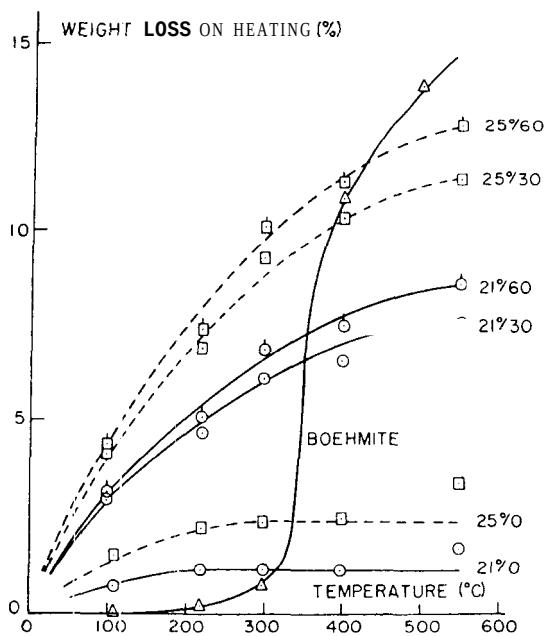


Fig. 12-67. Loss of water by anodic coatings on healing expressed as % loss of weight. The 0.6 mil (15 μm) coatings were produced by anodizing at 21" and 25°C and were tested unsealed and after sealing for 30 and 60 minutes[273]

The degradation of optical properties of sulphuric acid anodized aluminium exposed to vacuum-ultraviolet radiation has been studied by workers in the U.S.A.[274] They showed that such exposure caused fine cracking of the coating as a result of water loss and coating densification. This reduced coating transmittance and total reflectance, particularly in the short wavelength region.

On the barrier type films produced in ammonium tartrate solution Barrett and Winterbottom[275] found that the change in reflectivity with film thickness followed the predicted values for a uniform transparent film with constant optical properties.

12. THERMAL PROPERTIES

Heat resistance

The heat resistance of the anodic film is extremely high. Although fine cracks may be observed at 80-100°C, especially with the more brittle coatings, these do not appreciably affect the protective properties of the coating up to the melting point of the basis metal.

Cracking is caused by the low coefficient of expansion of the anodic film which is approximately 0.2 times that of the metal, though shrinkage caused by dehydration of the oxide during heating may also play a part. Again, the electrical insulation is not normally impaired at temperatures high enough to produce cracks, provided the coating remains adherent. The degree and type of sealing has a big influence on the temperature at which thermal crazing occurs, and this has been discussed in Chapter 11.

The heat resistance of anodized aluminium depends to some extent on the basis metal. Salt spray tests on aluminium alloys which had been anodized and heated for 8 to 100 hours at temperatures between 80 and 200°C showed that while the corrosion resistance of 1200 material was influenced very little in spite of some crazing, the anodized copper-containing 2024 alloy showed severe corrosion after heating.[276]

Thermal conductivity

The thermal conductivity of thick anodic coatings has been reported by workers in the U.S.A.[277] They found values of 0.5-1.0 W/m-K, which was more than an order of magnitude lower than the thermal conductivity of bulk, polycrystalline aluminium oxide (about 30 W/m-K), which is often used to estimate the thermal conductivity of anodic coatings. Their results are shown in Fig. 12-68. These coatings were produced by sulphuric acid anodizing, presumably under hard anodizing conditions, and were dichromate sealed.

Peterson and Fletcher[278] also examined thick anodic films from 60 to 160 microns in thickness, on 6061 alloy, and showed that thermal conductivity values were dependent on contact pressure, conductivity values rising as the contact pressure increased (Fig. 12-69). Their values were somewhat lower than those reported above, ranging from 0.02 to 0.2 W/m-K.

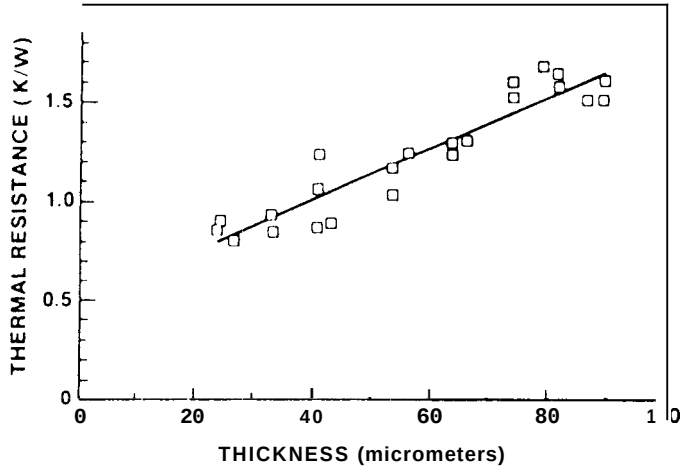


Fig. 12-68. Thermal resistance versus sample thickness for a typical thick anodic coating."

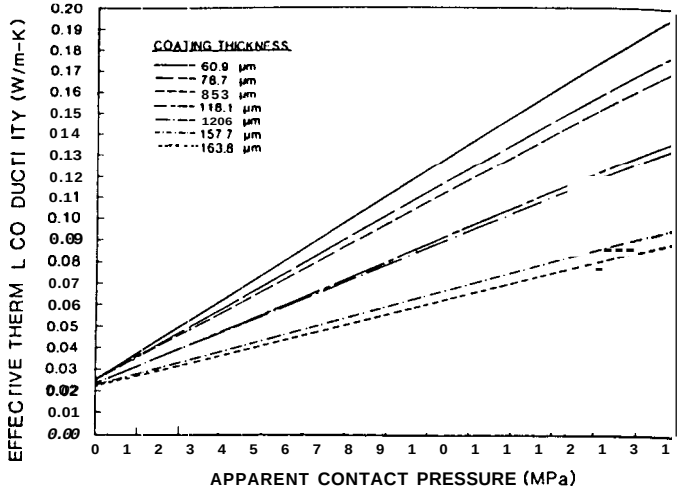


Fig. 12-69. Effective thermal conductivity as a function of pressure[278]

Heat emissivity

The heat emissivity of the anodic film has been studied by R. Hase,[279] whose figures for the radiation number of aluminium are given in Table 12-27.

TABLE 12-27

Radiation number of aluminium[279]

Condition of aluminium	*Radiation number* $[K\ cal/m^2 \times h\ (°K)^4]$	*Heat emissivity* %
Mirror polished	0.02-0.3	4.3-4.6
Etched	0.3-0.4	6.4-8.5
Bright rolled	0.25-0.35	5.3-7.4
Matt rolled	0.4-0.75	8.5-16
Aluminium painted	0.8-1.5	17-32
As diecast	0.75-1.2	16-26
As sand cast	1.2-1.7	26-36
Anodized	1.8-4.3	38-92
Black body	4.70	100

Tomashov[280] gives the coefficient of heat emissivity at 150-200°C as shown in Table 12-28. No details of the film thickness are given, however.

It is clear from the figures in these tables that an aluminium surface in the clean and bright state has a very low total hemispherical emissivity of about 3-5%, but as soon as this is subject to any of the natural hazards which entail surface roughening and the formation of oxide films, then this emissivity is rapidly increased to 3 or 4 times the value for the metal surface even in the commercially available conditions, and may reach the order of 30% in the case of cast aluminium surfaces.

When anodic oxide is formed on the surface even quite a thin coating can increase the emissivity from 3 to 8%,[281] curves produced by Tassara[282] at 38°C showing that the emissivity is 30% for 1 μm, 60% for 2 μm and 70% for 3 μm. Spectral emissivity curves obtained by Hase[279] for thick anodic coatings show two maxima, one at a wave length of 6 μm and the other at about 3 μm. Since the former wave length is in the range where the radiation from steam or water heated radiators will have its maximum energy, then anodized aluminium is an ideal material for functioning with radiators and heat exchangers. The

band near 3 μm is connected with the water content of the coating and varies with the thickness of the coating.

TABLE 12-28

Relative coefficients of heat emissivity[280]

Polished rolled aluminium	4
Matt-surfaced aluminium	6
Aluminium, as cast surface	18
Blackened aluminium surface	52
Graphited silicon surface	58
Anodized surface	80
Perfect black body	100

Burr and Hay[283] studied the effects of anodic coatings up to 20 μm thick on the heat losses from cylindrical containers by measuring the power needed to maintain the temperature at values from 23 to 100°C. They found that at 30°C they needed between **43** and 60% more energy to maintain the temperature than when the surface was polished aluminium, and at 90°C the increase in power was from 68 to 79%, the variations being due to differences in the colour and thickness of the coatings. They estimated the emissivity of the clear anodic coating to be 80% from the data, in agreement with the findings of others.

More recently there have been several studies of the spectral emissivity of anodized aluminium for potential infra-red radiation heating applications. Work in Japan[284] has shown that it is very suitable, particularly if anodized to thicknesses greater than 15 microns. They looked at a range of thicknesses produced by sulphuric acid anodizing, and their results are shown in Fig. 12-70. Values of up to 90% emissivity were obtained. However, in such applications there is benefit in having a high emissivity over the whole of the most important part of the infra-red wavelength region (about *3* to *10* microns). Clear anodized aluminium does not do this, as below a wavelength of 6 microns the emissivity is reduced. However work in India,[285] related to space applications, suggests that this can be improved by black anodizing. Integral colour anodizing processes gave values of up to 85% emissivity, but the best results were obtained by electrolytic colouring in a cobalt based electrolyte, followed by **a** further blackening dip in ammonium sulphide solution. Values of up to 90% were obtained, compared to 70-80% for clear anodized aluminium (Table 12-29).

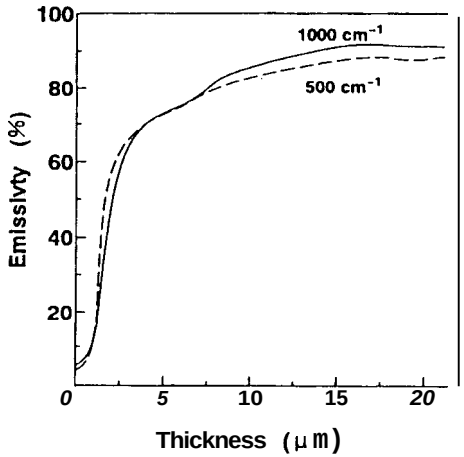


Fig. 12-70. Changes in emissivity with thickness of anodized film

TABLE 12-29

Influence of anodic film thickness on optical properties[285]

	*Solar absorptance**			*Infrared emittance**		
Film thickness (μm)	*1*	*2*	*3*	*1*	*2*	**3**
Alloy 1100						
7	0.23	0.80	0.82	0.74	0.77	0.78
10	0.29	0.86	0.88	0.77	0.84	0.84
15	0.34	0.93	0.94	0.79	0.86	0.86
19	0.37	0.93	0.94	0.81	0.86	0.86
25	0.40	0.92	0.94	0.84	0.89	0.90
30	0.39	0.94	0.94	0.85	0.90	0.90
34	0.37	0.93	0.94	0.85	0.89	0.89
Alloy 2024						
6	0.16	0.62	0.63	0.73	0.75	0.75
10	0.19	0.67	0.69	0.77	0.78	0.78
14	0.24	0.80	0.81	0.80	0.82	0.82
18	0.29	0.88	0.89	0.81	0.85	0.85
25	0.33	0.90	0.91	0.83	0.88	0.88
31	0.36	0.90	0.92	0.84	0.88	0.88
36	0.38	0.91	0.92	0.85	0.89	0.89
Alloy 6061						
6	0.30	0.70	0.71	0.70	0.72	0.72
11	0.39	0.77	0.78	0.75	0.80	0.80
14	0.38	0.85	0.88	0.78	0.82	0.82
20	0.48	0.94	0.95	0.82	0.86	0.86
25	0.49	0.96	0.97	0.83	0.89	0.90
29	0.47	0.95	0.96	0.83	0.88	0.88
34	0.48	0.96	0.97	0.84	0.90	0.90

* 1. Only anodized. 2. Anodized and inorganic black colored (one time). 3. Anodized and inorganic black colored (two times).

Infra-red reflectivity

Since the emissivity of anodized aluminium is high, then the complementary property of absorbing heat when the surroundings are at a higher temperature is also high. Accordingly the presence of any oxide coating on aluminium causes its reflectivity for infra-red radiation to drop quickly. The bright metal surface is of course a good reflector like all metals and the loss on anodizing does not depend much on the alloy type, but sealing of the anodic coating has an appreciable effect. The values in Table 12-30 are typical of the heat reflectivity of aluminium with various thicknesses of anodic coating, and refer to total radiation from a source at about 900°C which would have its maximum energy at 2.7 μm wave length.

TABLE 12-30

Heat reflectivity of sulphuric acid anodized 99.5%-99.99% aluminium

Film thickness (μm)	*Unsealed*	*Sealed*
none	95%	--
1	87	*83*
2	83	78
3	80	74
4	78	71
5	76	67

These values were measured using the method developed by Preston at the National Physical Laboratory which is the recommended procedure in BS 6161: Part 14. It is probably the least used test, firstly because the apparatus is difficult to acquire and lengthy to use, and secondly, because there is so little one can do to affect the heat reflectivity, other than by stipulating a maximum film thickness, that a measurement is not called for. The important thing to notice in these applications, which involve fire reflectors, laser reflectors operating in the infra-red, thermo-copying machines, heat shields, etc., is that a coating maximum is to be observed for thin coatings, which tends to be contrary to the psychology of the jobbing anodizer who is always anxious to give good value for money. Some film is required of course to prevent the metal tarnishing, which would soon reduce reflectivity.

British Standard test

The test is described in BS 6161: Part 14: 1987, and is carried out on a sample of flat sheet, preferably about 0.9 mm thick and 25-75 mm (1-3 inches) square. **A** thermo-junction of fine wires of about 0.25 mm (40 S.W.G.),e.g. of copper and constantan, is attached with adhesive to the back of the sheet near one corner. The face to which the junction is attached is then uniformly blackened with an optical black paint or other coating whose spectral absorption factor is substantially constant over the spectral range of the radiation used in the test, and whose total absorption factor for this radiation is known. **A** suitable black paint could be expected to have a total absorption factor of 0.96.

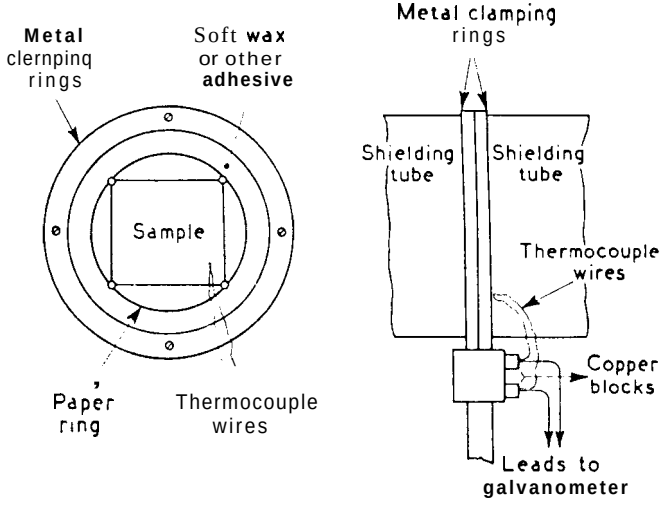


Fig. 12-71. Arrangement for infra-red reflectivity test

The sample is mounted in a thermally insulating mounting (see Fig. 12-71) which may incorporate shielding tubes against air currents. Clamping rings are mounted on a base to which are attached two insulated copper blocks forming the cold junctions for termination of the thermo-junction wires and from which copper leads go to a galvanometer. The whole apparatus can be turned through 180° about a vertical axis. The radiation source is a small grid of oxidized nickel-chromium resistance wire, heated electrically and held at a brightness temperature of 900°C as indicated by a calibrated optical pyrometer.

The sample is set up 600 mm (2 feet) from the source in a draught-proof enclosure and separated by a radiation screen with an aperture which limits the beam. **A** shutter, also in the form of a radiation screen, is arranged to close or open the aperture. The intensity of the source must remain constant. If desired, it may be augmented by a concave gold or copper mirror behind the wire grid.

The 'test' side of the sample faces the source. The shutter is opened and the sample allowed to heat until the temperature reading on the thermo-junction reaches about half the maximum (found by previous trial). Then the shutter is alternately closed arid opened at equal intervals of time (e.g. 2 minutes) and the temperature read at the moments of opening then closing the shutter. When the higher readings at the moments of closing, and the lower ones at the moments of opening, settle down to steady values, the mean difference between the two is found.

The black side of the sample is then turned to face the source, and a similar procedure is carried out. Finally, the sample is again turned and a second determination on the test side is made and averaged with the first.

The infra-red reflectivity is then given by $1 - \alpha.\frac{D_T}{D_B}$

where α is the absorption factor of the black side,

D_T is the mean difference between the temperatures on opening and closing the shutter on the test side,

D_B is the difference on the black side.

For the percentage value, multiply by 100.

Solar absorption/infra-red emittance ratio

The ratio of solar absorption to infra-red emittance of a surface is an important factor in the design of spacecraft, a low ratio normally being necessary to keep down the internal temperature of manned craft. The suitability of different anodizing processes for this purpose has been investigated in the United States.[286] Kelleher[287] has indicated that a ratio of solar energy absorption to emittance of less than 1 is desirable, and has indicated that this is readily obtainable with sulphuric acid anodizing where she obtained ratios between 0.3 and 0.5, while with chromic acid anodizing the ratios often exceeded unity unless the coatings were thicker than about 2 μm.

Much depends on the water content of the oxide coating. When this is low, as in coatings produced in chromic or boric acid, the reflectance is high, i.e. the infra-red emittance is lower than that of conventional sulphuric acid coatings or of coatings produced by hard anodizing (i.e. at low temperature) which have a higher water content. For tine same reason, sealing the sulphuric acid coatings decreases the reflectance while increase in thickness also helps to keep the absorptance/ emittance ratio low. Other factors, i.e. basis metal composition, heat treatment,

and pretreatment, have little or no effect. The influence of the anodizing bath is seen in Fig. 12-72. At higher temperatures in the vacuum of space, water tends to be driven off from the oxide coating, and where a somewhat higher ratio is permitted the more stable chromic or boric acid coatings may have an advantage.

One problem with space vehicles is the solar degradation caused by continuous exposure to ultra-violet light.[287,288] Although the coatings are highly stable towards visible and infra-red radiation the energy per quantum for ultra-violet radiation in the range 200-4000 Å can induce rupture of many chemical bonds, and since most of this is filtered out by the earth's atmosphere there can be 10-100 times as much radiation in space. By exposing surfaces for 200 hours to a radiation intensity of ten times that of the sun, Crow found that there was an increase in solar absorption for all alloys amounting to 31% for 2014 alloy, 40% for 1100, and 42% for 7075 alloy. Weaver[289,290] has indicated however that although the colour centres formed during ultra-violet exposure cause a gradual increase in the absorption/emittance ratio up to 120 hours, increasing it to 0.42, there was little further change, unlike most other organic and inorganic coatings.

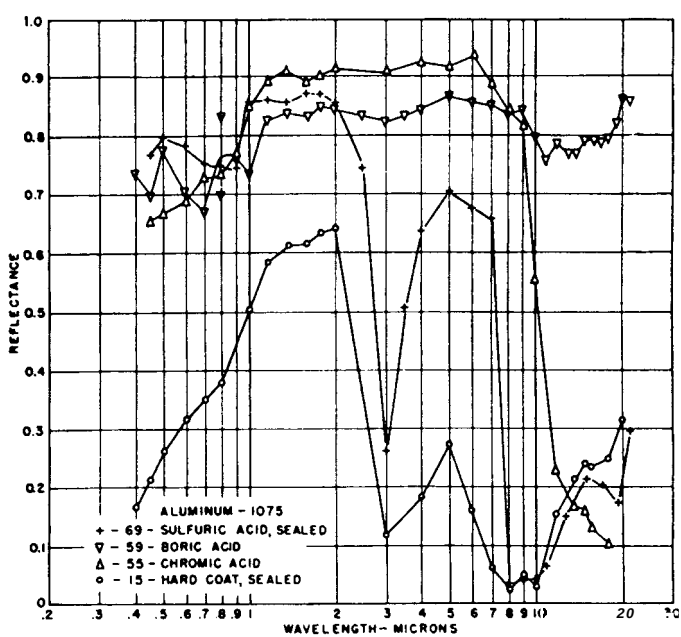


Fig. 12-72. Effect of anodizing on reflectance of aluminium at various wavelengths[286]

Hultquist and Sibert[291] have investigated absorption/emittance ratios for solar energy with Ematal coatings produced in 0.10M potassium titanium oxalate, 0.09M phosphoric acid, 0.065M citric acid and 0.10M sucrose at 49 mA/cm^2 and 30 minutes at 65-85°C, also varying the conditions. The ratios were 0.54-0.68 and could be extended down to 0.35 by impregnation.

More recent studies have included the potential effects of crazing during rapid thermal cycling[292] in low earth orbit, and the effect of long duration exposure of chromic acid anodized aluminium under these conditions.[293] Other workers have looked at the near UV and vacuum UV environments,[294] and the problems of outgassing in space situations.[295] In all cases the general performance of anodized aluminium has been good.

Amorphous aluminium phosphate layers have also proved of great interest for temperature control in space vehicles, giving low absorption/emittance ratios, and they have also been used for bonding other materials *to* the surface such as SnO_2 or Cr-Ni-Co-spinel to give coatings that will withstand high vacuum conditions.[295 296 297]

Ultra-violet reflectivity

The visible spectrum extends from 0.7 μm to 0.3 μm and below this comes the ultra-violet part of the spectrum. The anodic coating on pure aluminium is highly transparent to visible light and this continues in the ultra-violet down to 0.2 μm so that the near region can be regarded as an extension of the visible spectrum. The reflectivity of freshly evaporated aluminium on glass at various wavelengths and for various purities is given in Table 12-31.

TABLE 12-31

Reflectivity of aluminium to ultra-violet radiation[298]

Wavelength	*Aluminium purity*		
(μm)	*99 99%*	*99 7%*	*99 5%*
0.22	91	91	88
0.20	89	89	85
0.18	*85*	82	*77*
0.16	*12*	69	63
0.10	18	18	15

At short wave lengths even the natural oxide film has a big effect on reflectivity, as Hass[298] has calculated on the basis of Fresnel's laws:

Film thickness (μm)	*% Reflectivity at* 0.22 μm	0.1216 μm
0	92	47
0.01	85	4
0.02	82	19
0.06	91.5	–

The variations at 0.22 μm are interference effects which disappear with thicker films, but at short wavelengths the methods of preparation and storage of the aluminium surface have a big effect. Phillips[299] has also shown the interference effects occurring in the U.V. region, in his work with aluminium reflectors for lamps used for U.V. curing of lacquers. He found the best results with super purity aluminium protected by a thin anodic coating (less than 2 pm). He pointed out, as did Khan *et al.*,[46] that the separation of the peaks in the spectra can be used as a measure of anodic film thickness.

In the ultra-violet region from 0.2 μm to 0.0575 pm it is the practice to boost the reflectivity by depositing, by evaporation onto the freshly formed aluminium surface, a coating of magnesium fluoride, to prevent the formation of oxide.[300,301] At wave lengths below 0.05 μm in the extreme ultra-violet the oxide coating is a better reflector than the aluminium metal.

Values of the refractive index of aluminium oxide in the ultra-violet region are 1.85 at 0.22 pm; 1.75 at 0.12 μm; and 1.30 at 0.90 ym.

The effect of anodic coatings on the reflectivity of electropolished aluminium surfaces at various wavelengths has been given in detail in Chapter 3.

13. TENSILE STRENGTH AND FATIGUE EFFECTS

The tensile strength of aluminium is normally not greatly affected by anodizing unless the material is thin, when the brittleness of the coating may cause some decrease in the tensile strength. On the other hand, somewhat contradictory results were obtained in early investigations on the fatigue properties of anodized aluminium alloys. Oxalic acid anodizing caused a decrease in the endurance limit of Duralumin according to Igarashi and Fukai[302] though Mauksch[76] found no change after oxalic or sulphuric acid anodizing of either aluminium or aluminium-copper alloys. In sulphuric acid anodizing, Müller[303] found a decrease in endurance limit of 4 to 20% on aluminium-magnesium and aluminium-copper-magnesium alloys while Gerard and Sutton[304] obtained a 20% improvement on Duralumin at 50 million cycles. Stickley and Howell[305] found that the fatigue properties on

Al-Cu-Mg-Mn alloys were irnproved by applying a thin anodic coating. In the case of thicker coatings, the effect depended on the loading. When the specimen was highly stressed, anodizing was usually detrimental to the fatigue properties. It has become accepted that the sulphuric acid anodizing process does cause a reduction in fatigue strength of most alloys, as a result of crack initiation from the film.[306] Chromic acid anodizing is less detrimental, in part due to its much lower thickness, but the desire to move away from this for environmental reasons has led to alternative developments. One of these is a boric acid/sulphuric acid anodizing process developed by Boeing, and the effects of this process on fatigue properties have been evaluated by Cree and Weidmann.[307] They found that the fatigue properties of 2024-T4 alloy were markedly affected by this process, and a reduction of the fatigue limit of 22% was recorded, similar to that with sulphuric acid anodizing. An incresse in the fatigue crack growth rate was also experienced.

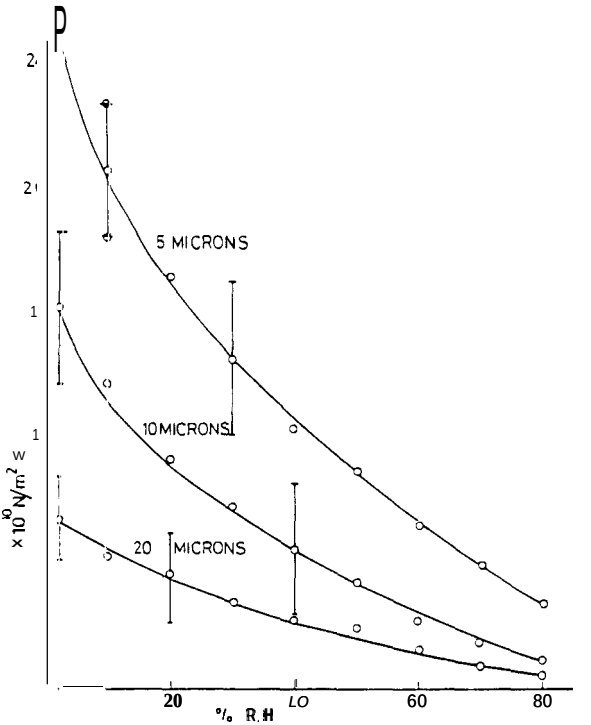


Fig. 12-73. Oxide modulus vs. relative humidity for three oxide thicknesses[309]

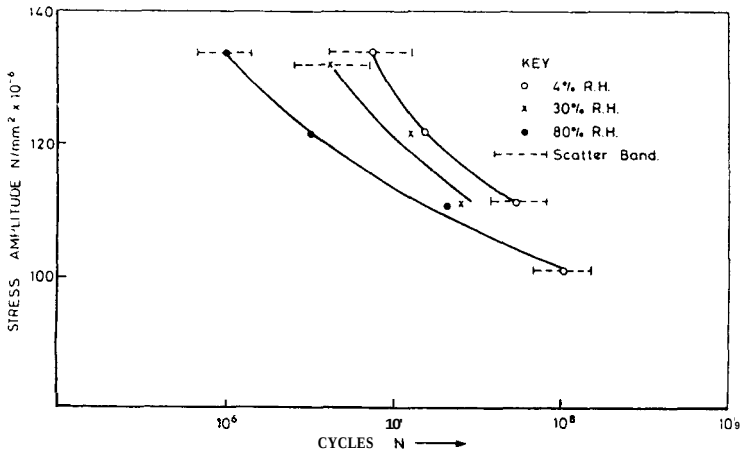


Fig. 12-74. Effect of humidity on fatigue of anodized AI alloy at 20 kHz[309]

In some applications where hard anodizing is regarded as an alternative to hard chromium plating, in which an appreciable drop in endurance limit may be experienced,[308] it appears that the anodizing process will generally give rather the better results (see also Chapter 9, p. 808).

Hockenhull *et al.*[309] have studied the mechanical properties of anodic oxides and their influence on fatigue behaviour. The Al-Cu-Mg-Ni alloy (RR58) specimens were anodized in a sulphuric acid electrolyte at 16°C to thicknesses of 5, 10 and 20 microns and were dichromate sealed. **A** vibrational technique was then used to measure the modulus of the anodic film in situ in varying humidity conditions. Results are shown in Fig. 12-73. As can be seen environmental humidity decreases the modulus as the humidity increases. The effect of these conditions on fatigue was then measured and fatigue life was also found to decrease with increasing humidity (Fig. 12-74) and this was explained in terms of the mechanical behaviour of the oxide film.

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CHAPTER 13

Plating on Aluminium

1. INTRODUCTION

The decoration and protection of aluminium and its alloys by the application of electrodeposits result in a very attractive combination of valuable properties of the basis metal with highly desirable surface attributes, and so on this account a great deal of interest has been taken in the development of efficient means of plating aluminium. Chromium plated aluminium of good quality, for example, possesses the following fbrmidable array of attractive properties: strength; ease of fabrication; lightness; attractive finish; relative economy.

The low specific gravity of aluminium, whereby approximately three times as many components may be produced from the same weight of material compared with ferrous or other common basis metals, is an important economic factor which makes it well worth while investigating the possibility of replacing heavier metals of construction by the light alloys, for example, replacing zinc-base diecastings with aluminium.

However, such substitution is not clear cut, as some aluminium alloys are not easily plated, and a caref'ul study needs to be made where substitution of the basis metal is sought in a manufacturing sequence. Partly for this reason and partly because the corrosion resistance of electroplated aluminium is not as good as that of other finished metals in outdoor conditions, the commercial plating of aluminium has not proceeded as rapidly as might have been expected. Nevertheless, the production of electroplated aluminium products is steadily increasing, albeit in certain well-defined fields rather than in any general manner. Additionally, the market for electroplated aluminium products is changing over the years. Thus

plated aluminium tableware such as tea and coffee sets, produced for half a century, have declined in production in the face of competition from cheap stainless steel articles produced in South East Asia. In contrast, there is increasing production of plated aluminium components where the high strength to weight ratio of aluminium alloys is important as in aerospace and also in fast moving machinery in general engineering applications.

2. METALS DEPOSITED ON ALUMINIUM

Decorative nickel plus chromium coatings are applied to cast, stamped and extruded articles for use as furniture fittings, motorcar components, domestic holloware and a wide variety of other consumer products. Hard chromium is applied to various forged, cast and wrought aluminium components, such as dies and moulds, printing rollers, pistons, cylinder liners, and aircraft landing gear parts, to give increased wear resistance. Electroless nickel (chemical nickel plating) is similarly applied to a wide range of engineering components for increased wear resistance.

While nickel and chromium are the metals most commonly deposited on aluminium, there are special applications making it desirable to apply other metal deposits. As aluminium is anodic to most of the metals commonly deposited on it, it is essential that the deposited metal should be largely pore-free if adequate protection is to be achieved.

Various metals have been applied to aluminium to provide a solderable surface. These include tin, copper. zinc, silver and nickel, while brass has been deposited to facilitate the bonding of rubber to aluminium surfaces. Tin and sometimes silver deposits are used on aluminium bus bar ends to improve the electrical conductivity at the joints, while precious metals such as gold and rhodium are used on aluminium components in electronic equipment. Lead tin alloy electrodeposits are applied to bearing surfaces.

In aircraft there are many cadmium plated aluminium components such as switch boxes and instrument panels where electrical earthing is needed together with protection from corrosion.

Aluminium wire with a co-extruded copper coating is being used for electrical installations in place of solid copper wire. A process' for the continuous electroplating of aluminium wire with copper from a pyrophosphate bath has been developed. Alternatively, nickel and/or tin can be electrodeposited on the wire in the same process. An aluminium wire with a nickel coating, deposited from either a fluoborate or a sulphamate bath,[2] has been patented,[3] and other metallic coatings for aluminium conductor wires are being investigated.

Difficulties connected with the plating of aluminium

The presence of the oxide film, and the extreme reactivity of bare aluminium which results in rapid re-formation of the film on exposure to air or to aqueous solutions, is the main difficulty connected with the plating of aluminium. Additionally, the following factors must be considered:

1. The amphoteric nature of the oxide, which complicates the possible reactions likely to occur either during or subsequent to preparing the surface for plating.

2. The position of aluminium in the electrochemical series (see Table 13-l), which leads to the ready formation of immersion deposits in plating solutions, obviously affecting adhesion of the plating.

TABLE 13-1

Electrode Potentials (wrt 0.1N KCl Calomel Electrode)*

(Measured in an aqueous solution of 53 g/l NaCl + 3 g/l H_2O_2 at 25°C)

	volt
Nickel	−0.07
Silver	−0.08
Copper	−0.20
Brass (61%Cu-39%Zn)	−0.28
Chromium (electrodeposited)	−0.37
Tin	−0.49
Mild steel	−0.58
Cadmium	−0.82
Aluminium	
Commercial purity 99.5%	−0.83
Super purity 99.95%	−0.85
Zinc	−1.10
Magnesium	−1.73

*Based on Binger, Hollingsworth and Sprowls[4]

3. The difference in potential between the aluminium matrix and second phase constituents which affects the deposition reactions and makes the plating of some aluminium alloys particularly difficult (see Table 13-2).

TABLE 13-2 (a)

Electrode Potentials (wrt 0.1N KCl Calomel Electrode)*

(measured in an aqueous solution of 53 g/l NaCI + 3 g/l H_2O_2 at 25°C)

			volt
(a)	*Second phase constituents*		
	Si		−0.26
	$NiAl_3$		−0.52
	$FeAl_3$		−0.56
	$CuAl_2$		−0.73
	$MnAl_6$		−0.85
	$CuMgAl_2$		−1.00
	$MgZn_2$		−1.05
	Mg_2Al_3		−1.24
(b)	***Cast aluminium** alloys*		
	AI-Si-Cu-Mg, 355, LM16	T4	−0.78
		T6	−0.79
	Al-Si-Mg, 356, LM25		−0.82
	AI-Si. 443, LM l	permanent mould	−0.82
		sand mould	−0.83
	Al-Mg, 520, LM10		−0.85
(c)	***Wrought aluminium** alloys*		
	Al-Cu-Mg, 2024	T4	−0.69
		T6	−0.8l
	Al-Zn-Mg-Cu, 7075, T6		−0.83
	Al-Mn, 3103,		−0.83
	Al-Mg-Si, 6063,		−0.83
	Al-Mg, 5251,		−0.85

*Based on Binger, Hollingsworth and Sprowls[4]

TABLE 13-2 (b)

Electrode Potentials (wrt 0.1N KCl Calomel Electrode)*

(measured in an aqueous solution of 53 g/l NaCl + 3 g/l H_2O_2 at 25°C)

Aluminium Alloy	*Temper*	*volt*
1060 99.60Al (min)		−0.84
1100 99.00Al (min)-0.12 Cu	all tempers	−0.83
1350 99.50.41(min) EC		−0.84
2011 5.5Cu-0.4Pb-0.4Bi	T3, T4	−0.69
2011 5.5Cu-0.4Pb-0.4Bi	T8	−0.83
2014 4.4Cu-0.8Si-0.8Mn-0.5Mg	T3,T4,T451	−0.68
2014 4.4Cu-0.8Si-0.8Mn-0.5Mg	T6, T651, T652	−0.78
2024 4.4Cu-1.5Mg-0.6Mn	T3. T4, T361	−0.68
2024 4.4Cu-1.5Mg-0.6Mn	T6. T81. T861	−0.80
2024 4.4Cu-1.5Mg-0.6Mn	Alclad 2024	−0.83
2036 2.6Cu-0.45Mg-0.25Mn		−0.75
2124 4.4Cu-1.5Mg-0.6Mn	T851	−0.80
2219 6.3Cu-0.3Mn-0.18Zr-0.10V-0.06Ti	T31, T37. T351	−0.64
2219 6.3Cu-0.3Mn-0.18Zr-0.10V-0.06Ti	T62. T81, T87. T851	−0.80
2618 2.3Cu-1.6Mg-1.1Fe-1.0Ni-0.18Si-0.07Ti	T61	−0.80
3003 1.2Mn-0.12Cu		−0.96
3004 1.2Mn-1.0Mg		−0.84
Alclad 3004.1.2Mn-1.0Mg 3004 core		−0.84
Alclad 3004 1.2Mn-1.0Mg 7072 cladding		−0.96
3105 0.55Mn-0.50Mg		−0.84
5005 0.8Mg		−0.83
5050 1.4Mg		−0.83
5052 2.5Mg-0.25Cr		−0.85
5056 5.0Mg-0.1Mn-0.1Cr		−0.87
5086 4.0Mg-0.4Mn-0.15Cr		−0.88
5154 3.5Mg-0.25Cr		−0.86
5254 3.5Mg-0.25Cr		−0.86
5356 5.0Mg-0.12Mn-0.12Cr		−0.87
5454 2.7Mg-0.8Mn-0.12Cr		−0.86
5456 5.1Mg-0.8Mn-0.12Cr		−0.87
5457 1.0Mg-0.3Mn		−0.84
5652 2.5Mg-0.25Cr		−0.85
6151 0.9Si-0.6Mg-0.25Cr		−0.83
7072 1.0Zn		−0.96
7178 6.8Zn-2.7Mg-2.0Cu-0.3Cr	T6	−0.81

* Based on Binger, Hollingsworth and Sprowls[4] and extracted from ASM International Metals Handbook[1]

The influence of alloying elements in solid solution on the potential is shown in Fig. 13-1 obtained with high purity binary aluminium alloys solution treated and quenched. The potentials were measured[4] (wrt O.lN KCl Calomel Electrode) in an aqueous solution of 53 g/l NaCI + 3 g/l H_2O_2 at 25°C.

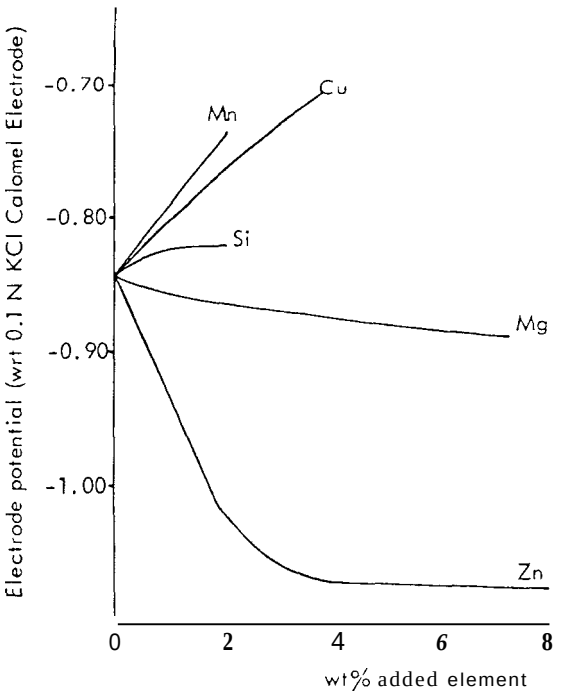

Fig. 13-1. Influence of alloying on electrode potential of aluminium. Based on Binger *et al.*[4] and Hollingsworth *et al*[5]

4. The coefficient of expansion of aluminium and its alloys, differing markedly from that of most of the metals commonly deposited on it. According to West[6], in applications in which considerable temperature changes occur, the differential expansion of aluminium and the metal coating may cause sufficient strain to rupture the bond between the deposit and the basis metal (see Table 13-3).

TABLE 13-3

Mean coefficient of linear expansion of the common metals per °C

Metal	x 10^{-6}	*Metal*	x 10^{-6}
Chromium	7	Silver	19
Steel	11	Aluminium	24
Nickel	13	Tin	27
Gold	14	Zinc	27
Brass	18	Cadmium	31
Copper	18		

5. The difference in atomic diameter and crystal lattice structure between the aluminium substrate and the plated metal deposit. Schwartz and Newkirk[7] have tabulated the properties of metals and alloys commonly plated on aluminium and compared the closeness of fit of atoms at the interface with reported adhesion of plating on aluminium (Table 13-4).

TABLE 13-4

Metals for possible direct deposition on aluminium

(Based on Schwartz **and** Newkirk[7])

Element	*Crystal Structure*	*Lattice parameter Å*	*Atomic diurneter Å*	*Valency*	*Solid solubility in Al*	*Plating process**	*Adhesion of plating on Al*
Al	fcc	4.0113	2.8577	3			
Cu	fcc	3.607	2.551	1,2	0.1%	I	poor
Ag	fcc	4.077	2.883	1	1.0%		
Au	fcc	4.070	2.878	1	nil		
Zn	cph	2.660	2.660	2	2.0%	I & E	good
Cd	cph	2.973	2.973	2	nil	I	poor
Sn	diamond	6.476	2.804	2,4	nil	I	fair
	tetragonal	5.830					
Pb	fcc	4.940	3.493	2	nil		
Cr	bcc	2.879	2.493	3,6	0.07%	E	good
Fe	bcc	2.861	2.411	2,3	nil	I	poor
Ni	fcc	3.517	2.487	2	0.005%	I	poor

TABLE 13-4 *(continued)*

Element	*Crystal Structure*	*Lattice parameter Å*	*Atomic diameter* Å	*Valence*	*Solid solubility in Al*	*Plating process**	*Adhesion of plating on Al*
Alloys							
Cu-Zn 70-30	fcc	3.693			0.2%	I	good
Zn-Ni 94-6	cph					I	good
Cu-Sn 70-30	fcc & or orthogonal					I	good
Cu-Pb 80-20	fcc					E	

* I = immersion; E = electroplating

Classification of methods for plating on aluminium

Many methods have been proposed for producing deposits on aluminium, but they may be broadly classified as follows:

1. Processes based on the zincate immersion technique
2. Processes based on the stannate immersion technique
3. Direct plating methods
4. Processes based on mechanical preparation
5. Chemical etching procedures
6. Processes based on preparation by anodic or chemical oxidation.

Of these methods, the zincate process is by far the most widely used. The stannate process is recommended for specific applications. The other methods for plating on aluminium are no longer used commercially and are of historical and academic interest only. Details of them were given by Wernick, Pinner and Sheasby[8]. They covered direct copper plating,[9-12] direct nickel plating,[13-15] direct chromium plating,[16-17] direct tin plating,[18-19] direct zinc plating including the Vogt process,[20-26] and processes based on mechanical preparation.,[27-32] They included chemical etching processes in acid mixtures,[28, 33] in trichloroacetic acid mixtures," and in etches containing heavy metals.[28-29, 35-43] They also included chemical oxidation prior to plating,[''-''] and anodizing prior to plating.''', [54-76]

Sallee, Cromer and Vittori[77] studied the use of direct and pulsed currents to plate copper on aluminium. Several parameters were optimized: current density, pulse and rest duration. When using direct current, it was observed that a current density lower than 4 A/dm^2 was suitable for obtaining adherent, compact and homogeneous deposits. The bath was 0.745M $Cu(NO_3)_2$-0.79M tetraethylene-pentamine and 0.19M NH_4NO_3 at pH 7.8 and 25°C. The best deposits were obtained for *2* ms pulse width and a current density of 20 A/dm^2. A positive current density during the rest time had to be avoided to prevent dissolution of aluminium. **A** study of the first stages of copper deposition was undertaken using 1-5 pulses. The deposits were shown to grow from a limited number of spherical aggregates ranging from 0.1 to 2.5 μm diameter. This explained why the stirring of the solution did not significantly increase the electrodeposition current. The kinetics of growth of the deposit seem to be governed more by the adatom diffusion than by the migration or diffusion of Cu^{2+} from the bulk, even when its concentration is as high as 0.75M.

A process[78] has been developed in which continuous aluminium wire (or strip) is made the anode as it passes through a bath which dissolves the anodic oxide as fast as it forms. The solutions are similar to those used for chemical polishing or electropolishing, for example, mixtures of concentrated phosphoric, sulphuric and nitric acids held above 80°C. The wire passes through the bath in 5-6 seconds with a high current density (100 A/dm^2) applied. The wire then passes into the plating solution and through a PTFE ring oscillated transverse to the wire to agitate the wire.

A similar process[79] uses an alkaline bath. Aluminium is anodically cleaned with a solution with **a** high dissolving power for aluminium oxide till it is substantially free from oxide. It is then plated either with a bronze strike or by immersion plating in zincate or stannate solutions. The anodic clean contains NaOH or KOH at a pH not less than 11, with at least 0.8 volts applied, and the aluminium is vigorously agitated.

3. CONVENTIONAL ZINC IMMERSION PROCESSES

Most electroplating on aluminium is currently carried out on top of zinc deposits applied by a chemical immersion process in modified zincate solutions. The zincate process has been developed into a relatively simple, cheap and reliable technique for plating on aluminium and a wide range of aluminium alloys. It is less sensitive to alloy composition than processes based on anodizing pretreatments, does not need the applied power requirements of anodizing and is cheaper than the stannate immersion process owing to the high price of tin.

The zinc immersion process was first developed by Hewitson[80] in 1927 in America but was shortly to be found in use in Germany[81,82] and in Britain.[83] Its development was soon followed by the double dipping technique of Korpiun[84] and much subsequent research has been carried out.[18,85-104]

Theory of the zinc immersion process

That the dissolution of aluminium in alkaline solution is electrochemical in character was established by Straumanis and Brakss,[94] Streicher[95] and Petrocelli.[96] The basic net reactions in the alkaline zincate solution are the dissolution of aluminium and the deposition of zinc. To a greater or lesser extent, some hydrogen evolution may also take place at the cathodic areas, though this is usually unimportant.

The basic reaction may be written as:

Anodic: $Al + 3OH^- \rightarrow Al(OH)_3 + 3e^-$

$Al(OH)_3 \rightarrow AlO_2^- + H_2O + H^+$

Cathodic: $H^+ + e \rightarrow H \rightarrow \frac{1}{2}H_2$

Dirkse[97] has shown that the zincate ion in strong alkaline solution is probably in the form $Zn(OH)_4^{2-}$. The deposition of zinc may therefore be expressed as:

Cathodic: $Zn(OH)_4^{2-} \rightarrow Zn^{2+} + 4OH$

$Zn^{2+} + 2e^- \rightarrow Zn$

The quantitative relationship between aluminium dissolved and zinc deposited was measured by Bengston,[85] who found that on commercial aluminium the changes were:

	mg/cm^2
aluminium dissolved	0.017
zinc deposited (found)	0.057
zinc deposited (theoretical)	0.062

The zincate solution is normally made up from zinc oxide and caustic soda and it has been shown that the ratio of these constituents has a profound effect on the adhesion of the subsequent electrodeposit. The physical conditions, time of immersion and temperature, can also affect the degree of adhesion.

Mechanism of zinc deposition

The mechanism of deposition of zinc from the zincate solution is not only of theoretical interest, because on the form the deposit takes depends the adhesion of a subsequent plating coating. Bullough and Gardam[88] considered that the adhesion between zinc and aluminium depended on the degree of epitaxy between the deposit and the substrate. As the lattice constant of aluminium is 4.04 Å compared with 2.66 Å for zinc (see Table 13-4), by replacement of two aluminium atoms by three zinc atoms the zinc deposit is formed on the (1 10) plane as an atomic layer with little distortion. Bailey[92] published an X-ray and electron diffraction study of zincated aluminium and concluded that the zinc film was covered with separated small single crystals of zinc. He also presented evidence to support the existence of small amounts of zinc hydroxide on the surface. In an extensive study of the zincating of aluminium, Lashmore[98,99] used transmission electron microscopy and electron diffraction and found that zinc initially

forms epitaxial semi-continuous films on all the principal lattice planes of aluminium. Subsequent zinc growth continued in the form of separate crystallites (2000 Å diam) which grew upon the initial film while continuing to maintain the epitaxial relationship.

Colby and Dennis[""] published scanning electron micrographs of commercial purity aluminium after 5 seconds and 30 seconds immersion in zincate solution.

In the first 5 seconds (Fig. 13-2a) zinc crystallites had nucleated preferentially around etch pits, while after 30 seconds (Fig. 13-2b) more of the surface had been covered with zinc and the growth centres had started to coalesce. However, even after 2 minutes immersion, the surface was still not completely covered though the preferential growth round etch pits was not as obvious.

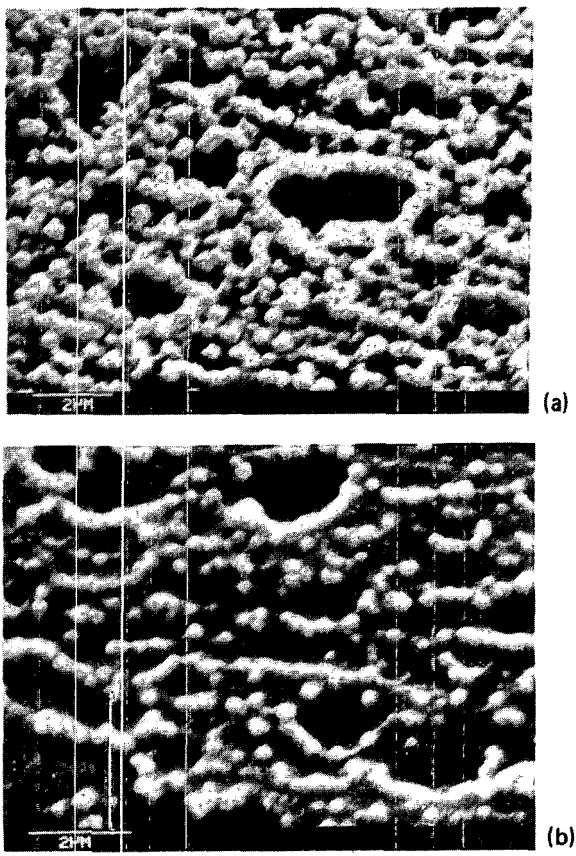

Fig. 13-2. Scanning electron micrographs of the surface of commercial purity aluminium pretreated by alkaline cathodic cleaning and etching for 1 minute in 5% HF, 50% HNO_3:
(a) after 5 seconds immersion in modified alloy zincate solution at room temperature,
(b) after 30 seconds immersion[101]

Bailey[92] found that from a dilute zincate bath (5 g/l ZnO + 45 g/l NaOH), thicker, large-grained zinc deposits (1,000 crystals per cm^2) are obtained with a tree-like structure 10^{-3} cm diameter x 10^{-5} cm high which may correspond to single crystals. This is in contrast to deposits from a more concentrated solution (100 g/l Zn + 500 g/l NaOH as used by Keller and Zelley[105]), which are finer grained and more compact. From theoretical grounds Bailey calculated the crystal size found in the concentrated solution as approximately one hundredth that in the dilute solution, with a correspondingly large increase in the adhesion between the zinc and aluminium in the former.

Wyszynski[100] used electron microscopy to examine the replacement zinc deposits formed on aluminium after treatment in both dilute and concentrated solutions. From a solution containing 20 g/l ZnO + 120 g/l NaOH the deposit obtained was irregular, while from a solution containing 100 g/l ZnO + 500 g/l NaOH a uniform but coarse deposit was formed but with a tendency for the development of a dendritic growth.

Effect of solution composition

Bailey found there was a lower limit to the concentration of the zincate solution below which adhesion was generally poor. He found that ½ minute zincate treatment was insufficient to obtain good adhesion, and that the adhesion after 3 minutes was approximately similar to that after 5 minutes. He attempted to correlate adhesion with solution composition. For good adhesion, he considered a suitable solution composition could be based on a ZnO/NaOH ratio approximately as follows:

zinc oxide	40-50 g/l
sodium hydroxide	400-450 g/l

The adhesion evaluation of nickel deposits onto aluminium which had been treated in a range of zincate solutions was carried out by Wyszynski.[100] The results obtained indicated that the treatment in the very dilute zincate solutions did little to increase the adhesion between aluminium and the deposited nickel, while treatment in the concentrated solutions generally improved the adhesion of the plate to the substrate.

The weights of the immersion zinc deposits obtained in both the dilute and concentrated zincate solutions have been determined and the differences reported are only slight, but the dilute solutions produce thicker coatings than the concentrated solutions, which must therefore be of lower density.[92, 96]

Robertson, Ritchie and Druskovich[86] used an aluminium sample in the form of a rotating disc to investigate the effects of varying the zinc concentration (0.01-0.5 M), disc rotation speed (66-1380 rpm), temperature (5-72°C), and sodium hydroxide concentration (1.5-9.0 M) on the kinetics of zinc deposition on aluminium from zincate solutions. It was found that the reaction was usually first order. When the zincate concentration was 0.1 M, the reaction was chemically

controlled with an activation energy of 35.7 kJ mol^{-1}. At high zincate concentrations, high disc rotation speeds and low sodium hydroxide concentrations, a thin film of zinc metal was formed on the aluminium surface, blocking the subsequent reaction. It was found that the most compact and adherent zinc films were formed at high zincate concentrations. This finding is consistent with industrial practice. These results were explained using mixed potential measurements and Evans' diagrams.

The effect of alkali concentration of the zincate solution on the weight of the deposit formed is seen in Fig. 13-3, which shows that the higher the caustic soda concentration, the lower the weight of zinc initially deposited. After the first 15 seconds (approximately), the gain in weight of the deposit is approximately independent of alkali content.

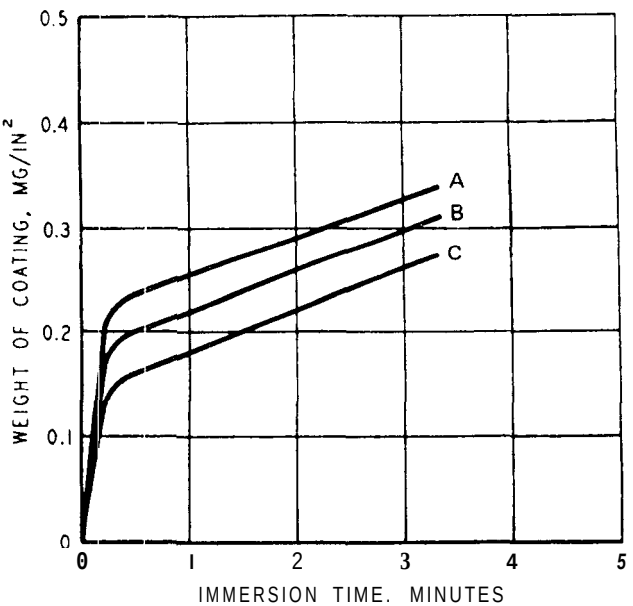

Fig. 13-3. Effect of concentration of zincate solution on weight of deposit formed on commercial purity aluminium at 21°C[91]

A. 400 g/l NaOH
B. 600 g/l NaOH
C. 800 g/l NaOH
0.1mg/in^2 = 0.155 g/m^2

Numerous modifications to the basic zinc oxide/caustic soda solutions have been suggested with the object of producing a thin, uniform, firmly adherent layer of zinc which will promote adhesion of a plated deposit to aluminium and its alloys.

Korpiun[84] in 1935 proposed the addition of copper, in the form of potassium copper cyanide, and sodium sulphite to a zincate solution containing 80 g/l ZnO + 400 g/l NaOH to confer improved adhesion of various deposited metals to aluminium. Three modified solutions proposed by Zelley[108] are stated to give uniform zinc coverage of aluminium and many alloys, and to improve the adhesion of a number of deposited metals. The nominal solution compositions proposed by Zelley are the following:

	Solution 1	*Solution 2*	*Solution 3*
sodium hydroxide	525 g/l	50 g/l	120 g/l
zinc oxide	100 g/l	5 g/l	20 g/l
ferric chloride	1 g/l	2 g/l	2 g/l
potassium sodium tartrate	10 g/l	50 g/l	50 g/l
sodium nitrate	–	1 g/l	1 g/l

Zelley found that small amounts of ferric chloride in conjunction with the tartrate ion improved the adhesion of deposits, particularly on magnesium containing alloys. The sodium nitrate present in the dilute solutions is claimed to limit the weight of zinc deposited. The use of any of these three solutions, in conjunction with a double immersion treatment, is further stated to improve the adhesion of plated deposits on a number of casting alloys and on magnesium-containing alloys, as well as the Al-Zn-Cu-Mg and the Al-Cu-Mg-Mn alloys. Good plating adhesion on the high magnesium alloys is claimed by increasing the sodium potassium tartrate to 100 g/l in the concentrated solution. Surface preparation, as well as time and temperature, are particularly critical in the dilute baths. Treatment should be carried out at 21 to 24°C, and the immersion time should not exceed 30 seconds.

Such and Wyszynski[106] have indicated that the presence of nickel in the zincate solution improves the adhesion of nickel plated directly onto the zinc deposit. Copper also assists adhesion to some alloys, and a substitution of zinc oxide by zinc sulphate was found to give a further improvement. A typical solution as described by Wyszynski,[100] and referred to as the Bondal process,[109] contains:

nickel sulphate	30 g/l
zinc sulphate	40 g/l
nickel sulphate (hexahydrate)	30 g/l
zinc sulphate (heptahydrate)	40 g/l
sodium hydroxide	106 g/l
potassium cyanide	10 g/l
potassium hydrogen tartrate	40 g/l
copper sulphate (pentahydrate)	5 g/l
ferric chloride (hexahydrate)	2 g/l

X-ray microanalysis of the thin, fine grained, immersion film formed on aluminium from this modified alloy zincate solution showed it to be approximately 86% zinc, 8% copper and 6% nickel.[96] Chemical analysis[102] of films stripped from commercial purity aluminium gave a typical composition of 84.5% zinc, 10% copper, 3% nickel and 2.5% iron, while the simple zincate films contained only zinc. Results from X-ray microanalysis suggest that copper and nickel codeposit on the zinc crystallites, retarding their growth and providing sites for strong metallic bonding with subsequent copper or nickel electrodeposits. Monteiro and Ross[103] also used X-ray microanalysis to study modified alloy zincate deposits on aluminium, and noticed that copper (and to a lesser extent, iron) deposited preferentially round the perimeter of those bare parts of the surface where no deposit formed. They also used Auger electron spectroscopy coupled with argon ion milling to analyse the composition of the coating and found that copper is deposited preferentially to zinc at the substrate/film interface in the initial stages (Fig. 13-4). As the film thickens the concentration of copper falls and that of zinc predominates. Iron and nickel are present at the 1-2 at.% level throughout the film.

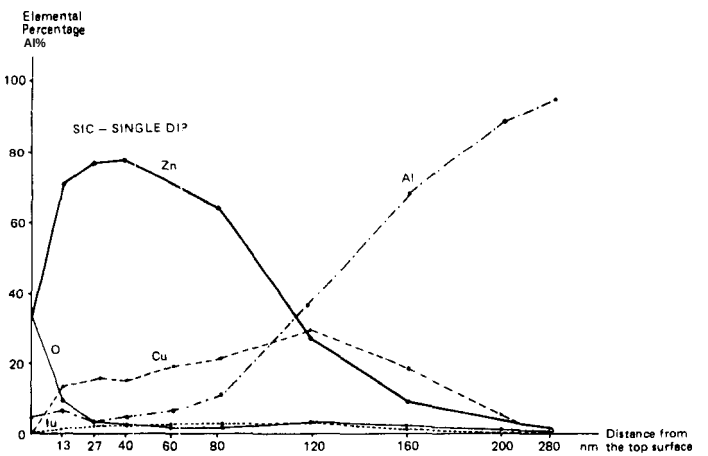

Fig. 13-4. Auger electron spectroscopy results of modified alloy zincate film after 90 seconds of single dip treatment of commercial purity aluminium, expressed as atomic percentages of the main constituents versus distance from the outer surface[""]

The low coating weight and growth rate of the modified alloy zincate (MAZ) film was compared with those formed in dilute (DSZ) and concentrated *(CSZ)* simple zincate solutions by Golby, Dennis and Wyszynski (Fig. 13-5).[102]

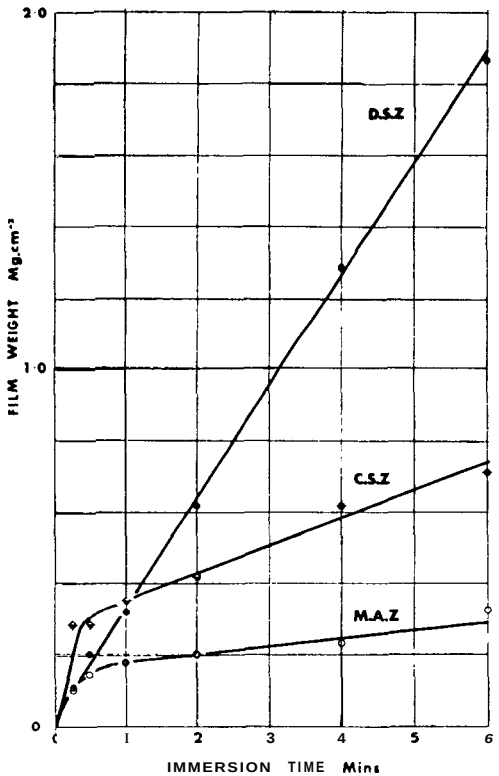

Fig. 13-5. Relationship between film weight and immersion time in various solutions at room temperature on commercial purity aluminium:[102]

DSZ Dilute Simple Zincate (10 g/l ZnO + 120 g/l NaOH)
CSZ Concentrated Simple Zincate (100 g/l ZnO + 500 g/l NaOH)
MAZ Modified Alloy Zincate

The viscosities of the three zincate solutions, relative to water, measured at 20°C were as follows:[102]

DSZ =2.711
MAZ =3.538
CSZ =46.412

The aluminium content of the modified alloy zincate solution increases with use. According to Wyszynski,[100] an increase to the level of 15 g/l aluminium does not affect generally the adhesion of the deposit to most alloys. However, for some alloys (e.g. Al-15%Si), deposit adhesion decreases with increase in aluminium

content in the bath. Wyszynski found that since aluminium forms an insoluble cyanide it can be precipitated out of solution by the addition of potassium cyanide, without interference with the composition of the modified alloy zincate solution.

The transference of lead from jigs used for tin-lead plating of aluminium-tin bearings has been found to cause blisters on the aluminium alloy. Analysis of zinc alloy deposit in the blisters revealed the presence of lead.[100] Plating on free-cutting aluminium components containing lead is not recommended as they contaminate zincate baths. Blisters can be avoided by keeping the lead contamination to a low level by plating the lead out of solution onto scrap aluminium from time to time.

Effect of alloy composition

The way in which zinc deposition varies with alloy composition is shown in Fig. 13-6 for a concentrated simple zincate solution and Fig. 13-7 for a modified alloy zincate solution.

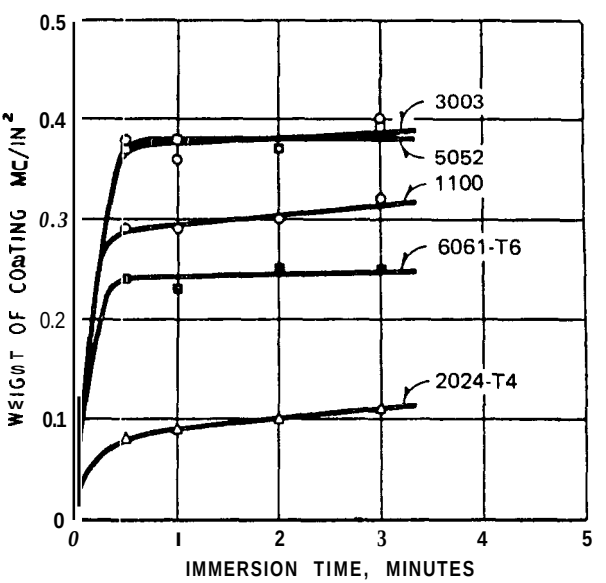

Fig. 13-6. Weight of zinc immersion coating obtained on different wrought alloys in concentrated simple zincate solution (100 g/l ZnO + 525 g/l NaOH)[105]

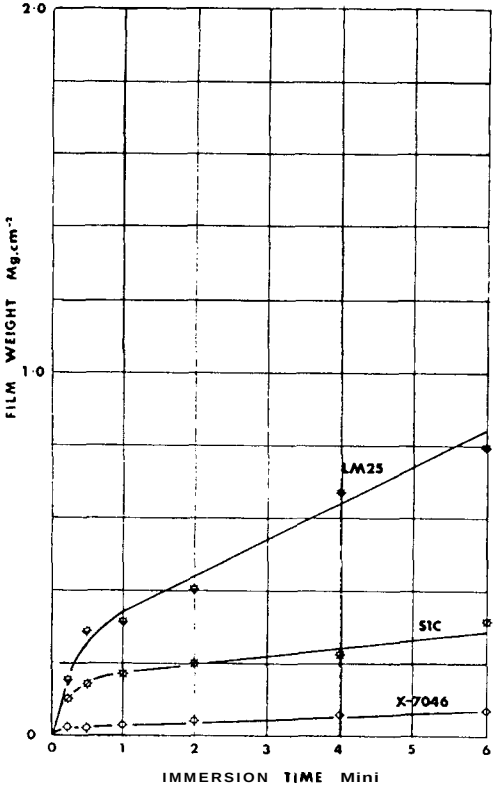

Fig. 13-7. Weight of zinc immersion coating obtained on different alloys in modified alloy zincate solution[102] (S1C = 1100 alloy)

Results which differed in some instances were obtained by Bengston[85] who found rather lighter deposits on Al-1¼%Mn alloy (3003) and heavier deposits on Al-1%Mg-0.5%Si type alloys (6061) which showed a rise in the rate of growth after one minute. As has been seen, the thinner, more compact, deposits generally show the better adhesion properties. In practice, however, the process may have to be adapted to suit varying alloy compositions or structures.

The effect of alloy composition is in some cases due to variations in the potential differences between the alloys and zinc in the alkaline solution, e.g. aluminium and the aluminium-magnesium alloys have a higher potential difference with respect to zinc than the heavy-metal-containing alloys, resulting in a thicker zinc deposit for the same conditions.

Table 13-1 (see page 1115) shows the potentials of a number of aluminium alloys and other metals compared with zinc.

Local potential differences between alloy constituents may also play a part. The potentials of several second phase intermetallic particles, also measured in 53 g/l NaCl + 3 g/l H_2O_2 were given on page 1116 (Table 13-2). However, as noted by Golby, Dennis and Wyszynski[102] the relative nobility of metals, aluminium alloys and second phase particles in alkaline zincate solutions is different from that in 53 g/l NaCl + 3 g/l H_2O_2. In the latter solution, the natural oxide tends to remain on aluminium alloys, whereas the oxide is dissolved in alkaline zincate solutions. A qualitative assessment of the relative nobilities in modified alloy zincate solution was made[102] but it was soon realised that in a solution as complex as modified alloy zincate, the potential of an aluminium alloy changed with time (Fig. 13-8) as copper, nickel, iron and zinc deposited and progressively covered the alloy substrate.

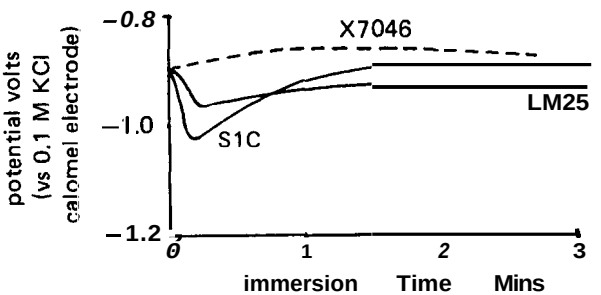

Fig. 13-8. Change in potential of aluminium on immersion in modified alloy zincate solution at room temperature using a single dip sequence[101]

The aluminium-silicon casting alloys such as LM25 (Al-7%Si) have a heterogeneous microstructure with regions of eutectic. The etching response is also heterogeneous and the silicon platelets within the eutectic are clearly seen in the scanning electron micrograph (Fig. 13-9) of the etched surface prior to zincating. Golby and Dennis[101] found that on immersion in zincate solution there was preferential nucleation and growth of the zinc deposit on the eutectic regions, due to the potential difference between the silicon platelets and adjoining aluminium being larger than the differences within the single phase non-eutectic regions.

When studying the characteristics of immersion zinc films on Al-3%Cu-5%Si and Al-10%Cu-2%Si casting alloys LM4 and LM12, Wyszynski[100] showed that there was incomplete development of the zinc deposit in areas rich in alloying constituents at which the adhesion of a deposited metal would be weak.

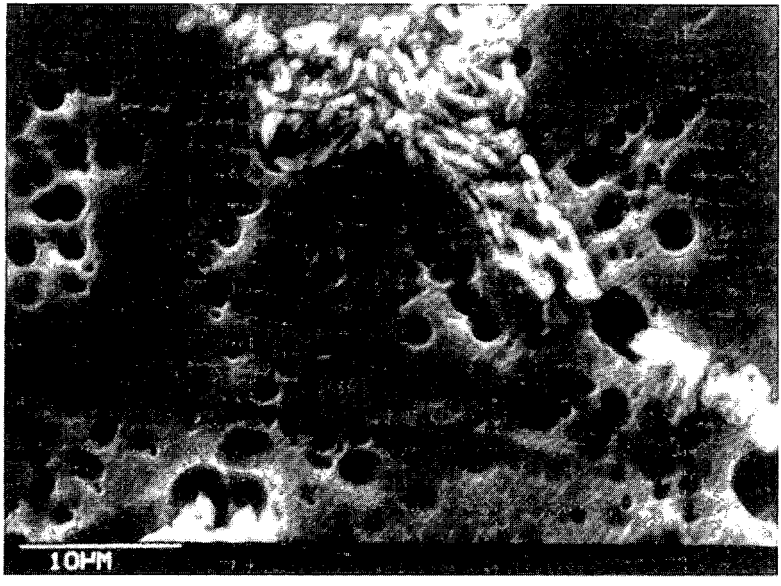

Fig. 13-9. Scanning electron micrograph of Al-7%Si casting alloy after alkaline cathodic clean and one minute dip in 50% HNO_3 showing the surface structure immediately before immersion in zincate solution. Clearly visible (white particles) are silicon platelets in the eutectic regions and etch pits. Single dip zincating results in preferential deposition on eutectic regions. The double dip technique reduces the galvanic heterogeneity of the surface and results in improved adhesion[101]

Effect of temperature

The effect of operating temperature on the deposit thickness obtained from the concentrated simple zincate solution is shown in Fig. 13-10.

As is seen, the initial rate of deposition is increased appreciably by the use of high temperatures.

Bailey[92] showed that in 100 g/l ZnO + 520 g/l NaOH, good adhesion was obtained with 1-3 minutes immersion at room temperature, while at 85°C adhesion was good after 1 minute but poor after 3 minutes. Below room temperature, longer immersion times were required to secure good adhesion and at -6°C the reaction had slowed down so much that a 20 minute immersion was needed to give good adhesion.

Wyszynski[100] studied the influence of temperature on the composition of the film formed from the modified alloy zincate solution. Whilst increase of temperature is beneficial in the case of some alloys, since it enables the optimum film thickness

of 0.2-0.3 μm to be reached more quickly, it cannot be allowed to increase in the case of high copper and high magnesium alloys. Furthermore, as the rate of film build-up increased, its composition also altered, becoming progressively richer in copper with the subsequent reduction of adhesion of the deposit

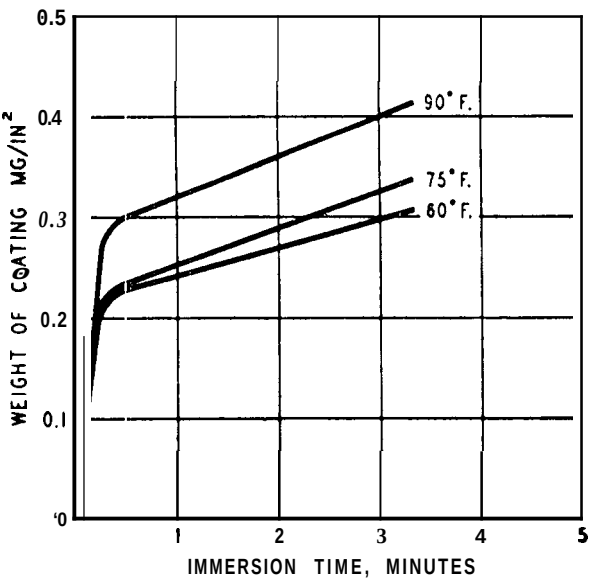

Fig. 13-10. Effect of temperature of the concentrated simple zincate solution (100 g/l ZnO + 525 g/l NaOH)[91]

The effect of temperature on process characteristics has a considerable practical significance since dissolution of aluminium in sodium hydroxide is an exothermic reaction. Unless the volume of the process solution is substantial or artificial cooling is introduced, its temperature can rise fast during use, with a progressive reduction of bond strength.

Effect of pretreatment

As in the case of variations in alloy composition, the pretreatment may affect zinc deposition via the potential of the aluminium.

Fig. 13-11 shows the potential difference between commercial purity aluminium treated in various ways and zinc in a concentrated simple zincate solution, while the effects of these treatments on the zinc deposit is shown in Table 13-5.

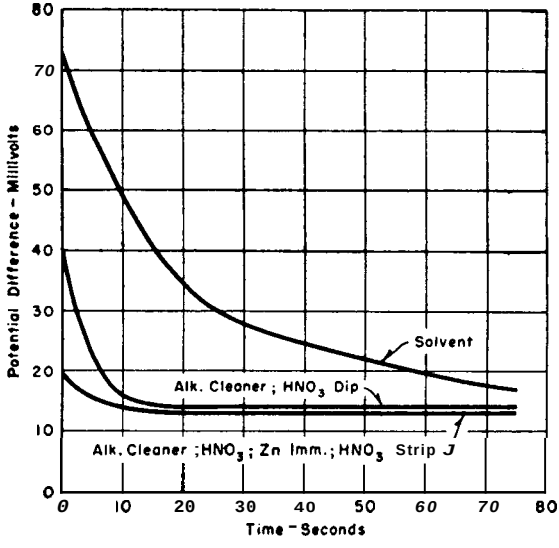

Fig. 13-11. The potential difference between commercial purity aluminium after various pretreatments and high purity zinc in a concentrated simple zincate solution (100 g/l ZnO + 500 g/l NaOH)[93]

TABLE 13-5

Effect of pretreatment on the zinc immersion deposit on commercial purity aluminium[93]

Treatment	*Coating weight* *(mg/in²)*	*(g/m²)*	*Zinc content* (%)	*Resistance** *(micro-ohms)*
Electrodeposited zinc	–	–	–	**5**
Solvent cleaned, 30 sec Zn immersion	1.0	1.6	93.8	10
Alkali cleaned, HNO_3 dip, 30 sec Zn immersion	0.33	0.53	83.0	15
Alkali cleaned, HNO_3 dip, double 30 sec Zn immersion	0.16	0.26	72.5	70

* The surface resistance was measured by a Kelvin Bridge using 0.25 in² (1.6 cm²) contacts and 50 lb (22.7 kg) pressure.

The type of cleaning and etching procedure adopted before the immersion in the zincate bath may have a significant influence on the deposit obtained. This is shown in Fig. 13-12.

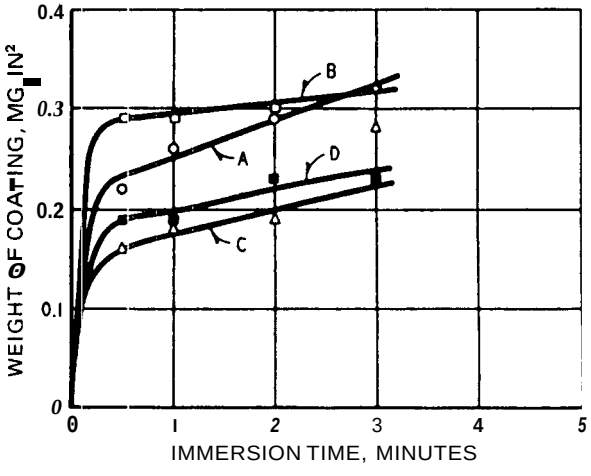

Fig. 13-12. The effect of different pretreatments on the weight of the zinc immersion coating on commercial purity aluminium. **A:** carbonate-phosphate cleaner –– zinc dip; B: As A but cleaning followed by 25% sulphuric acid etch; C: as **A** but double zinc dip; D: phosphoric-nitric acid chemical polishing solution (Alcoa R5) plus zinc dip''

Although the modified alloy zincate process was initially formulated for commercial purity aluminium, Wyszynski[100] found its extension to the complete range of aluminium alloys proved that the original etch solution (50% v/v nitric acid) was not satisfactory in every case. Although no universally excellent etch was found, the nearest to the optimum was based on 30% v/v nitric acid, 3% w/v sodium hydrogen bifluoride, 1% ferric chloride 70% v/v water. Although individual etches of greater efficiency can be compounded for individual alloys, the acid etch quoted can be regarded as the nearest compromise to the universal etch.

Golby and Dennis''' found that the immersion film morphology and its adhesion were influenced significantly by aluminium alloy response to the pretreatment sequence. For optimum adhesion a particular process sequence is likely to be necessary for each alloy.

4. DOUBLE ZINC IMMERSION TECHNIQUE

The double zinc immersion technique, by which the first zinc coating is stripped in nitric acid and a new zinc deposit applied was suggested by Korpiun.[84] This method has been found useful in plating many alloys which are difficult to plate satisfactorily by the single immersion method. Golby, Dennis and Wyszynski[102] have shown by scanning electron microscopy that the second coating is more compact and consists of a larger number of fine grains. Applying and removing the first zinc deposit thus results in the production of a surface with a more uniform potential (see Fig. 13-13).

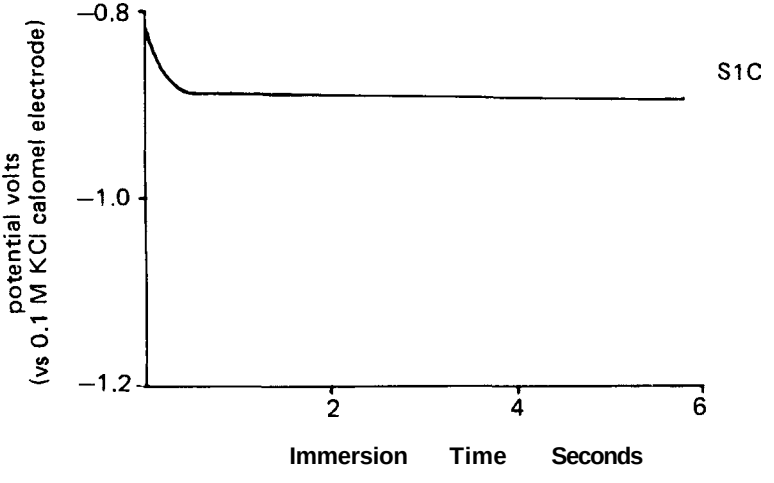

Fig. 13-13. Change in potential of aluminium on immersion in modified alloy zincate solution at room temperature using a double dip sequence. (Compare with single dip Fig. 13-8) (S1C = 1100 alloy)

Table 13-6 gives details of deposit weights on three alloys treated by various methods including double immersion treatment. As is seen, the second zinc immersion treatment gives thinner deposits, despite longer treatment.

TABLE 13-6

Weight and thickness of zinc deposit obtained on aluminium alloys given various pretreatments before zinc immersion[93]

		Zinc immersion		*Zinc deposit*	
Alloy	*Pretreatment*	*Time mins*	*Temp °C*	*Weight g/m²*	*Thickness μm*
1100, commercially pure	A, B, C	1	23	0.16	0.020
	A, C		24	0.35	0.048
	A, C	3	24	0.59	0.084
3003, Al-1¼%Mn	A, B, C	1	25	0.21	0.030
	A, C	1	24	0.51	0.074
	A, C	3	24	0.72	0.104
2024-T4, Al-4½%Cu-1½%Mg-0.6%Mn	A, D, C	1	24	0.13	0.018
	A, D, C	3	32	0.18	0.028

A. 1 min carbonate-phosphate cleaning etch.
B. 1 min zinc immersion dip.
C. ½ min immersion in 1:1 nitric acid or, when after zinc immersion, until zinc appears removed.
D. 5 min in 25% sulphuric acid at 80°C.

Lashmore[99] used Rutherford backscattering to analyse surfaces at successive stages of a double zinc immersion sequence. After 1 minute immersion in a zincate solution which contained ferric chloride and Rochelle salts, iron and zinc were present in a relatively thick deposit. This was then dipped into 50% nitric acid for 30 seconds and thoroughly rinsed. Both zinc and iron were still detected on the surface in roughly equal quantities, corresponding to about four atomic layers in total. Lashmore concluded that iron plays an important role in the deposition process and a surface alloy exists that is relatively insoluble in nitric acid.

Monteiro and Ross[103] compared the composition of single dip (Fig. 13-4) and double dip (Fig. 13-14) deposits from modified alloy zincate solutions using Auger electron spectroscopy and argon ion milling to measure the change in composition through the film from the substrate to the outer surface. The double dip film was only 12.0nm thick (compared with 280 nm for the single dip film) and contained a higher proportion of aluminium and copper with a corresponding lower proportion of zinc, compared with the single dip film.

The number, size, distribution and composition of intermetallic particles in the aluminium surface affect the roughness of the surface after zincating. The alkaline cleaner and sulphuric acid etch in the pretreatment stages of the zincating process preferentially attack the intermetallic particles (or the aluminium at their interface, depending on their relative potentials). Phosphoric acid cleaners, though, have a slight polishing effect (see chapter 3) and when they are used, the resultant zincate immersion coatings are denser and more uniform.

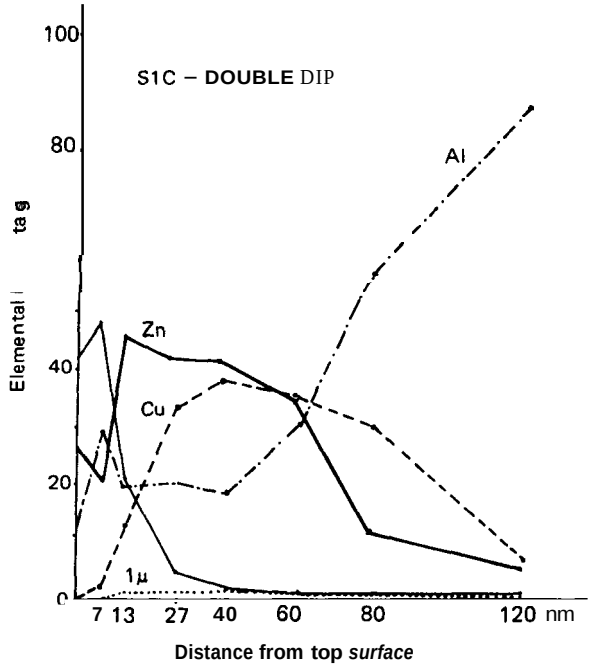

Fig. 13-14. Auger electron spectroscopy results of modified alloy zincate film after 90 seconds of double dip treatment of commercial purity aluminium, expressed as atomic percentages of the main constituents versus distance from the outer surface.[103] (Compare with single dip Fig. 13-4)

Williams and Davison[110] studied the influence of intermetallic particles on the substrate surface roughness after various stages of the double dip zincate process. Reducing the size and number of intermetallic particles, determining their behaviour, and understanding the alloy electrochemical characteristics led to increased reliability and higher bit densities in plated 5086 Al-4.0Mg-0.4Mn-0.15Cr used for computer memory hard discs. Relatively slight reductions in iron and silicon levels were found to have a large impact on disc performance.

Fig 13-15 shows the typical size and distribution of the iron-bearing intermetallic particles in standard and improved purity aluminium-magnesium memory disc alloys. Reducing and equilibrating the electrochemical potential of the aluminium surface through modification of alloy electrochemistry and reduction of the number and size of intermetallic particles, decreased the surface reactivity during the double dip zincate process and resulted in a smoother and more uniform surface (Fig 13-16).

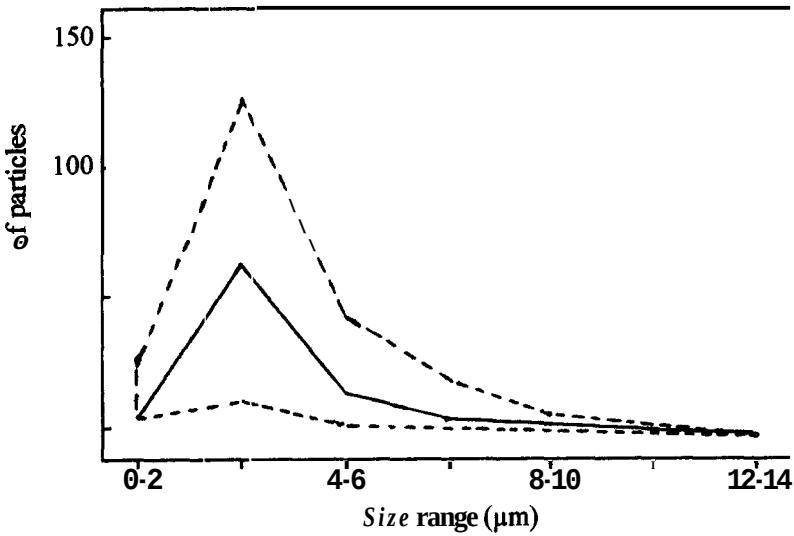

Fig 13-15 LeMont analysis of the typical size and distribution of inter-metallic particles in 5086-type alloys.

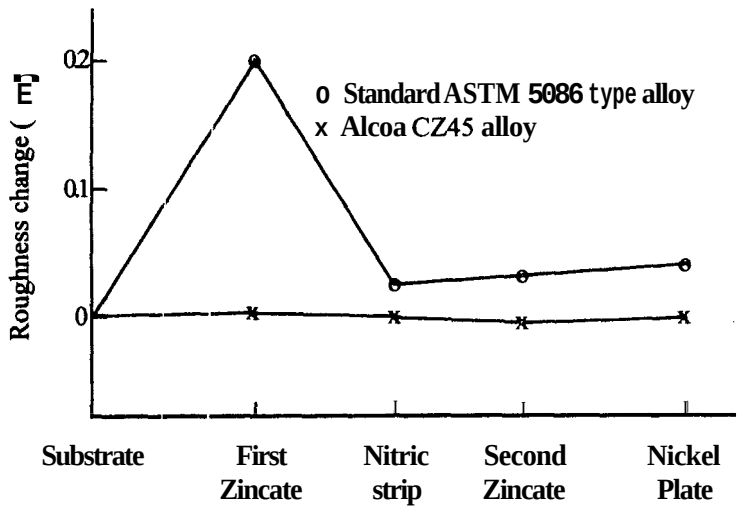

Fig 13-16 Substrate surface roughness alter various steps of the electroless nickel plating process.

The electroless nickel layer deposited on this smoother surface was itself smoother, had fewer pitting defects, reduced the nickel thickness required and the amount of polishing needed, and enabled the electroless deposition of a more uniform cobalt alloy magnetic layer with a higher memory density.

5. ULTRASONIC ZINCATE PROCESS

Ultrasonic agitation in the zincate solution as well as in subsequent copper or silver plating has been used in electroplating aluminium bus bars at Westinghouse Electric Corp.[111,112] in the **U.S.A.** where, it is stated, a previous 11-stage pretreatment and plating sequence was reduced to the following four stages: ultrasonic zincate, rinse, ultrasonic silver plate, rinse. The zincate bath contained 125 g/l ZnO + 400 g/l NaOH and was operated at 24-52°C. When the work was placed in the solution, it was first made cathodic when the solution acted as an ultrasonic electrolytic cleaner, after which the current was turned off for the immersion deposition stage, where the effect of the ultrasonic vibrations is stated to remove any loosely-adherent zinc.

This process is carried out in a local plating cell where only the contact areas of the bus bars are plated. Ultrasonic vibrations are provided by a high frequency generator, and four immersible transducers for each operation, operating at 20kHz.

6. OTHER ZINC IMMERSION PROCESSES

Immersion in zinc fluoborate solution containing a trace of nickel fluoborate, for example:

zinc fluoborate	150 g/l
nickel fluoborate	0.05 g/l
ammonium chloride	20 g/l

at pH 3.0 at room temperature for 4 minutes has been suggested as a pretreatment for aluminium before copper plating.'" It was found satisfactory by Wittrock[114] for plating on aluminium bus bars.

Of some interest is a range of solutions for immersion deposition developed by Heiman[18] who proposed a zinc solution containing:

zinc sulphate	719 g/l
hydrofluoric acid	35 ml/l

though the composition is by no means critical. This solution is used at 25°C with mild agitation for immersion times varying from 5-60 seconds. Good adhesion was obtained cn commercial purity aluminium as well as on Al-Cu-Mg-Mn and a number of other alloys, adhesion values above the ultimate tensile strength of the basis metal being obtained by the Ollard test on aluminium plated by this method. Fig. 13-17 shows the comparative growth of the zinc deposit in this solution.

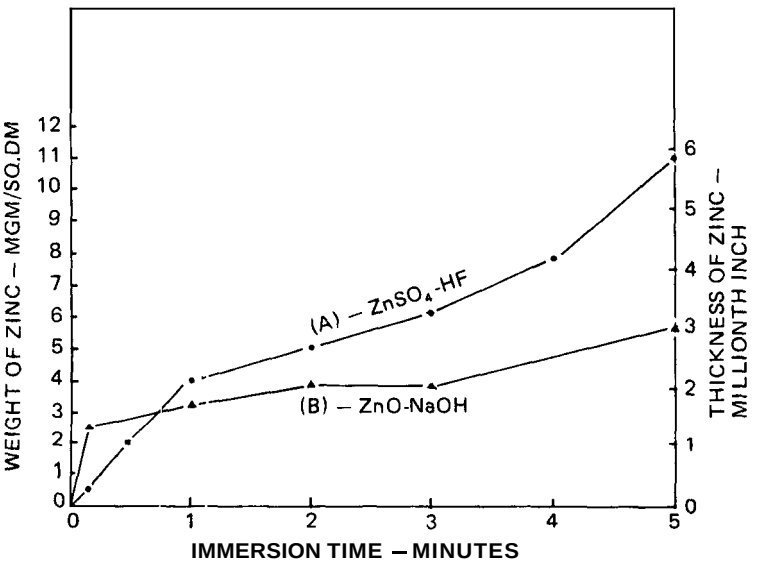

Fig. 13-17. Thickness of zinc deposited on commercial purity aluminium immersed in: A: $ZnSO_4$ 5N, HF 0.5N; B: 100 g/l ZnO+ 500 g/l NaOH[18]

Another method of pretreatment, the Alcoa 661 process,[115] employs a zincate immersion step to remove the aluminium oxide and then coat the work with zinc. The zinc coating is then dissolved in a nickel plating solution followed by nickel electrodeposition on the oxide free aluminium. The dissolution of the zinc is monitored by measuring the electrode potential difference, and plating is started when a pre-determined potential is reached. This patented process has the advantage of being cyanide free.

A process which enables very thick zinc deposits *to* be produced for corrosion resistance involves the use of zinc fluoride tetrahydrate in suspension.[116] The

amount of zinc deposited from conventional simple zincate solutions is about 1.0 g/m^2 depending on duration of immersion, temperature and the conditions of prior pretreatment. Concentrated simple zincate solutions suffer the disadvantage of high viscosity. With aqueous zinc fluoride, its solubility is so low that the viscosity of a saturated solution is little different from that of water so that with a little wetting agent the solution will penetrate recesses and drain readily. For uniformity, 5-120 g/l undissolved $ZnF_2.4H_2O$ is suspended in water at pH 5.1 at 25°C and gives an immersion deposit of 15-20 g/m^2 on aluminium in 15-20 minutes. The work is then heat treated to form a diffusion layer 50-150 μm deep containing 1-7% zinc.

7. THE PLATING SEQUENCE FOR ZINCATING PROCESSES

A typical flow sheet for plating by the zinc immersion method is shown in Fig. 13-18.

Polishing

The aluminium is first polished if a decorative coating is to be applied. Procedures have been described in Chapter 2.

Jigging

Jigging for plating should be carried out with care. It is important that contacts should be positive, because of the light weight of metal. Spring contacts should be used whenever possible.

Jigs should be of springy aluminium alloy from which most deposits can be removed in 50% nitric acid. Stripping in sulphuric acid should be used for phosphor-bronze contacts or can be carried out by anodic treatment in 60% sulphuric acid or 75% phosphoric acid.

As compared with copper, a 40% larger cross-sectional area should be used to obtain the same electrical conductivity. As a general rule, contacts should then only be of heavy metals, e.g. phosphor-bronze, if the area adjacent to the contact does not show.

If jigs of brass, bronze, etc., are used, they must be stopped off adequately, not only due to the risk of corrosion but also because, if left bare, the aluminium may be anodic in the zincate solution.

Cleaning

To obtain a consistent and uniform deposit, it is necessary to produce a clean active surface for the zinc immersion treatment. Often the work is first degreased in either trichlorethylene or perchlorethylene or in an emulsion cleaner. Whether

this operation is necessary depends on the degree of contamination, but in any event, it is normally essential to precede the remainder of the sequence with an alkaline cleaner.

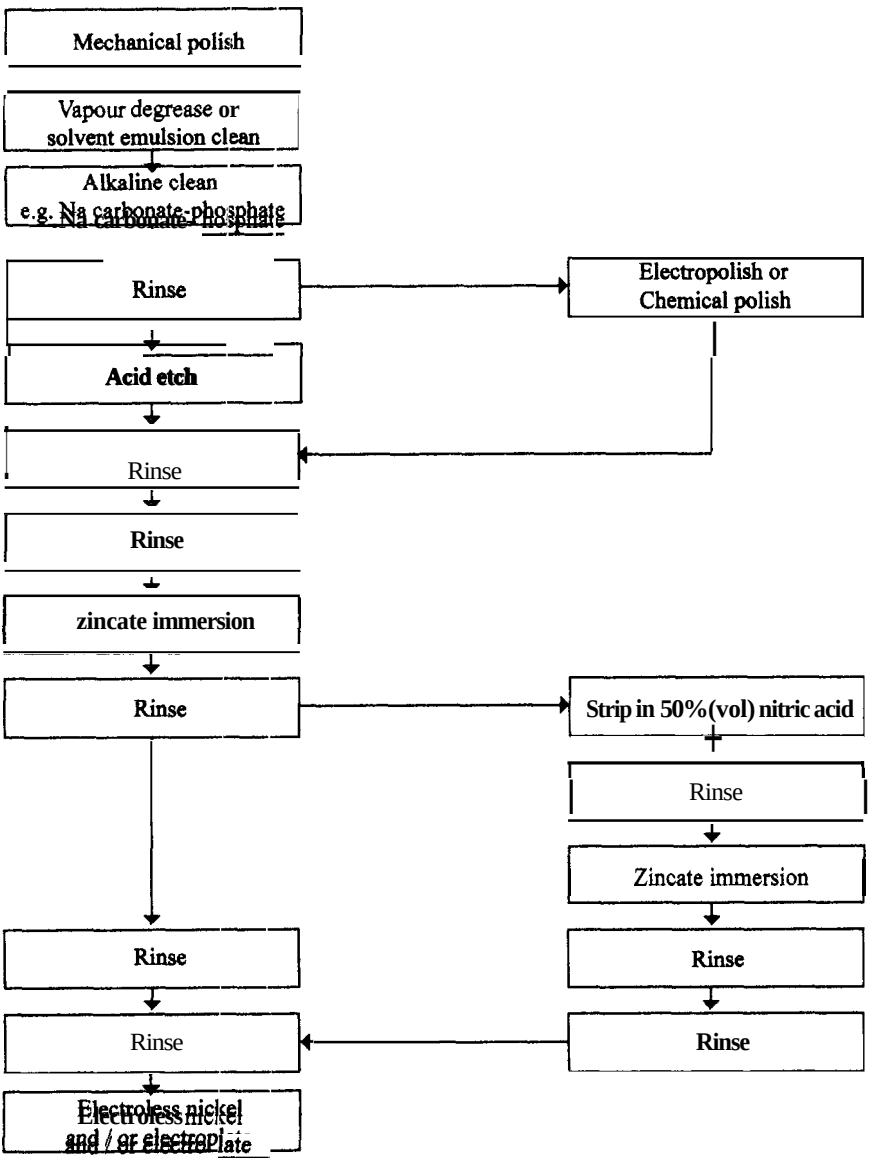

Fig. 13-18. Flow sheet for zinc immersion process of plating aluminium alloys

The formulation of an alkaline cleaner may vary. One that has been suggested for this purpose contains:

sodium carbonate	23 g/l
trisodium phosphate	*23* g/l

and is used at 60-80°C for 1-3 minutes. Other formulations are also suitable (see Chapter 4).

Acid ***etch***

After alkaline cleaning, the work is rinsed thoroughly and is then taken through an acid etch which has the dual function of removing micro constituents from the surface and of removing the original oxide film. **A** number of acid solutions have been found suitable.

One of the most effective is 15% (vol) sulphuric acid used at about 90°C for 2-5 minutes. The time depends on the alloy used, and is generally kept fairly short for castings. This etch has been proved particularly suitable for magnesium containing alloys but gives good results on most wrought and cast alloys.

For many wrought alloys the single 1:1 (vol) nitric acid dip may be sufficient and is somewhat faster since only a 30 second immersion is usually required.

A nitric-hydrofluoric acid mixture containing:

hydrofluoric acid (40%)	10% (vol)
nitric acid *(SG* 1.42)	10% (vol)
water	80% (vol)

used for 1 minute at temperatures up to 40°C has been recommended, while some casting alloys with high silicon contents are preferably treated in a somewhat more concentrated solution containing:

nitric acid	75% (vol)
hydrofluoric acid (48%)	*25%* (vol)

for *3-5* minutes at room temperature.

For many wrought alloys a chromic-sulphuric acid etch has been suggested by Bengston[85] containing:

chromic acid	30 g/l
sulphuric acid	150 g/l

This dip, operated at 65°C, is stated to give good adhesion when used for 3 minutes. It is usually followed by a 50% nitric acid dip. The chromic-sulphuric acid etch offers advantages over sulphuric acid but has the attendant risk of leaving an adherent chromate film on the surface.

Zinc immersion

The zinc immersion process itself can be carried out in solutions of various compositions, a number of which have been discussed above.

The work should be agitated when it is introduced into the solution to ensure uniform contact of the whole surface area with the solution.

In some cases, e.g., with the high silicon casting alloys, a short zinc immersion treatment of 5-10 seconds may be suitable. Tanks are of steel or stainless steel. Ceramic is suitable but has a tendency to crack due to heat evolution when the solution is made up. In operation the components should not be allowed to touch the steel tank as the aluminium may become anodic, preventing zinc deposition. The zinc deposit should be uniform in colour.

Double zinc immersion

Where the double zinc immersion treatment is used, the component is immersed in 50% (vol) nitric acid at room temperature to remove the first deposit. Subsequently it is rinsed and the zinc immersion treatment repeated.

Unmodified zincate solutions give zinc deposits with a dendritic structure and poor adhesion to the substrate. Solutions can be modified with other metals which inhibit crystal growth, giving a finer grained thinner deposit, and the resultant zinc alloy is usually less chemically active than a pure zinc deposit. This allows the production of adherent deposits from electrolytes such as Watts type nickel which would normally be too aggressive for use on pure zinc.

The two main types of alloy zincate in commercial use are iron or copper modified. Compared with the copper modified solutions, those modified with iron are much simpler in formulation, effluent treatment tends to be easier, but good adhesion is restricted to a more limited range of alloys. They can give good results, especially on extruded alloys and also prior to an electroless nickel topcoat. The iron content is between 8 - 12 %.

Copper modified zincate processes can be applied to a very wide range of alloys and produce consistently good results[105]. The copper content is between 10 - 23 %. Copper modified baths usually also contain cyanide, 0.5 - 2.5 % iron, and 0.5 - 2.0 % nickel. These additives assist in controlling the rate of copper deposition and the growth rate and morphology of the zincate coating. The copper modified processes are the most versatile, and allow plating of the widest range of alloys and topcoats. Those containing cyanide are currently more robust, but the toxic waste needs treatment. The new non-cyanide processes use pretreatments that need more care in use.

8. NON-CYANIDE MODIFIED ALLOY ZINCATE PROCESS

Pearson and Wake[104] have developed a more environmentally acceptable and safer process which has eliminated cyanide and operates at lower metal contents

to minimise sludge generation. They have also reduced or eliminated the use of nitric and, in the case of high silicon alloys, hydrofluoric acid, by using a commercial oxidizing acid dip combined with ultrasonic agitation.

Pearson and Wake compared the performance of the non-cyanide modified alloy zincate process (MAZ 2) with the former cyanide process (MAZ 1). The baths were analysed for sodium hydroxide, zinc, copper, iron, nickel, solids content and specific gravity. The metal, sodium hydroxide and cyanide contents of the solutions are shown in Fig. 13-19.

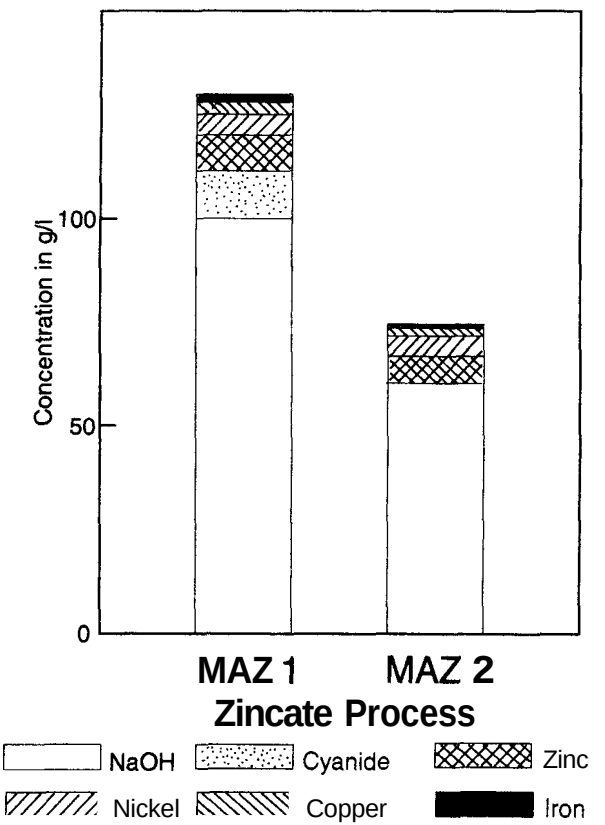

Fig. 13-19. Concentrations of components in Modified Alloy Zincate solutions[104].

The approximate solids content and specific gravity of the solutions used in tests is shown in Table 13-7.

TABLE 13-7

Solids Content and S.G. of Modified Alloy Zincate solutions[104].

Solution	*Solids content*	*S.G.*
MAZ 1 (cyanide)	25%	1.165
MAZ 2 (non-cyanide)	15%	1.096

Results of tests comparing the amount of dragout are shown in Fig. 13-20.

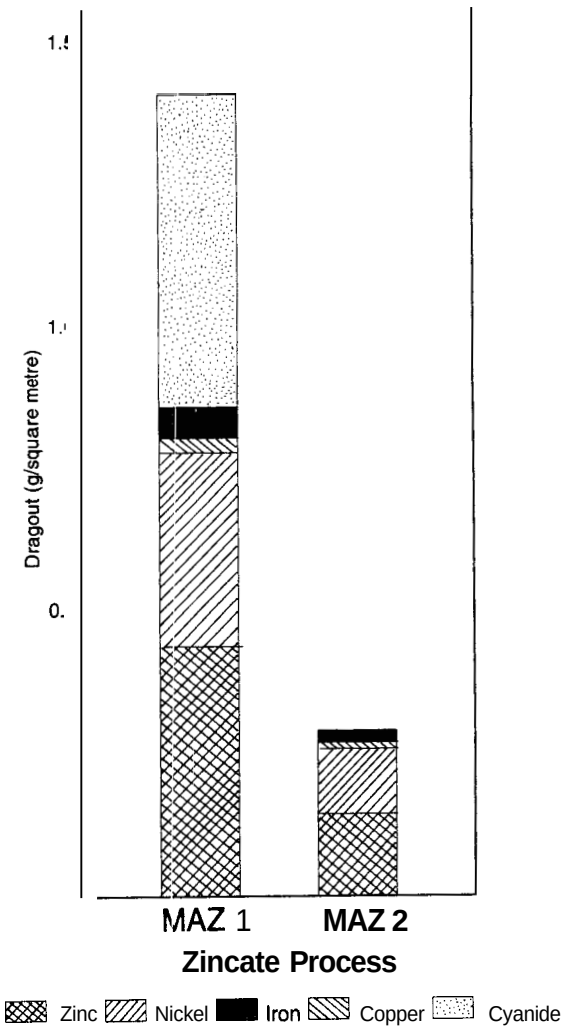

Fig. 13-20. Dragout of constituents from Modified Alloy Zincate solutions[104].

The results show the amount of dragout is related to the solids content of the solutions. The amount of sludge generated from treatment of rinse waters from MAZ 2 is very considerably lower than from MAZ 1. Furthermore the treatment for cyanide from MAZ 1 is not required when using the non-cyanide MAZ 2.

The deposits from both solutions were very similar; both were very fine grained, and both had good adhesion to the substrate (24 kN/m from MAZ 1 and 23kN/m from MAZ 2). The alloy compositions from both solutions were also very similar, each producing an alloy containing approximately 16% copper, as shown in Table 13-8.

TABLE 13-8

Alloy compositions of deposits from Modified Alloy Zincate solutions[104].

Solution	*Zn*	*Cu*	*Fe*	*Ni*
MAZ 1 (cyanide)	80%	16%	2.5%	1.5%
MAZ 2 (non cyanide)	82%	16%	1.0%	1.0%

9. NITRATE AND FLUORIDE FREE PRETREATMENTS

For many years, nitrate and fluoride have been used in the pretreatment of aluminium prior to zincating. Fluoride has been used to remove the loose silicon smut produced during the alkaline etching stage of high silicon alloys (containing more than 5% Si). For low silicon alloys (usually extrusions), it is normally sufficient to use a nitric acid dip to remove the metallic smut produced during alkaline etching. The use of nitrate and fluoride are becoming subject to increasing legislation. Hydrofluoric acid is a highly dangerous material and the use of nitric acid is becoming increasingly restricted due to generation of nitrogen oxides.

Pearson and Wake[104] have developed the following alternative pretreatments for most platable aluminium alloys which avoid the use of nitrate and fluoride. Most extrusion alloys are low in silicon which avoids the need for fluoride in the pretreatment sequence. The use of nitric acid can be avoided by the use of a proprietary oxidizing acid bath (referred to as ME 1). This has been shown to give improved results when compared with the use of nitric acid. Test pieces of 6061 T6 alloy were plated using the following process sequence:

1. Non silicated soak cleaner, 3 minutes, 65°C
2. Alkaline etch, 30 seconds, 65°C
3. Rinse
4. MEI, 2 minutes, 25°C
5. Rinse

6. Zincate (MAZ 2), 60 seconds, 25°C
7. Rinse
8. MEI, 40 seconds, 25°C
9. Rinse
10. Zincate (MAZ 2), 30 seconds, 25°C
11. Rinse
12. Plate

Using this sequence, an average quantitative adhesion value of 9.6 kN/m was obtained. Substitution of 50% nitric acid for the ME1 (stages 4 and 8) and using the same process times and temperatures, an average adhesion value of 3.8 kN/m was obtained. A double dip process sequence was used as it gives a finer grained, thinner deposit on this difficult-to-plate alloy. It is usual commercial practice to use a double dip sequence on hardened extrusions.

Aluminium alloys designed for castings usually contain a fairly high proportion of silicon. After alkaline etching, silicon remaining on the surface causes poor adhesion. Usual practice is to use a fluoride-containing nitric acid dip to dissolve the silicon smut as silicofluoride. Fluoride free chemical treatments are nor capable of dissolving silicon, but a combination of the use of the oxidizing dip ME1 with the use of ultrasonic agitation in an alkaline cleaner has been found to give good adhesion"'. The mechanical action of the ultrasonic agitation dislodges loose silicon smut that would otherwise cause poor adhesion.

Pearson and Wake[104] processed samples of LM 26 alloy containing 12% silicon (average) using ultrasonic agitation in the following pretreatment sequence:

1. Non silicated soak cleaner with ultrasonic agitation, 3 minutes, 65°C
2. Alkaline etch, 30 seconds, 65°C
3. Rinse
4. MEI, 2 minutes, 25°C
5. Rinse
6. Non silicated soak cleaner with ultrasonic agitation, 3 minutes, 65°C
7. Rinse
8. ME1, 2 minutes, 25°C
9. Rinse
10. Zincate (MAZ 2), 60 seconds, 25°C
11. Rinse
12. ME1, 2 minutes, 25°C
13. Rinse
14. Zincate (MAZ 2), 30 seconds, 25°C
15. Rinse
16. Plate

Scanning electron microscopy of the LM 26 (Al-12%Si) alloy after the alkaline etch shows the presence of loose particles ("smut") on the surface, Fig. 13-21.

Fig. 13-21. Surface of Al-12%Si after alkaline etch showing loose "smut".

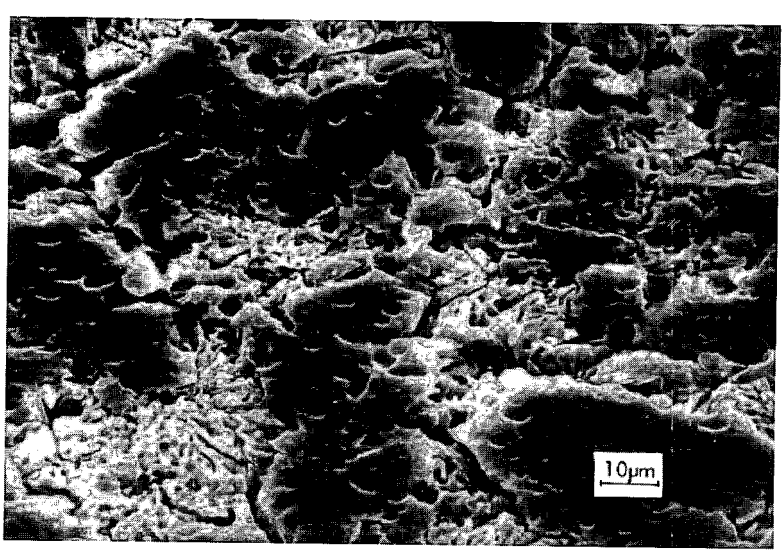

Fig. 13-22. Surface of Al-12%Si after de-smutting in nitric/hydrofluoric showing removal of silicon but some surface damage.

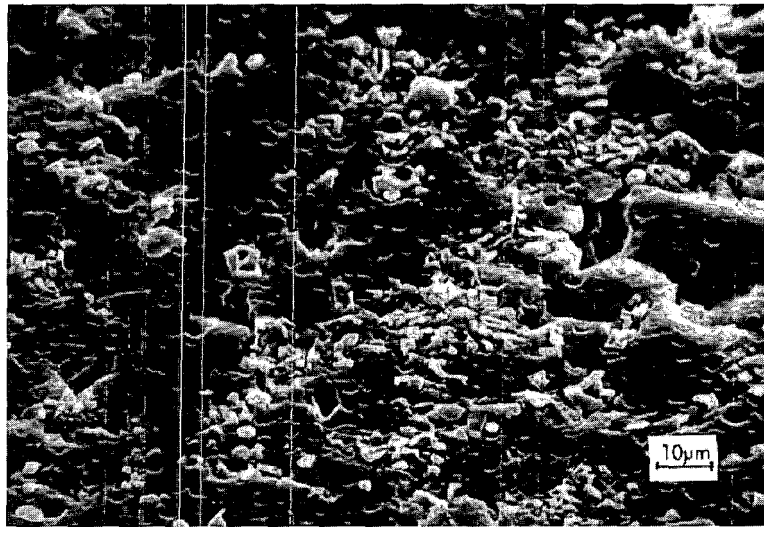

Fig. 13-23. Surface of Al-12%Si after the oxidising acid dip combined with ultrasonic agitation showing less surface damage than in Fig. 13-22, some silicon particles in the surface, and removal of all loose smut.

De-smutting in nitric/hydrofluoric removes silicon from the surface by chemical dissolution but leaves some surface damage (Fig. 13-22). Minimising this surface damage by using the oxidising acid dip combined with ultrasonic agitation (Fig. 13-23) results in slightly higher adhesion. Silicon particles can be seen on the surface but the loose smut has been removed.

Aluminium alloy containing more than 2% zinc do not give satisfactory results in zincate processes and need special treatment. The zincate is applied electrolytically using a current density of 0.5-1.0 A/dm^2 for 30-60 seconds.

10. ELECTROPLATING ON THE ZINC DEPOSIT

After the zinc deposit has been formed, other metals can be plated by normal methods suitable for plating onto zinc, keeping in mind that the zinc deposit is very thin.

The metals that can be plated directly include nickel, copper, zinc, brass, cadmium, silver and chromium.

Copper plating

Copper is usually plated directly onto the zinc deposit and is frequently used prior to decorative nickel-chromium plating, but deposits obtained from a

nickel-containing zincate solution[109] have been used for the direct application of nickel. As in plating on zinc-base diecastings, a cyanide copper solution has been found most generally useful. Typical cyanide copper solutions used for this purpose contain:

	1	2	*3*
copper cyanide	40 g/l	30 g/l	12-21g/l
total sodium cyanide	50	38	17-26
sodium carbonate	30	38	12-25
free sodium cyanide	4 (max)	–	3-6
Rochelle salt	–	50	–
pH	10.2-10.5	9.5-10.5	–

Baths 1 and 3 are operated at 38-55°C. Bath 2 is used at 40°C.

In order to avoid dissolution of the zinc as the work enters the plating bath, electrical contact should be made with the work before it is introduced into the solution. **A** high strike current density, about 2.5 A/dm^2 (25 amp/sq ft) is usually employed. The total plating time is usually between 5 and 10 minutes.

A tendency may be noted for the pH of the copper plating solution to rise due to drag-in from the zincate solution. This can be corrected by adding dilute tartaric acid. High pH, high free-cyanide content and high operating temperatures may all lead to blistering of the copper deposit.

The copper pyrophosphate solution has also proved satisfactory for plating on zinc immersion coating. A typical solution contains:

pyrophosphate (as P_2O_7)	210 g/l
copper (as Cu)	30 g/l
ammonia (as NH_3)	*3* g/l
pH	7.5-8.5

This solution should be operated at 40-60°C and approximately 2-4 A/dm^2 with air agitation.

An alkaline zincate solution containing a chelating agent and approximately 6 g/l copper has been recommended for the treatment of aluminium prior to plating from a copper pyrophosphate bath.

Wilding[118] describes the use of a periodic reversal process for the copper plating of aluminium alloy memory drums for mainframe computers, prior to the magnetic coating of nickel.

Brass plating

The standard brass plating solution can be used on the zinc immersion deposit at room temperature. A solution containing:

copper cyanide	26 g/l
zinc cyanide	11 g/l

sodium cyanide	45 g/l
sodium carbonate	7.5 g/l

is suitable for use at 1.1 A/dm^2 (10 amp/sq ft) at 27-32°C and using 75% Cu-25%Zn anodes. Brass plating is sometimes carried out instead of copper plating before decorative nickel/chromium plating of aluminium. The reason for this is the suggestion that the corrosion resistance obtained is somewhat better.

An important application of brass plating is its use in rubber bonding.

Zinc plating

Zinc can be plated either from alkaline or acid solutions onto aluminium treated by the zinc immersion process. A suitable alkaline zinc plating solution for use on the zinc immersion deposit contains:

zinc cyanide	60 g/l
sodium cyanide	40 g/l
sodium hydroxide	80 g/l

and is used at 25-35°C, 0.5-5 A/dm^2 (5-50 amp/sq ft). As in the case of copper plating, electrical contact should be made before the work enters the solution.

Cadmium plating

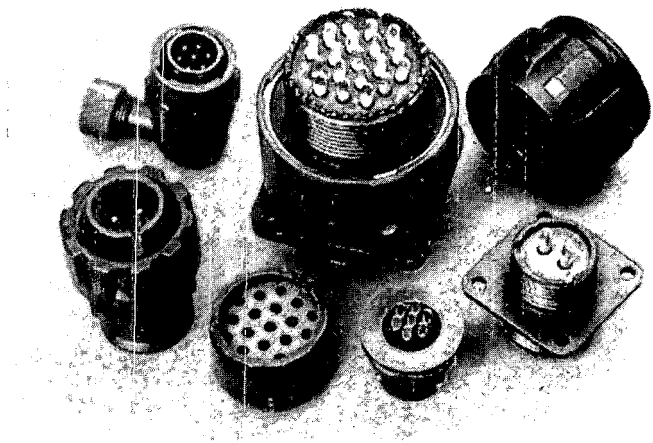

Fig. 13-24. Aluminium military connectors plated with cadmium over Bondal and subsequently passivated drab olive
[Courtesy **A.B.** Electronics and W. Canning Materials Ltd.]

Cadmium is plated mainly for the protection of mixed assemblies of aluminium with heavy metals. For the best results a dilute strike solution is used for 1 minute at room temperature and 2.5 A/dm^2 (25 amp/sq ft) before transferring to the main bath, used at 1.5-5 A/dm^2 (15-45 amp/sq ft). Typical solutions are given below:

	Strike bath	*Main bath*
cadmium oxide	7.5 g/l	26 g/l
sodium oxide	60 g/l	100 g/l

Brighteners are sometimes added to the main bath. The plating of cadmium on a copper-nickel undercoat has also been used.

Iron plating

A process for the hard iron plating of aluminium alloys (such as Al 390 for pistons) has been patented.[119] The aluminium is first zincated, then plated with electroless nickel, and electroplated with iron from a sulphamate/sulphate solution.

Tin plating

Tin, where it is electrodeposited for soldering, is usually applied over copper, and a flash nickel deposit may be interposed to prevent too-rapid diffusion of the tin into the copper. The normal stannate bath is used.

Silver plating

Silver is plated mainly for electrical contacts. Silver should be plated for 10 seconds each in two strike baths, or the second strike can be used by itself after applying a copper deposit from the copper solution given. The second method is generally more satisfactory. Typical compositions and operating conditions are as follows:

	1st strike bath	*2nd strike bath*
silver cyanide	1 g/l	5.3 g/l
sodium cyanide	90 g/l	67.5 g/l

Both solutions are operated at 27°C, 1.5-2.5 A/dm^2, 6 volts for 10 seconds.

After the strike treatment the following silver solution may be used at 27°C and 0.5 A/dm^2:

silver cyanide	30 g/l
potassium cyanide	56 g/l
potassium carbonate	45 g/l
free potassium cyanide	41 g/l

According to Halls,[113] copper or silver or combined copper-silver coatings should be applied in the following thicknesses:

extreme service conditions	50 μm (2 mil) (average)
intermediate conditions	25 μm (1 mil)
dry conditions and arc lighting	12 μm (0.5 mil)

The local minimum should be at least 50% of the average thickness. In combined copper and silver coatings the copper may be approximately two thirds of the total thickness.

Silver plating over electrodeposited zinc has been suggested,[?] zinc plating being preceded by acid etching and immersion in 5% hydrogen peroxide (1 20 vol) solution.

Precious metal plating

The surface resistance of silver plated aluminium bus bars is very small and does not depend significantly on the pretreatment method.[114] On the other hand, the contact resistance: of copper plated aluminium is rather higher. **A** recommended method[114] for silver plating on bus bars of EC, 55EC, 1100, 3003, 2024, 5052 and 6063 alloys is as follows:

Inhibited alkaline clean at 45-60 g/l, 82°C for 5-10 minutes.
Rinse.
Etch in 15% (vol) sulphuric acid **at** 82°C for 5 minutes.
Rinse.
Desmut in 50% (vol) nitric acid.
Rinse (the last two steps may be omitted with high purity material).
Zincate treatment using 75 g/l ZnO + 500 g/l NaOH at 15-30°C for 2 minutes.
Double spray rinse.
Nitric acid dip (as above).
Double spray rinse.
Second zincate treatment (as above) for 30-45 seconds.
Double rinse.
Immerse in the silver strike bath containing:

silver cyanide	20 g/l
copper cyanide	6 g/l
sodium cyanide	75 g/l

at 20-30°C, 2 A/dm² (18 amp/sq ft) for 10 seconds with the current on.
Transfer to the main silver bath to obtain a semi-bright deposit.

Lack of adhesion is revealed by heating to 340°C for ½ hour.

Ricks[''] describes a silver plating procedure which uses an electrolytic etch in sulphuric acid followed by zincate treatment and a silver strike in a bath containing:

silver nitrate	1-5 g/l
sodium cyanide	65-90 g/l

A silver plate is finally electrodeposited on the silver strike. An ultrasonic silver plating process has been used in conjunction with the ultrasonic zincate process described previously.

Except for silver, precious metals are not plated directly onto the zinc immersion coating but are plated on top of a heavy metal undercoat. Thus gold is normally deposited after first plating with copper (or brass) and nickel. The same procedure may be used for plating rhodium, or this metal is also sometimes plated on a silver undercoating.

Bismuth has been deposited on pretreated aluminium from EDTA solutions containing perchlorate, chloride or nitrate ions.[122] A procedure for the electrodeposition of tantalum onto aluminium foil has been described which uses freshly-formed tanatalum chloride dissolved in ethyl alcohol at a concentration of 28 g/l.[123] Coatings of uranium oxide have been formed on aluminium by electrolytes of weak uranyl nitrate.['?']

Nickel plating

Although the use of nickel strike solutions suitable for plating directly onto zinc immersion deposits is described in the literature, in practice it is more convenient to plate the nickel on a copper undercoating. If a strike solution is used, a high current density is needed, the pH should not be too low and the temperature should not be higher than 60°C. Electroplating in the normal Watts-type, bright nickel or sulphamate solutions may be used under standard conditions.

Deposit thicknesses are between 7 and 12 ym (0.3 and 0.5 mil) nickel for non-corrosive indoor conditions and 25-50 ym (1-2 mil) for conditions where corrosion is encountered.

In the past, the use of dull nickel deposits was often preferred as the earlier bright nickel deposits were usually more brittle and prone to develop cracks.

Both cracks and pores in the nickel deposit must be avoided rather more strictly than in plating on heavy metals, as any discontinuity in the coating is liable to promote corrosion of the anodic basis metal. For this reason, too, continuous filtration and frequent purification of the nickel plating solution, e.g., with activated carbon, are important. For decorative purposes a chromium deposit is almost always applied.

Missel and Kishi[125] have described an improved acetate buffered nickel glycolate strike solution for plating on zincate immersion coated aluminium, stated to provide superior wear characteristics in long-term field operation. Other advantages

claimed are improved throwing power, elimination of cyanide, elimination of the need for live entry, lower porosity, lower stress, pH stability, room temperature operation and long bath life. The strike solution contains:

nickel acetate	65 g/l
boric acid	45 g/l
nickel glycolate	60 ml/l
saccharin	1.5 g/l
sodiuni acetate	50 g/l

The solution also contains a wetting agent. It is operated at room temperature and at pH 6.0. Electrodeposition in the same solution is carried out for 5 minutes at 2.7 A/dm^2 with cathode or solution agitation and nickel or inert anodes.

Chromium plating

For decorative purposes, 0.25-0.5 μm (0.01-0.02 mil) chromium is deposited on nickel in the normal way.

Chromium is plated directly on the zinc immersion deposit in hard chromium plating and also where the low-temperature chromium plating process is used for decorative purposes.

In hard chromium plating over a zinc immersion coating, a solution containing:

chromic acid	250 g/l
sulphuric acid	2.5 g/l

has been found suitable. In practice it has often been found useful to make up two solutions, the first being kept at 18-20°C. After plating at the low temperature for 1-2 minutes, the work can be transferred to the second solution, which is kept at 40-42°C, where it is plated at 16 A/dm^2 (150 amp/sq ft), gradually building the current density up to 32 A/dm^2 (300 amp/sq ft) if required.

At low temperatures, 18-20°C, a slate-grey deposit is obtained from the chromic acid bath. This, however, adheres well to the zinc immersion deposit and may be polished to a high finish.

The fatigue strength of aluminium alloys will be considerably reduced as a result of hard chromium plating. Morgan and Brine[126] have however shown that the use of shot peening prior to plating can virtually prevent a reduction in the fatigue strength of 2014 alloy (Al-4¼%Cu-0.8%Mn-0.8%Si-0.5%Mg).

Other metal plating

Among other metals applied after zinc immersion treatment and copper plating are lead and indium, which have been used for aluminium bearing shells.[127] Klingenmaier[128] has described the hard iron plating of aluminium pistons. A thin copper coating is applied to the zinc immersion coating and is followed by a coat

of hard iron for wear resistance and an outer coat of tin for corrosion protection. Precision racking of parts is required to direct deposition onto significant areas.

When plating with electroless nickel, it is necessary to use a double dip process. The best adhesion is obtained with Watts nickel. Adhesion is better after high temperature heat treatment but if electroless nickel is used then the temperature must be below 300°C, otherwise the nickel re-crystallises and loses corrosion resistance.

Barrel plating can damage the zincate layer and is not recommended.

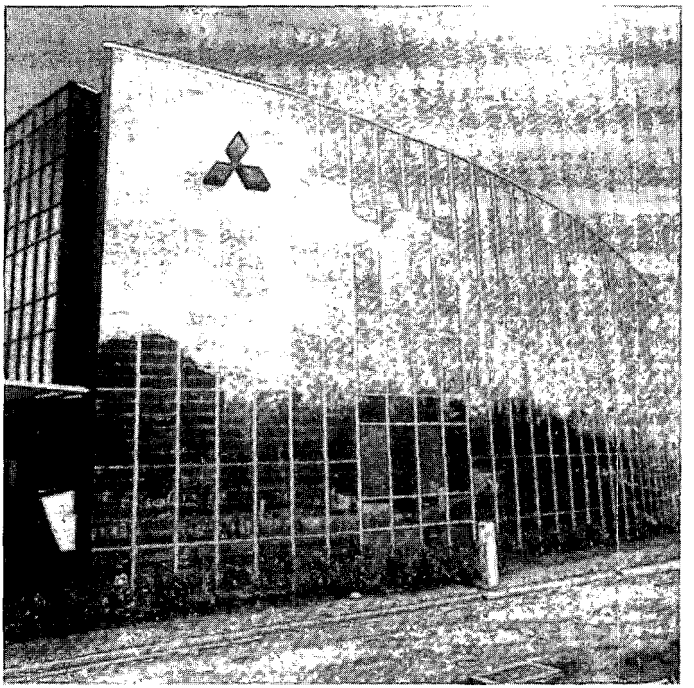

Fig. 13-25. Building clad in nickel/chrome plated aluminium mirror sheet [Courtesy Mitsubishi Metal Industries and W. Canning Materials Ltd.]

Brush plating of aluminium

Wasserman[129] and Rubinstein[130] have reported commercial processes for brush plating on aluminium. The former involves an activation stage, brush plating and heat treatment. Rubinstein gives examples of brush plating applied to the repair of plated aluminium components, using a brush anodizing stage to condition the surface for brush plating.

Turner and Dennis'[131] have studied brush plating on aluminium and compared several different pretreatment and plating sequences including single and double zincate immersion techniques in modified alloy zincate solutions. Satisfactory coatings were obtained though the adhesion level was not as high as that obtained using conventional immersion deposition.

Dennis, Turner and Eastham[132] brush plated a tin-cobalt alloy onto zincate treated aluminium for bearings. Work with brush plated lead-tin alloys gave less satisfactory results than tin-cobalt.

11. IMMERSION TIN PROCESSES

Tin has been deposited on aluminium to facilitate soldering, to improve electrical conductivity (particularly at joints in bus-bar systems), and also to give a lubricated surface to aluminium alloy pistons for internal combustion engines during the running-in period.

While electrodeposition of tin can be made onto aluminium surfaces which have been pretreated by the zincate or anodic oxidation processes, deposition of tin by chemical displacement methods has been used for many years with considerable cost advantages. A number of processes have been proposed for this purpose, including deposition from a stannous chloride solution with and without additions of ammonium alum or sodium hydroxide[133,134] and Rochelle salt. Sodium stannate solutions[134-137] and stannous sulphate-fluoride solutions[138] have produced good immersion deposits of tin. A 2.0 N solution of tin fluoride[139] produced a soft ductile deposit of tin on aluminium which remained firmly adherent during a subsequent buffing operation.

The majority of solutions investigated have been for the production of a tin deposit for use without any further plating operation, but there has been a considerable interest, although only a limited application, in immersion tin coatings as substrates for subsequent electroplating.

Stannate solutions

The stannate solution is in use in America for plating tin on aluminium pistons.[134-137] In the UK it has been described by Hoare,[140] and has been investigated by Bryan.[141] One of its main applications is for bus-bar and electrical connectors.

Bryan studied a typical stannate sequence as follows:

1. Degrease.
2. Etch at room temperature in 50 g/l NaOH for 5 minutes.
3. Rinse.
4. Dip in 60 parts H_3PO_4 (SG 1.75) + 40 parts HNO_3 (SG 1.42) by volume for 5 minutes at 60-65°C.

5. Rinse.
6. Plate by immersion in 100 g/l sodium or potassium stannate solution at 55°C for 1 minute.

Bryan obtained slightly brighter and more adherent deposits by using potassium stannate in place of the sodium salt.

Effect of free alkali

In operation, the pH of the bath increases, and this adversely affects the adherence of the deposit. Immersion times must then be shortened. **As** no buffer will operate at the high pH encountered (pH 12-13), attempts have been made to add compounds to counteract the alkalinity directly or to act as corrosion inhibitors. The addition of ammonium sulphate, which liberates sulphuric acid in the solution during the deposition (ammonia is evolved), was partially successful in improving the adhesion but gave a bronze-coloured deposit. Similar results were obtained by direct addition of sulphuric acid to maintain the pH at 12.1.

Weimer and Price[142] found that the upper limit for the sodium hydroxide content varied with the type of aluminium alloy being processed. Control of the free alkalinity was found to be possible using additions of either acetic acid or sodium bicarbonate.

Bryan found that at higher potassium stannate concentrations (above 200 g/l) the solution had a pH of 12.47 and no preliminary acid etch was required to obtain satisfactory adhesion.

Addition agents

Of several addition agents tested in the potassium stannate solution,[141] potassium dihydrogen phosphate and a combination of zinc acetate and m-cresolsulphonic acid have given some improvement. Good deposits have been obtained by etching in 50 g/l sodium hydroxide solution for 1 minute at 75°C, etching in cold 50% (vol) nitric acid for 1/, minute, rinsing and plating for 5-10 minutes in a solution containing:

potassium stannate	200 g/l
potassium dihydrogen phosphate	100 g/l

for 5-10 minutes at 60°C. Small additions of potassium dihydrogen phosphate are made during use.

The most promising solution using the second type of addition agent contained:

potassium stannate	100 g/l
zinc acetate	2 g/l
m-cresolsulphonic acid	33 g/l

This solution, used at the normal operating conditions for 2 minutes plating time, eliminated the need for an acid etch, was somewhat more stable than the

plain stannate bath and gave deposits with better adhesion which could be polished easily to a bright reflecting finish.

The thickness of deposits obtained in this way varies from about 1.1-1.4 μm (0.045-0.055 mil), the thinner deposits being obtained on polished aluminium. The life of the solution is approximately 61 dm^2/l (30 sq ft per gallon).

In Russia, Matulis[138] proposed a stannate solution which contained:

sodium stannate	20-80 g/l
potassium pyrophosphate	30-120 g/l
ammonium oxalate	10-20 g/l
sodium hydroxide	1.5-7 g/l

Operation of stannate processes

Jongkind[144] outlined the steps of a stannate process referred to as the Alstan 70 process:

1. Vapour degrease or emulsion clean to remove grease or oil.
2. Alkali clean with either etch or non-etch type cleaners depending on applications.
3. Water rinse.
4. Acid dip for 30 seconds at room temperature. The formulation of the acid depends on the type of aluminium alloy being processed. For example, (1) 6061 alloy for bus-bars is dipped in 30% (vol) HNO_3 (SG 1.41) + *30* g/l NH_4HF_2 (2) *380* alloy (Al-8.5%Si-3.5%Cu) for castings is dipped in 3:1 (vol) HNO_3 (SG 1.41) + 120 g/l NH_4HF_2.
5. Water rinse.
6. Jmmersion in alkaline stannate solution for 30 seconds at 300°C.
7. Electrolytic strike in bronze bath containing copper, tin, free cyanide, free KOH and additive.
8. Water rinse..
9. Final plating operations as required.

The Alstan process[145-151] is one of the few proprietary treatments used in the preparation of aluminium and aluminium alloys for electroplating which uses the stannate immersion coating technique. This process has been found to give good adhesion of copper, tin, nickel and other electrodeposited metals to aluminium and aluminium alloys including the high copper-containing alloys. It has however, been suggested[152] that some of the magnesium-containing alloys have exhibited adhesion problems when treated by this process.

Aluminium components are treated in sodium, or preferably potassium, stannate solution containing approximately 30 g/l tin, with a sodium or potassium concentration of 4 g/l. The solution is operated at a pH of 12, and certainly at above pH 11.5, to avoid precipitation of tin, and the temperature is controlled at between 25 and 80°C. The immersion time is from 1 to 6 minutes and depends on

the thickness of tin required and on the alloy being processed. The addition of an inhibitor such as gluconic acid, and a chelating agent (e.g., ethylene diamine tetra-acetic acid) is advocated, particularly when plating magnesium containing alloys. After treatment in the proprietary stannate solution the components are given a bronze strike before further electroplating.

Comparisons have been made between electroplated aluminium components which have been pretreated by the zincate and stannate processes in papers by Jongkind,[144,153] Wrzecian,[154] Gowman,[155] DiBari,[156] Laser and Meyers,[157] Enger[158] and Lashmore.[159]

The Alstan 70 process has been replaced by an improved Alstan 80 process in which the stannate immersion stage is changed to a short electrolytic strike in the stannate solution at a low current density — 30 seconds at 10 amp/sq ft (1.1 A/dm'). The work is entered 'live' into the stannate solution and then transferred 'live' directly into the bronze strike solution without rinsing and keeping the transfer time less than 30 seconds. Such short transfer times present difficulties on some automatic lines, but these have been overcome[160] by using polymeric additives in the stannate bath to slow down reactions occurring on transfer. The bath contained sodium or potassium stannate (10-70 g/l as Sn), sodium or potassium hydroxide (1.2-12 g/l) and 0.001-25 g/l of either methyl cellulose ether, polyvinyl alcohol, polyethylene oxide, or polyethylene glycol.

Mechanism of the tin immersion process

The mechanism of the zinc immersion process has been discussed in detail earlier. The double zincate dip was shown to give a more uniform distribution of zinc on the surface. Similarly in the stannate process, Jongkind[144] has stated that it is necessary to equalize the activities of different areas on the surface of the aluminium or aluminium alloy. This is done by an acid dip in nitric acid or nitric acid-hydrofluoric acid mixtures, the exact composition depending on the alloy used, whether cast or wrought, and whether bright or not. For many applications 30% (vol) HNO_3 (SG 1.41) + 30 g/l NH_4HF_2 is excellent, but the addition of hydrofluoric acid is necessary for some alloys such as casting alloys containing silicon.

The stannate dip follows the acid dip and water rinse. The alkaline stannate solution first dissolves the thin aluminium oxide film on the surface.

$$Al_2O_3 + 2KOH \rightarrow 2KAlO_2 + H_2O$$

Then after about twenty seconds hydrogen is evolved at cathodic sites with corresponding anodic dissolution of aluminium.

Anodic reactions

$$Al + 3(OH)^- \rightarrow Al(OH)_3 + 3e^-$$
$$Al(OH)_3 \rightarrow AlO_2 + H_2O + H^+$$

Cathodic reactions

$$2H^+ + 2e^- \rightarrow H_2$$
$$Sn(OH)_6^{2-} + 4e^- \rightarrow Sn + 6(OH)^-$$

where $Sn(OH)_6^{2-}$ is the complex ion formed by hydration of the stannate ion SnO_3^{2-}. Although the details of the electrochemical reactions have yet to be established, it is known that hydrogen is evolved, tin is deposited, and both the aluminium content and the hydroxyl content of the stannate solution increase with use.

Lashmore[99] dipped 99.99% purity aluminium in stannate solution for 60 seconds and found that the etch patterns caused by aluminium removal in the stannate solution were exactly the same as in zincate solution. Lashinore also found a concentration of 0.26×10^{17} tin atoms/cm^2 (equivalent to about 15 monolayers of tin) on the surface. The tin deposited preferentially along zones on either side of grain boundaries. The distribution of tin obtained by Lashinore from a stannate dip was similar to the distribution of zinc obtained by Golby and Dennis[101] from a zincate dip as shown in Fig. 13-2. Studies of deposits on single-crystal aluminium spheres show that the same crystallographic orientations are active in both stannate and zincate processes.[99]

Stannous chloride solution

In 1948 Suchy[133] described a solution containing 10 g/l of stannous chloride for the immersion deposition of tin on aluminium and aluminium alloys. After treatment in the stannous chloride solution, the aluminium component was heated to 500-600°C for 5 minutes which caused the tin to diffuse into the surface of the aluminium, forming a tin-rich layer which was found to improve the adhesion of subsequently electrodeposited coatings of other metals. A treatment cycle as proposed could, however, seriously affect the mechanical properties of many aluminium alloys, and this type of process was not developed for commercial use.

An immersion tin plating solution proposed by Hunt and Webb[161] contained:

sodium hydroxide	25-37.5 g/l
copper chloride	37.5 g/l
stannous chloride	37.5 g/l

and was used at a temperature of 95-96°C. After the tinning operation the aluminium specimen was dipped in 48% H_2SO_4 + 2% HNO_3 until the colour was completely removed. The adhesion of a nickel deposit on aluminium treated by this method was found to be poor, but could be improved considerably by the addition of a small amount of sodium chromate to the tin solution.[162]

Watson and Ward[163] described a sodium stannate solution and a stannous chloride solution for the tinning of aluminium as a basis for electroplating. Two examples of the solutions used are as follows:

Solution 1:	sodium hydroxide	85.0 g/l
	sodium carbonate	7.0 g/l
	sodium stannate	28.0 g/l
	nickel chloride	10.0 g/l

Solution 2:	sodium hydroxide	100.0g/l
	sodium carbonate	7.0 g/l
	stannous chloride	28.0 g/l
	nickel carbonate	7.0 g/l

The solutions were both used at between 65 and 82°C with an immersion period of 30-60 seconds. An acid cleaning bath containing 40% nitric acid was used after tin deposition from either of the baths.

Stannous solutions without addition agents are not satisfactory for plating on aluminium. Stannous chloride gives somewhat better results than stannous sulphate, but to obtain smooth deposits without pitting, addition agents are essential and the pH of the solution must be increased to near neutrality.

A solution which has been stated to give smooth deposits 5 μm (0.2 mil) thick and with an adhesion of 23 N/mm^2 (1.5 tons per sq inch) contains:

stannous chloride ($SnCl_2.2H_20$)	100 g/l
Rochelle salt	200 g/l
hydrolysed glue	5 g/l
sodium hydroxide	added to give pH 7.0 - pH 7.5 (approximately 25 g/l)

This solution is operated at 70°C for 4 minutes. Prior to plating the aluminium is etched in 50 g/l sodium hydroxide solution containing a wetting agent (e.g., Lissapol N, 3 g/l) for 5 minutes at room temperature, after which it is etched in an acid solution.

A suitable acid etch given by Bryan[141] contains:

hydrochloric acid (conc.)	5.5 ml/l
trichloroacetic acid (melted crystals)	5.0 ml/l
phosphoric acid (SG 1.75)	250.0 ml/l
lactic acid (SG 1.21)	200.0 ml/l
Lissapol N	3.0 g/l

The time of etching is fairly critical; 1 minute at 75°C gives the best results; shorter etching giving pits and longer etching, rough deposits.

An organic bath has also been developed by Berezyuk[164] which uses 50 g/l stannous chloride in dimethylformamide.

Stannous sulphate-fluoride solution

The stannous sulphate-fluoride solution, developed by Heiman,[18] in many ways appears one of the most promising. A typical solution used on commercial aluminium contains:

stannous sulphate ($SnSO_4$)	161.1 g/l
hydrofluoric acid (48%)	70.0 g/l

hydrolysed glue	1.0 g/l
goulac	0.1 g/l
purified residue acid	1.3 ml/l
pH	0.2-1.0

The hydrolysed glue is prepared by boiling with caustic soda solution in a vessel fitted with a reflux condenser and acidifying with sulphuric acid. Goulac is a sulphite paper pulp waste containing lignin sulphonates. The purified residue acid is a mixture of high-boiling coal-tar phenols with a distillation range: initial boiling point 102°; 5% = 212°; 50% = 235"; end point 90%= 276°C.

The working temperature of this solution is 25°C and the time of immersion varies from 5 to 10 seconds. Fairly vigorous agitation is recommended. The plating sequence used by Heiman is as follows: alkaline clean; rinse; acid etch (0.5N HF, 25°C, 2-3 minutes); rinse; 70% HNO_3 (SG 1.42) dip at 25°C for 10-20 seconds, rinse; tin immersion plating. The plating time is fairly critical and should not generally exceed 10 seconds. The adhesion obtained is stated to be superior to that obtained with deposits from the stannate bath. A solution given in another patent[165] is similar but has ammonia added to pH 5.5-6.5.

12. IMMERSION COPPER, SILVER AND NICKEL DEPOSITS

Immersion copper deposits

As a pretreatment for applying tin solder, aluminium has been immersion copper plated[166] by etching the degreased aluminium in a 400 g/l sodium hydroxide solution for 30 seconds, rinsing, and 'sensitising' for 10 seconds at room temperature in a solution containing:

cupric chloride ($CuCl_2.2H_20$)	15 g
water	1 litre

with addition of a few drops of hydrochloric acid.

Finally, the aluminium is plated at room temperature in a bath containing:

cupric chloride	140 g
concentrated ammonia solution	1 litre

for 10 minutes.

Adherent copper deposits have also been obtained in Russia from solutions of cupric chloride in ethyl, isopropyl or other alcohols.""

Immersion copper plating has also been carried out in solutions of copper salts with palladium chloride as a catalyst and using ultrasonic vibrations at 20-40 kHz for 2 minutes to ensure wetting.[168]

Immersion silver deposits

Immersion silvering may be applied to aluminium after it has been anodized, when the process may be carried out in much the same way as silvering glass. In one such process[169] the aluminium is degreased, etched in dilute hydrochloric acid with or without nitric acid, and rinsed in distilled water.

The actual silvering is carried out with 3.33 ml of a 10% silver nitrate solution to which a solution of 86 ml/l ammonium hydroxide (0.880) is added until the precipitate first formed is just redissolved. Subsequently, 30-50 ml excess ammonium hydroxide solution are added. The total volume of the solution is then approximately 660 ml.

The reducing solution is made up by dissolving 30 g Rochelle salt or 40 g potassium citrate in distilled water and making up to 330 ml.

Both solutions are filtered and are then mixed in a glass or porcelain vessel for use.

Immersion nickel deposits

Honma and Kobayashi [170] found that the adhesion of electroless nickel was higher if an immersion nickel process was used instead of zincate. Adhesion depended on the rate of the displacement reaction which can be controlled by changing the kind of complexing agent and plating conditions.

13. HARD CHROMIUM PLATING

Hard chromium plating of aluminium is applied to such components as cylinders, pistons, bearings and brake drums to produce hard, wear-resistant and in some cases, oil-retaining surfaces for many industrial and engineering applications.

The corrosion resistance of hard chromium plated aluminium is generally good and this is an important factor in the life of cylinders, particularly under conditions where sulphuric acid may be formed. As the coefficient of expansion of aluminium is approximately three times that of chromium (see Table 13-3, p. 1119), heating of hard chromium plated aluminium parts will cause cracking of the deposit; this, however, is not detrimental to the adhesion because the mosaic crack structure produced ensures that no stress is present in the coating which would cause exfoliation in service.

The use of the single zincate process has sometimes been applied to hard chromium plating. In the process described by Mall[171] the parts are first polished to a high finish, degreased, etched in an alkali solution, rinsed and dipped in an alkaline sodium zincate solution. Subsequently, the parts are rinsed and transferred to the chromium plating solution where the zinc is dissolved before the current is applied. The double zincate treatment is generally preferable to a single zincate immersion in preparing aluminium alloys for hard chromium plating.

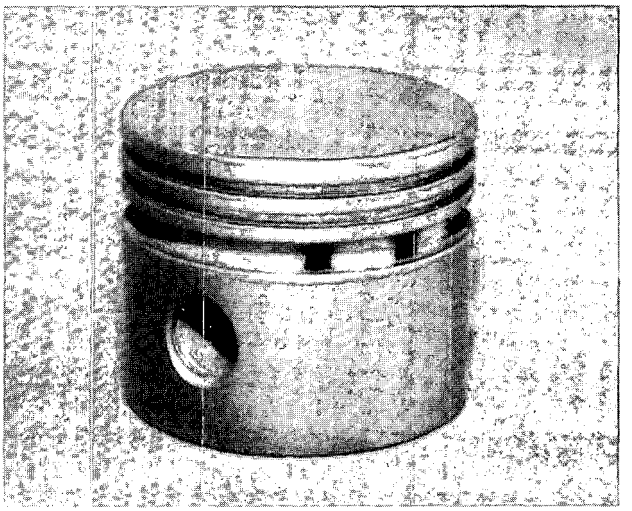

Fig. 13-26. Hard chromium plating on aluminium alloy piston for lightweight engine

[Courtesy Ionic Plating Co.]

After preparation of the surface, the chromium plating operation does not usually differ essentially from that used on other metals and adequately described elsewhere.[138] The most usual solution is one containing:

chromic acid	250 g/l
sulphuric acid	2.5 g/l

operated at 32-54 A/dm^2 (300-500 amp/sq ft) at 4-8 volts, giving deposits of 1000 VPN hardness. Components are entered live into the plating bath. Chromium plating solutions containing fluoride or silicofluoride, such as SRHS (Self Regulating High Speed) chromium plating solutions, rapidly attack aluminium and can only be used over a nickel or copper undercoat.

Engine cylinder!; are one of the most common aluminium components to be hard chromium plated. The use of such cylinders rests on the light weight and good heat conductivity of the light metal, coupled with the wear resistance of a hard chromium deposit of up *to* 150 μm (6 mil) thickness. According to Meyer-Rässler[166] a 7% higher efficiency is obtained over cast iron, while in addition fuel consumption is reduced at the lower operating temperature of the cylinder. According to this author, the wear of a chromium plated cylinder averages approximately 5 μm in 10,500 km (0.2 mil in 6,250 miles), with greatly reduced wear of the piston rings as compared with cast iron. In Germany, the performance of these cylinders in the motor, aircraft and motorcycle industries has been

described in a number of pubhcations,[173-177] heat resistant cylinder alloys of the aluminium-silicon and aluminium-copper-nickel type being used for pressings, while cast cylinders are made of aluminium-silicon-copper and aluminium-magnesium alloys. Similar applications have been described in the USA[171] and in Hungary.[178,179]

In practice the cylinder bore is mechanically ground and polished, cleaned in alkali and pretreated as described above. The cylinder is placed in a fixture in which the round anode is exactly concentric with it to obtain a uniform electrode distance. As cylinders vary in diameter and length, it is usually necessary, however, to proceed by trial and error with each new type in order to find the optimum plating conditions. Edges should be rounded to avoid local build-up of the deposit and holes plugged, for example with a low melting point metal.

Jongkind[180] used the following sequence for hard chromium plating on the internal diameter of cylinders cast in alloys 356 (Al-7%Si-0.3%Mg; LM25), 360 (Al-0.5%Si-O.5%Mg; LM9), and 380 (Al-8.5%Si-3.5%Cu; LM24):

1. Vapour degrease or emulsion clean.
2. Alkali etch clean, followed by two water rinses.
3. Acid dip in:

nitric acid (SG 1.42)	2 parts
sulphuric acid (SG 1.84)	1 part
water	1 part
NH_4HF_2	1 lb/gal (100 g/l)

   Dip for one minute at room temperature followed by two water rinses.
4. Acid dip in:

nitric acid (SG 1.42)	2 parts
water	1 part

   Dip for 30 secs at room temperature followed by two water rinses.
5. Hard chromium plate;
   Transfer the racked part to the chromium bath, allow a few seconds for temperature equilibration and then make contact.
   16-48 A/dm^2 (150-450 amp/sq ft) at 52-54°C.

Porous chromium deposits

Porous chromium deposits can be obtained for applications where oil retention is required.[138] In addition to such chemical and electrolytic etching methods, depressions can be obtained mechanically before plating, particularly for pressed aluminium cylinders. The depressions are applied by a pressing technique after which the surface is rough turned and lightly honed before chromium plating.

The chromium deposit should not be applied more than approximately 5 μm (0.2 mil) oversize and it is important therefore to pay strict attention to the arrangement of cylinders and anodes in the plating bath. According to Meyer-Rässler,[172] series production is best carried out by placing the cylinders end to end with gaps of only *2.5* μm (0.1 mil).

Stripping of the chromium deposit from rejects or repair work is carried out by anodic treatment in chromic-sulphuric acid solution, which does not attack the aluminium to any extent if the cylinder is removed without undue delay. Before re-plating, the cylinder bore is re-ground.

Even better results are stated to be achieved in very dilute sulphuric acid. According to Csokan,[178 179] cylinders stripped in 1% sulphuric acid at 46-54 A/dm^2 (430-500 amp/sq ft) and 25-35 volts can be reconditioned three or four times in this manner as no attack takes place on the basis metal.

A number of other applications of hard chromium plating of aluminium have been proposed, among them the treatment of the bearing surface of aluminium pistons (in which case the cylinder itself would not be plated), parts of the pistons exposed to high temperatures,[181] piston rings, nuts and aluminium brake drums, aluminium water taps and miscellaneous other components.

There are two complementary processes to hard chromium plating for some of the applications described. One of these, hard anodizing, has been described in Chapter 9 and the other is the application of ferrous and hard facing metals by metal spraying. However, hard chromium plating must be used instead of hard anodizing where electrical conductivity is required in addition to wear resistance.

For aluminium cylinders of motor-bicycle engines a process involving lead plating, tin plating and graphiting has been developed in Italy.[182]

14. ELECTROLESS NICKEL PLATING ON ALUMINIUM

Applications of electroless nickel plating on aluminium

Electroless nickel plating is also known as chemical or autocatalytic nickel plating. It is an immersion process in which nickel is deposited from solution without the use of an applied current. The process depends on the catalytic reduction of nickel ions on the surface being plated. Unlike displacement deposits, the surface is not dissolved and thick deposits can be produced.

The electroless process has the advantage of simplicity in that the need for complicated jig and anode arrangements is avoided. The main advantage of the electroless process is the unique throwing power of the solution in which even long, small-diameter tubes may be plated internally provided that a flow of the solution is maintained through the tube. For similar reasons the process may also be suitable for plating threaded parts, while another application of the process is the plating of the interiors of tanks and large vessels. Electroless nickel will penetrate into narrow, through and blind holes, providing these are positioned so that gas trapping does not occur.

For applications where the major requirements are chemical resistance, hardness and resistance to wear and abrasion, electroless nickel provides an effective

alternative to hard chromium particularly on complex shapes where the need for elaborate anode arrangements is avoided. Where however, high operational temperatures are involved or a low coefficient of friction is a major requirement then electrodeposited hard chromium may still be preferred.

Electroless nickel plating provides a simple technique for the application of coatings which are hard (450-500 VPN as plated and up to 1100 VPN after heat treatment) and have a high resistance to wear and abrasion. Typical applications include: gears, bearings, pump components, hydraulic cylinders, automotive components including ball studs, transmission thrust washers and differential cross shafts on which improved resistance to galling is obtained. The deposit has good wettability and therefore tends to hold a lubricant film better than chromium.

Treatment for one hour at 400°C will increase the hardness to 1100 VPN. At elevated temperatures there is a reduction in hardness as there is with electrodeposited chromium, but unlike chromium, it can regain considerable hardness on cooling.

In building up worn or over-machined parts, deposits up to 200 μm (20 mil) can be applied under suitable conditions. The uniform thickness of the coating permits accurate control of the deposit so that in many cases subsequent machining will not be required.

An interesting application is operated in standard production by the Wright Aeronautical Corporation in America.[183] Here electroless nickel is applied for the protection of annular grooves in light alloy pistons used at 280°C. In this application, axial clearance must be given between the piston ring and the side wall of the groove to leave room for the ring to expand and contract radially. The purpose of the deposit is to protect the walls from damage by the striking of the ring during service. Pretreatment in this instance is by cleaning in a chromic-sulphuric acid or nitric-hydrofluoric acid mixture, followed by plating with 12-30 μm (0.5-1.2 mil) nickel from an alkaline solution. Following deposition the parts are heated to 230°C for 30 minutes to increase the hardness to 600 VPN. A number of other applications have been found for the process in the aircraft[184] and aerospace industries.

Special protective applications of electroless nickel on aluminium in the electronics industry include plating on dissimilar aluminium alloys,[185] plating modular electronic packages, mass course adjustors, high frequency signal selectors and wave guides. While the minimum thickness plated on the components is 7.5 μm (0.3 mil), thicknesses up to 40 μm (1.5 mil) have been plated. Gyro shells, hydraulic cylinders, lock nuts, piston ring grooves, shafts, slide valve plates and threaded fittings are instances in which electroless nickel is plated for wear and abrasion resistance or for good frictional and anti-galling properties. Here thicknesses of 12-127 μm (OS-5 mil) may be specified and, after plating, the components are frequently heated to 190-245°C to harden the coating and improve its adhesion.

One of the purposes of electroless nickel plating of aluminium is to enable the parts to be soldered with lead-based solders. Electronic components and instrument

housings are among typical applications which receive 7.3-20 μm (0.3-0.8 mil) coatings, while another specialised use of electroless nickel is to increase the breaking strength of aluminium alloy structural components.[185]

Occasionally aluminium parts assembled to semi-conductors, such as germanium or silicon, have been electroless nickel plated. In these cases the parts may be introduced together into the bath when any transition layer between the two materials is short circuited by the nickel deposit.[186]

Electroless nickel baths

The most widely used electroless nickel is deposited by the catalytic reduction of nickel ions with sodium hypophosphite in acid baths at pH 4.5-5.0 and at a temperature of 85-95°C.[187] The deposit contains typically 3 to 12% phosphorus hy weight. The alloy obtained is dependent upon the chemical composition of the solution and the operating conditions. The phosphorus content significantly influences its chemical and physical properties in both the as-plated condition and after heat treatment.

There are three main types of electroless nickel — nickel-phosphorus, nickel-boron and polyalloys. Nickel-phosphorus is generally used for engineering applications. Nickel-boron is very often used in industrial wear applications for its as-plated hardness which is higher than that of nickel-phosphorus. The boron content can be varied from 0.1 to 10%.The reducing agent used is dimethylamine borane or sodium borohydride depending on the desired alloy composition. Polyalloys are a combination of nickel, boron *or* phosphorus **and** other metals such as cobalt, iron, tungsten, rhenium or molybdenum. Composite deposits such as electroless nickel-PTFE and electroless nickel-diamond have been developed for special applications.

Aluminium alloys plated with electroless nickel

In addition to pure aluminium, most aluminium alloys can be plated directly with electroless nickel. All aluminium alloys, however, can be reliably plated with electroless nickel if pretreated with zincate using the conditions appropriate to the aluminium alloy to be zincated.

Mallory[188] studied electroless nickel deposition on aluminium and found that the type of zincate solution used has a pronounced influence on the subsequent adhesion of the electroless nickel. Each zincate solution deposits a zinc film of characteristic thickness and composition. A zinc rich zone is formed in the electroless nickel next to the aluminium substrate. The best zincate is the one that results in the thinnest zinc rich zone. The distribution of zinc in the zinc rich zone is influenced by the chemistry of the electroless nickel bath. The best electroless nickel solutions give diffuse distributions of zinc in the zinc rich zone and result in low intrinsic tensile: stress.

Miscellaneous electroless nickel plating processes

A chromic-sulphuric acid or a nitric-hydrofluoric acid dip has been used before plating piston ring grooves,[183] while Reschan and Krieg[189] claim that the addition of nitrate to the bath permits plating after normal pretreatment. In yet another method,[190] the aluminium is etched and rinsed in ammonia solution containing a complexing agent, such as an amino-carboxylic acid, before electroless nickel plating.

Bosdorf and Muller[191] found that the best adhesion is obtained after preparing the surface by the zincate process, plating in the alkaline electroless nickel bath and finally transferring to the acid electroless nickel bath.

Brown and Jarrett[192] also recommend the use of a zincate treatment as a preparation for electroless nickel plating, and consider that heat treatment at 130-140°C for at least 2 hours is essential to ensure good adhesion. Alternatively, aluminium may be anodized after which it can be plated with electroless nickel in the usual way for plating on non-conductors.

In a French process,[193] aluminium alloy can be plated directly in a solution containing 23 g/l nickel sulphate, 24 g/l sodium hypophosphite, 27 g/l lactic acid and 20 g/l sodium succinate at pH 4.7. The aluminium is first made the cathode in the bath at 1.7 A/dm^2 (16 amp/sq ft) and 14 volts for 30 seconds, and the parts are then plated with electroless nickel for 1 hour at 96-98°C to deposit 23 μm (0.9 mil) nickel, which is heat treated at 165°C for 1 hour.

Takeuchi and Tohyama[194] use a jet of electrolyte containing silica particles to smooth a zincated aluminium surface prior to electroless nickel plating. An inclined jet is more effective in creating a hooked surface which anchors the deposit and improves the adhesion. Impact of the silica particles gives beneficial residual compressive stress.

Other electroless deposits

Aluminium is etched in a sulphuric-nitric acid solution before electroless palladium plating.[195] Electroless plating of lead and antimony have also been described using aqueous salts containing tartrates, alkaline zincate compounds and a ferric salt.[196]

The Alniclad process

Under severe corrosion-erosion conditions where conventional electroless nickel has corroded, the Alniclad process can be used. In this process, aluminium alloys are first anodized, after which a rubber bonding material is applied by immersion.[197]

Carbonyl plating

Nickel carbonyl plating on aluminium has been patented in America.[198] In this process the work is cleaned and treated in a mixture of gaseous nickel carbonyl and inert gas at 80-200°C. Oxide films on aluminium can also be removed by passing the work through molten cryolite. Subsequently, the work is heated to 260-450°C in carbon dioxide and exposed to nickel carbonyl gas at a temperature high enough to cause deposition. Relatively porous deposits between 1 and 4 μm (0.05 and 0.15 mil) thick are obtained but it is doubtful whether the process has much commercial significance at the moment. The nickel carbonyl process requires special equipment and is described in greater detail in the literature.[199]

Electrodeposition of tantalum and uranium

The electrodeposition of tantalum onto 8 μm aluminium foil has been described[123] for use as a source of beta-rays in spectroscopy. The solution used was freshly prepared tantalum chloride ($TaCl_5$) in ethyl alcohol at a concentration of 28 g/l using a current density of 1 1.2 mA/cm^2. Deposits were between 0.08 and 1.34 mg/cm^2, equivalent to a thickness of 0.1-0.8 μm of tantalum. Adhesion remained good up to temperatures of 260-300°C.

Deposits of uranium oxide (UO,) up to 7 mg/cm^2 have been obtained by the electrolysis of weak uranyl nitrate $UO_2(NO_3)_2$ for use as a source of *a*-particles.[200]

15. TESTING AND PROPERTIES OF ELECTROPLATED ALUMINIUM

Adhesion tests

Various methods for testing adhesion have been reviewed in the literature.[""[206] The simplest and most common test of adhesion is the bend test which is used for a quick qualitative assessment of adhesion. Schaer,[207] in developing processes for plating copper on aluminium wire, used a wrap test where the plated wire was wrapped round itself and was a fast comparative test of adhesion.

A number of quantitative adhesion tests have been developed for use with plated aluminium. fimong those used are the Bullough and Gardam[88] test in which a shank fits flush with a collar of the basis metal under test. The whole is polished, degreased and stopped-off before applying the immersion treatment and nickel plating. The shank is then detached from the collar by direct tension in a tensile testing machine. This test and other variations of the Ollard test[208] were used by

Roehl,[209] and by Bailey.[92] Dini and Johnson[204] developed three quantitative adhesion tests: (1) a Ring Shear test which was favoured for speed and low cost, and which was used[210] for measuring the adhesion of electroless nickel and of electrodeposited nickel to aluminium, (2) a Conical-Head Tension test used for evaluating procedures for plating on three aluminium alloys,[203] and (3) an I-Beam test with the advantage that a piece of plated aluminium of a given size will yield many more I-beam specimens than it will specimens for other tests, giving a considerably lower cost per specimen and ideally suited to statistical evaluations or multi-variant test programmes.

Kelly[211] developed a test giving good results where low adhesion forces were to be measured. It was designed for testing the adhesion of electrodeposited zinc on aluminium starting sheets used in the refining of zinc.

The Jacquet[212] peel test has been used qualitatively by a number of workers[106, 107, 213] for assessing the adhesion of nickel deposits to zincate treated aluminium. It has been modified to give quantitative values by Dennis and Tipping[214] and independently by others including Klingenmaier and Dobrash,[205] who mechanised it for measuring the adhesion of plated aluminium alloy pistons to show the applicability of the peel test to production components.

Corrosion tests

In general, corrosion tests for aluminium are also suitable for testing plated aluminium. The copper-accelerated acetic-acid salt spray **(CASS)** test and the Corrodkote test have been specified for the evaluation of electroplated coatings of nickel and chromium on aluminium.[215]

A useful test designed by Heussner has been used by Keller and Zelley for rapid evaluation of plated coatings on aluminium.[216] In this test the samples, consisting of panels 150 × 62 × 0.8 mm (6 x 2% × 1/32 inch), are marked with a V-shaped threading tool so as to form an X-pattern across the panel. The grooves extend through the plating and poor adhesion is marked by lifting at the sides of the grooves and particularly at the point of intersection.

These samples are then exposed to the atmosphere or to salt spray. Poor performance is marked by blistering and lifting of the deposit along the grooves. This test may be regarded as a combined corrosion and adhesion test and has given good results in comparing various methods of surface preparation.

Corrosion resistance of electroplated aluminium

As aluminium is anodic to most coating metals, plated aluminium is liable to pitting corrosion if pores, scratches or other discontinuities are present in the metallic coating. Electroplated aluminium commonly fails by blistering followed

by rapid lateral spread of corrosion underneath the deposit and exfoliation. For this reason it is usually necessary to apply thicker coatings than would generally be applied to other metals. Some figures for corrosion resistance of various aluminium alloys, plated and unplated, are shown in Figs. 13-27 and 13-28, and these show that a thickness of 37-50 μm (1.5-2 mil) nickel is generally desirable.[217]

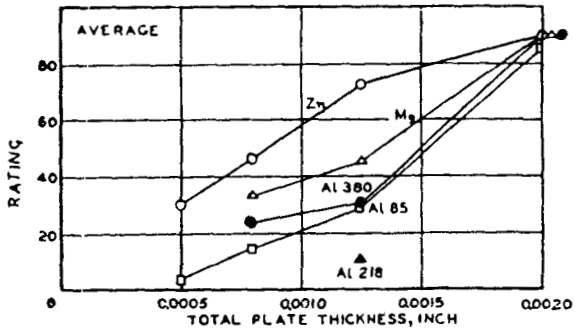

Fig. 13-27. Effect of thickness of nickel electrodeposit on corrosion rating of zinc alloy Zamak 3 (marked Zn), magnesium alloy Dowmetal R (Mg) and aluminium alloys Alcoa Nos. 380 (Al-9%Si-3½%Cu), 85 (Al-5%Si-4%Cu) and 218 (Al-8%Mg) after outdoor exposure in an industrial atmosphere for 12 months.'"
0.001 in = 2.5.4 μm

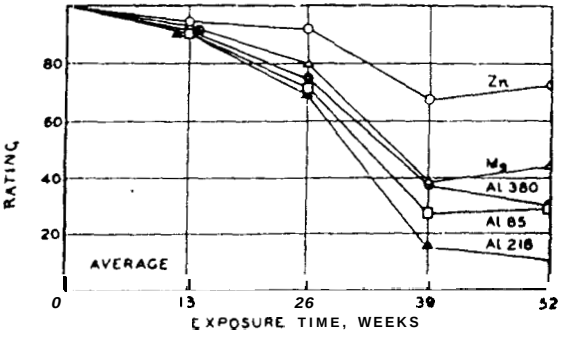

Fig. 13-28. Relation between exposure time and corrosion rating of the bare metals as used in Fig. 13-27.[217]

These results are also interesting in that they give a comparison of alloys of aluminium with zinc and magnesium alloys. It is, however, fair to state that the results showing a better life for plated magnesium alloys are contradicted by industrial experience using the best method of applying the coating. Nickel-chromium plated aluminium is in general inferior to plated zinc.

The service life of electroplated aluminium can vary within fairly wide limits. Keller and Zelley[216] found that the life of samples plated by the zincate method varied with the weight of zinc deposited, which is a function of solution composition and operating conditions, as well as with the type of alloy and the method of pretreatment used. According to Zelley[93] the best results are obtained on the thinnest practicable zinc deposits, while the alloys likely to give the best results are those with the lowest potential difference to the basis metal, i.e., heavy metal containing alloys will give better results than pure aluminium.

A mechanism for the corrosion of such deposits has been advanced by Zelley[93] and is illustrated in Fig. 13-29. In this diagram (a) shows the cross-section of a groove that has cut through the deposit into the basis metal. As is shown in (b), the first stage is the anodic dissolution of the zinc which carries on until, when the zinc has been dissolved to a certain distance, the anodic current density is insufficient to protect the aluminium. From current-distribution considerations it follows that the thinner the zinc deposit the smaller the distance to which the zinc will be dissolved, and the smaller the area on which the initial lifting of the deposit around the crack occurs.

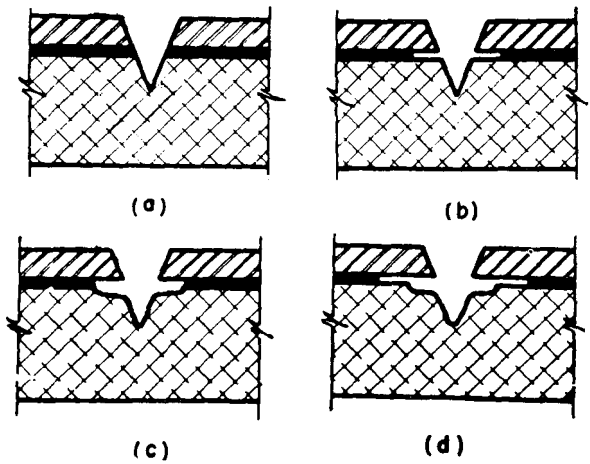

Fig. 13-29. Corrosion mechanism of aluminium plated by the zinc immersion process"

Zinc versus stannate pretreatment

In 1967, following corrosion tests at Kure Beach, North Carolina, Jongkind[144] reported that after 10 months exposure nickel-chromium plated aluminium specimens which had received a zincate treatment showed extensive exfoliation of the deposit as a result of severe undercutting associated with preferential attack of the zinc layer. Stannate-treated specimens with a bronze strike but otherwise plated in the same manner as the zincate samples showed no evidence of undercutting.

Heat treatment prior to corrosion testing was found by Jongkind to accelerate the lateral corrosion on zincate-treated specimens.

In 1977, DiBari[156] reported the corrosion test results of an extensive programme designed to evaluate methods for plating on aluminium. Four different processes were assessed:

(1) Conventional double zincate process as specified in ASTM B253-73 in which a copper cyanide strike follows zincating.
(2) As (1) but replacing the specified copper cyanide strike with a nickel strike from a low-chloride sulphamate bath.
(3) Proprietary GMR double zincate process incorporating a neutral nickel strike.[118]
(4) Proprietary Alstan 70 stannate process.

Four aluminium alloys were used and replicate panels were plated with nickel/chromium and copper/nickel/chromium coatings. Scribed and unscribed panels were subjected to several corrosion performance tests — exposure at Kure Beach (a moderately severe marine environment), exposure at the industrial corrosion site in Kearney, New Jersey, and CASS tests. The scribing was done with a carbide cutting tool through the coating and into the basis metal to assess the tendency of coatings to blister and become undermined by the corrosion process.

The corrosion performance of nickel/chromium plated aluminium was influenced by the type of pre-plating process, the nature of the aluminium alloy, and the type of chromium. The stannate process minimized the tendency for intentionally damaged coatings to become undermined by the corrosion process. The use of micro-discontinuous chromium significantly improved the performance of nickel-chromium plated aluminium alloys in corrosive environments.

Mechanical properties of plated aluminium

Most electrodeposits were found by Paige, James and Williams[218] not to influence the tensile strength of aluminium, though as would be expected the elongation and ductility decreased. The exception to the latter was the nickel/chromium deposit, which surprisingly had a superior elongation to specimens

which were only nickel plated. After atmospheric exposure, elongation fell in all cases, but least in the case of the nickel-chromium coatings.

In fatigue tests the life of the specimen was shown to be dependent on the type of deposit, i.e., one bright nickel deposit tested was superior to other types. If the component was subsequently chromium plated this effect was largely lost, indicating that the chromium deposit was the main factor in determining fatigue properties.

Adhesion of plated aluminium

The influence of the pretreatment sequence on the nature of zincate films and the subsequent adhesion levels of electroplated nickel coatings was studied by Golby and Dennis.[101] The nucleation and growth of the zinc deposit depended on both the type of aluminium alloy processed and the pretreatment sequence used. In turn, the distribution of zinc influenced the adhesion of the electroplated nickel coating. To obtain maximum adhesion, the pretreatment sequence has to be adjusted for each type of alloy. Some alloys, such as aluminium-silicon casting alloys are much more critical than, for example, pure aluminium on which good adhesion could be obtained from a wide range of conditions. The peel adhesion values obtained are detailed in Table 13-9.

TABLE 13-9

Process: MAZ (Modified Alloy Zincate)

Etch stage	*Zincate dip*	*Alloy*	***Peel** Adhesion (mean) N/cm*
50% HNO_3	Single	Pure AI	121
		Al-2%Mg (5251)	62
		Al-0.7%Mg-0.5%Si (6063)	7
		Al-11%Si (LM6)	7
		Al-7%Si-0.3%Mg (LM25)	7
50% HNO_3 + 5% HF	Single	Pure AI	170
		5251	74
		6063	16
		LM6	7
		LM25	7
50% HNO_3	Double	Pure AI	236
		5251	115
		6063	131
		LM6	41
		LM25	104
50% HNO_3 + 5% HF	Double	Pure AI	121
		5251	58
		6063	40
		LM6	18
		LM25	12

These results confirmed the benefit of the double zincate dip which gave a thinner, more uniform and more complete coverage of the underlying aluminium. A similar result was obtained by Klingenmaier and Dobrash[205] who also measured the peel adhesion of nickel plated aluminium alloys (Table 13-10) and found that better adhesion was obtained when a nickel strike was used in place of a copper strike.

TABLE 13-10

Peel strength of nickel plated aluminium

Strike Deposit	*Zincate Dip*	*Post Treatment*	*Alloy*	*Mean Peel Adhesion N/cm*
copper	single		Al-1¼%Mn (3003)	81
	single	150°C, 1 h		128
	double			98
	double	150°C, 1 h		180
nickel	single			103
	single	150°C, 1 h		208
	double			196
	double	150°C, 1 h		257
copper	double		Al-1%Mg-½ %Si-¼%Cr-¼%Cu(6061)	89
	double	150°C, 1 h		144
	double	150°C, 24 h		149
	double	175°C, 12 week		144
nickel	double		6061	107
	double	150°C, 1 h		210
	double	150°C, 24 h		228
	double	175°C, 12 week		245
copper	double		Al-2½ %Mg-¼%Cr (5052)	77
	double	150°C, 1 h		123
nickel	double			142
	double	150°C, 1 h		280
copper	double		Al-9½%Si-3%Cu-1%Mg(F132)	77
	double	150°C, 1 h		107
	double	150°C, 24 h		109
	double	175°C, 12 week		91
nickel	double			105

Also, the influence of heating for 1 hour at 150°C on adhesion was very pronounced for the wrought alloys, resulting in 50 to 100% improvement in peel strength. Klingenmaier and Dobrash also investigated the peel strength of plated anodized aluminium, (Table 13-11)

TABLE 13-11

Influence of anodizing and type of preplate treatment on the peel strength of nickel plated aluminium

Preplate Treatment	*Alloy*	*Mean Peel Adhesion*
Double zincate	Al-1¼%Mn (3003)	196
Phosphoric acid anodize, IS V		198
Double zincate	Al-1%Mg-½% Si-¼%Cr-¼%Cu(6061)	107
Phosphoric acid anodize, 15 V		51
Phosphoric acid anodize, 20 V		79
Phosphoric acid anodize, 30 V		105
Phosphoric acid anodize, 40 V		140
Double zincate	Al-7%Zn-1¼%Mg (7046)	156
Phosphoric acid anodize, 20 V		0
Phosphoric acid anodize, 30 V		26
Phosphoric acid anodize, 30 V		*19*
Phosphoric acid anodize, 50 V		96

It is seen from the results in Table 13-1I that different anodizing voltages were required for the three alloys to obtain satisfactory adhesion. This confirms the extensive work of Wittrock[66, 219] who showed that the adhesion level depended on the alloy, the anodizing voltage, the temperature and the concentration of phosphoric acid.

16. APPLICATIONS OF ELECTROPLATED ALUMINIUM

Various metals are plated on aluminium to obtain a decorative or engineering finish. The coatings usually applied are chromium, nickel, copper, brass, silver, gold, tin, lead, cadmium, zinc and combinations of these. Gold, silver or tin is applied to electrical components to decrease contact resistance or to improve surface conductivity. Brass, copper, nickel or tin is applied to improve solderability. Chromium is applied to reduce friction and increase resistance to wear. Zinc is applied to threaded parts where organic lubricants are not permissible. Tin or lead or their alloys are applied to bearing surfaces to reduce friction. Nickel plus chromium or copper plus nickel plus chromium are used in decorative applications.

The main applications of electroplated aluminium are given in Table 13-12.

TABLE 13-12

Principal applications of electroplated aluminium

Application	*Plated coatings (undercoatings are given in brockets)*
Decorative, mainly for indoor oi light outdoor exposure	Chromium (copper-nickel) Silver (copper) Gold (copper) Rhodium (copper-silver, copper-nickel)
Corrosion resistance of assemblies with, for example. steel *or* copper	Cadmium
Electrical contacts	Silver (copper). rhodium (copper-silver)
Soldering	Tin, tin-lead (copper), copper-nickel, and also immersion tinning Copper Nickel (copper.)
Rubber bonding	Brass
Wear resistance, hardness	Chromium (direct or copper-nickel) Nickel (copper)
Lubricating properties, sliding surfaces	Chromium (direct or copper-nickel), tin (copper) and also immersion tin

One of the principal applications for electroplated aluminium is for decoration under conditions where little or no corrosion is encountered. The most common plated finish is the copper/nickel/chromium system. Typical examples are camera parts (finished in bright or satin chrome), flash-gun holders, spraygun parts and fishing equipment, hand iron covers, and refrigerator door handles and decorative trim.

In the motor industry, nickel/chromium plated aluminium hub-caps have been used, while other applications quoted include plated wrought aluminium bumpers and overriders, and permanent mould castings.[220]

Brass plating has been used on household goods such as cast window locks, coat hangers, door stops and wrought door knobs, many of which have been barrel plated.

There are many instances of aluminium parts plated with copper, cadmium, tin or nickel for soldering. Examples are aluminium wire connectors plated with copper-tin and wire sheathing plated with lead-tin alloy. Nickel plated containers can be hermetically sealed with high-melting solders. For lower temperature use, copper deposits can be used. For anti-friction applications, aluminium slide

fasteners have been zinc plated for use in tropical parts, while zinc has also been plated on threaded components. Nickel plating has been used on aluminium aeroplane landing struts, while an important application is the use of lead-tin alloy plating on aluminium bearings.

On electrical equipment and in the aircraft industry, cadmium is plated to prevent corrosion where aluminium is in contact with mild steel and stainless steel, copper, etc. Many aluminium wire terminals are silver, copper, or tin plated for resistance to high temperature oxidation.[221, 222] Aluminium switchgear and bus-bar ends have been silver or tin plated for the same reason. Silver plating is carried out also on electric and electronic chassis and high-frequency conductors. Rhodium plating has been used for similar applications. Electrical connector boxes in aircraft have to be electrically grounded and for this reason coupled with corrosion resistance, they are cadmium plated and then chromated with a thicker than usual chromate conversion coating.

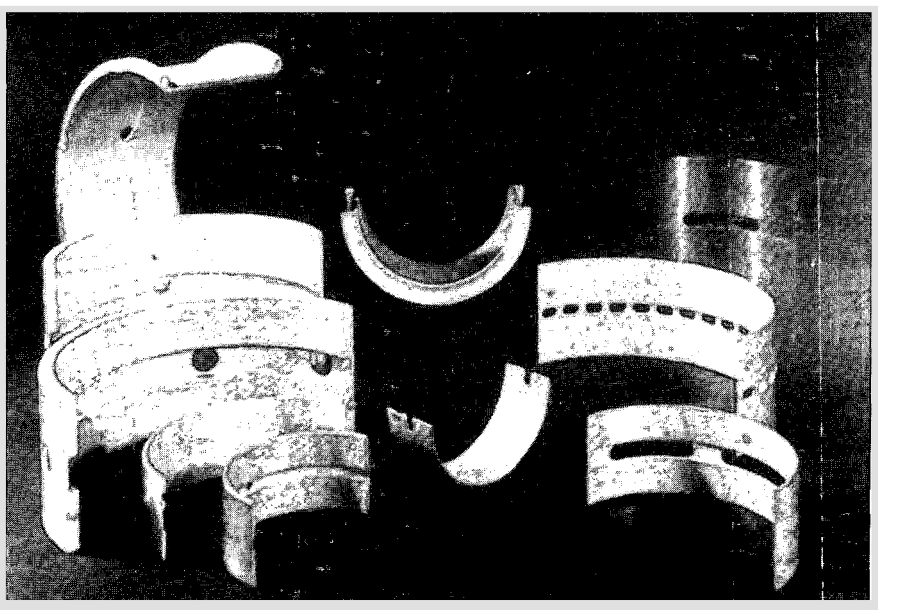

Fig. 13-30. Selection of thick and thin wall shell bearings aluminium/tin plated in soft metals and alloys over Bondal

[Courtesy Glacier Metal Co.]

17. SPECIFICATIONS

There is no British Standard for plating on aluminiuni but in America there is ASTM standard B253-83 Standard Practice for 'Preparationof Aluminium Alloys for Electroplating'. It covers cleaning and conditioning treatments used before metal deposition, and immersion deposit/strike procedures which include the following:

1. Zincate immersion with optional copper strike.
2. Zincate immersion with neutral nickel strike.
3. Zincate immersion with acetate buffered, nickel glycolate strike.
4. Stannate immersion with bronze strike.

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CHAPTER 14

Organic Finishing

Of all the finishing treatments for metals, painting is probably the oldest, and although its place is most important in the protection of the less corrosion resistant and cheaper ferrous metals, a substantial volume of aluminium is painted both for protection against corrosion and for decorative purposes. That organic finishes often constitute the most economical method of decoration is due in part to the low cost of modern paint application methods and in **part** to the ready availability of a wide range of colours and finishes.

In many cases the paints for finishing aluminium, and the painting processes used, are the same as those used for finishing other metals, and therefore this Chapter will try to concentrate on factors that are more specific to aluminium painting.

However paint finishes on aluminium have become very important in many parts of the world, particularly in architectural applications, and the area of painted sheet and extrusions now exceeds the area processed by anodizing in most countries. An exception is Japan where the combination of an anodic coating with an electrophoretically applied lacquer coating (described in Chapter **8** and Chapter 11) is still the dominant finish. In many other areas it is the increased quality and colour range of paint finishes, and the availability of simple application techniques such as powder coating, that has increased their market share.

1. PRETREATMENT

In many situations paints are being used to achieve a decorative effect, more than as a protection for the aluminium, but the continued retention of a satisfactory decorative effect, for example in architectural applications, is of great importance.

Therefore the long-term weathering resistance of the paint finish used, and its barrier properties as a resistance to corrosion will be of great significance. Because all paints are to some degree permeable to moisture, the pretreatment used before painting will be of particular importance in the overall durability of the finish, and the use of an inadequate pretreatment system or the poor application of a pretreatment can lead to rapid failure of paint finishes, either through loss of adhesion of the paint, or localised corrosion effects such as filiform corrosion. Pretreatment is particularly important in the organic finishing of aluminium, and Chapter 5 is largely devoted to this subject. In the past chromate containing conversion coatings were predominantly used, but the health and environmental problems in dealing with chromate solutions and effluent have led to the development of many chromate-free pretreatments. Unfortunately many of these do not provide equivalent corrosion protection to the chromate-containing pretreatments used previously.'.' In part this may have been responsible for the marked increase in the incidence of filiform corrosion in the 1980's and 1990's. However specifications in many countries still insist on a chromate pretreatment for paints in external architectural applications, so this is not the only reason.

With factory-applied paint coatings the type of pretreatment system used will often depend on the nature of the plant and the method of application of the paint. Thus aluminium coil coating lines almost universally now use no-rinse pretreatments, both chromate containing and chrome-free. Extrusion coating plants use dip or spray chromate conversion coatings, or sulphuric acid anodizing, before wet-spray or powder coating, but plants using electrophoretic paint coating systems generally use a simple degreasing and alkaline etching pretreatment. In the aircraft industry thin anodizing pretreatments produced by chromic acid or phosphoric acid anodizing are almost always used, and phosphoric acid or sulphuric acid anodizing as a coil preparation for roll-coated light-sensitive coatings in the lithographic industry. On the other hand the car industry, because of the mixed metal systems generally involved, uses phosphate coatings as a pretreatment for paint. In the case of aluminium these have to be modified with fluoride additions to cope with the presence of aluminium in the phosphate solution (see Chapter 5).

However aluminium is painted in many other situations where factory finishing is not possible. In such situations adequate adhesion may be achieved by mechanically roughening the surface, for example by sand or grit blasting, and then thoroughly degreasing and cleaning the surface chemically. Such treatments are often applied to castings and for site painting in structural applications, but they are followed by the application of an etch primer, and these are described in a later section of this Chapter.

The mechanism of corrosion protection by paint is complex and has been extensively studied, particularly using potentiometric and impedance techniques, but these studies are beyond the scope of this book. What is more important with aluminium is the interaction between the metal, its surface preparation and pretreatment, and the paint coating, and this is well exemplified with the recent studies that have been carried out on filiform corrosion.

Filiform corrosion

The mechanism of filiform corrosion on aluminium has been described in Chapter 1 (pp. 15-17), and it is now widely accepted that it is driven by a differential aeration cell between the anodic filament head and the cathodic tail.[2,3,4] Water and oxygen must be continuously supplied to the cell for growth to continue, and the presence of chloride ions is necessary to provide electrical conductivity and to stimulate the initiation of corrosion. This is, of course, why the effect is more prevalent in marine environments.

Filiform corrosion has been known for many years, and Guminski and Meredith[5] showed in 1963 how it could take place within very short periods of time with clear lacquered aluminium. Again it occurred most readily in marine atmospheres, but the rate of formation of filiform corrosion was strongly dependent on the nature and quality of the pretreatment used. Clear lacquering at this time was considered as a potentially cheap alternative to clear anodizing, but the problems of filiform corrosion ensured that this did not happen.

Some cases of filiform corrosion have always been reported with painted aluminium, and it was well documented in a paper in 1968 by Sick,[6] but in the 1980's many more occurred and these were often more extensive and more serious than problems experienced previously. They occurred most frequently in marine environments in Northern Europe, particularly in countries such as Belgium and Holland. This increaie corresponded with many changes in the industry, including the increased production of painted products, the use of alternative pretreatments to chromating, the increased use of powder coatings, and the availability of a wider range of paint types. However the problem occurred at times with all paint types and application methods, including coil-painted aluminium sheet and wet-spray and powder coated extrusions, and it appeared to be independent of these factors,[7] so there was no simple answer as to the cause.

In the last ten years very extensive investigations of filiform corrosion have taken place in Europe, both on a national and international basis, and this section can do no more than summarise some of the most important findings. Probably the most significant has been the joint study carried out by Alcan and other European aluminium companies with Trondheim University in Norway and Delft University in Holland. The work at Trondheim in particular has been widely reported,[1,2,8] and has shown that there was an important factor in the initiation of filiform corrosion that had not previously been considered. This was the nature of the aluminium surface before pretreatment, and in particular the surface layers associated with the high temperature annealing and deformation processes involved in the production of sheet aluminium. If this layer, 1 micron or more in thickness, was removed in the cleaning or etching processes prior to pretreatment, then sensitivity to filiform corrosion was significantly reduced. Scamans *et al.*[3] in further investigations described this as a thermomechanically or mechanically disturbed layer on the surface of the rolled aluminium. They showed that second-phase particles of the Al-Fe-Si type had a significant role, and that magnesium had an

important effect on the reactivity of surface films and thermomechanically processed surfaces. Significantly most of the alloys used in architectural applications are of the Al-Mg or Al-Mg-Si type. They again showed that removal of these disturbed surface layers markedly improved corrosion performance.

Earlier work reported by Defrancq[9] from the University of Ghent, covering filiform corrosion of 6063 (Al-Mg-Si) extrusions, had concluded that the problem was associated with particular levels of magnesium, iron and silicon in the alloy, and impurity levels of elements such as zinc, lead or copper. He based this on a statistical analysis of the chemical composition of samples which were taken from sections that had shown or not shown filiform corrosion in service, and concluded that the alloy composition should be as follows to avoid the problem:

Zn	< 0.02
Pb	< 0.005
Cu	< 0.015
Fe/Si	< 0.5
Mg/Si	between 1.05 and 1.3

Subsequent studies have not supported these conclusions,[10,11] and it is generally accepted that extrusions within the existing 6063 specification can give a satisfactory paint performance. However, as with rolled sheet, extrusions will have a disturbed surface layer which will need to be removed in any pretreatment process.

It was generally thought that in-service occurrence of filiform corrosion was mainly taking place at defects or weak points in the paint coating, typical examples being physical damage of the film, bare edges from cutting or drilling after painting, or locally low paint thicknesses. However it was important to be able to predict the occurrence of filiform corrosion by laboratory testing and a number of test methods were developed. These all involved the principles of physically damaging the paint by scratching through the paint layer (as in many paint corrosion tests), initiating corrosion by exposing the damaged panel above a chloride containing solution for a short time, and finally exposing the panel to elevated temperatures and high humidity for periods of 1,000 hours or more. The degree of filiform corrosion arising from the scratches was then evaluated.

Two evaluation methods have become standardised and widely used. The first is described in the German Standard DIN 65472. This was first issued in 1989 and uses a 20 ± 2 ml/l solution of concentrated (36%) HCl. The test panel, with its painted side downwards, is held 100 mm above the test solution for 1 hour at ambient temperature in a closed glass container. After this time it is exposed in a humidity chamber at $40 \pm 2°C$ and 85% relative humidity for 1,000 hours.

The other test, specified in ISO 4623: 1984, involves initiation by exposure for 24 hours in a standard salt spray test, and then again exposure to high humidity and tempcrature. The importance of the high humidity in both tests has been indicated in work by Gaszner,[12] and earlier by van Loo,'' and the effect is illustrated in Fig. 14-l. His work also compared the effect of HCI and NaCl initiation, and showed that HCI produced a 40 times stronger degree of filiform corrosion aver the same test period (3,000 hours). **As** a result, at least in Europe, it is the DIN 65472 method that is usually used. More recently a very similar test has appeared as BS EN 3665: 1997 in the aerospace series of European Standards.

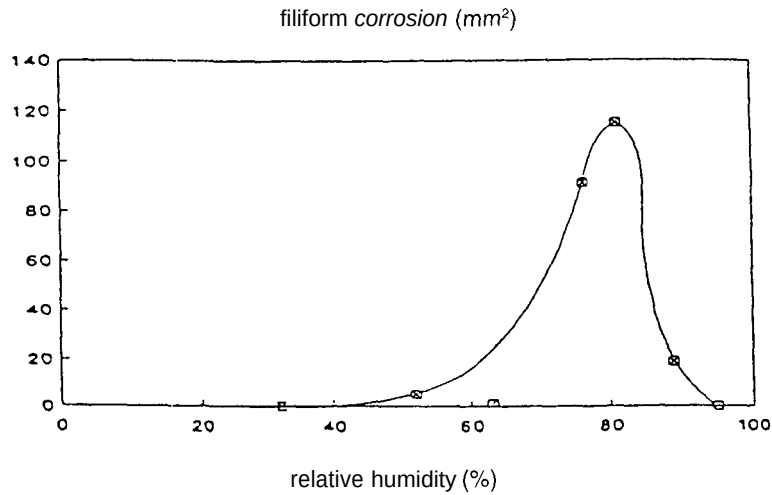


Fig. 14-1. Influence of the rel. humidity on the filiform corrosion after 3000 h at 40°C (Initiator: NaCl)[12]

Having developed an accelerated method of evaluating sensitivity of paint systems to filiform corrosion, the possibility of establishing systems with increased filiform corrosion resistance was open. Much work was carried out both on existing pretreatment systems and on trying to develop systems with improved filiform corrosion resistance. It was generally concluded that a correctly applied chromate pretreatment gave good results, but the importance of removing sufficient surface metal in the pretreatment stages is shown in Leth-Olsen's work' in Fig. 14-2. In this Figure pretreatment 1represents degreased and yellow chromated material, whereas the superior pretreatment J is degreased, etched and yellow chromated. The other successful pretreatments F, G and H all involve anodizing as a pretreatment and this will be discussed later.

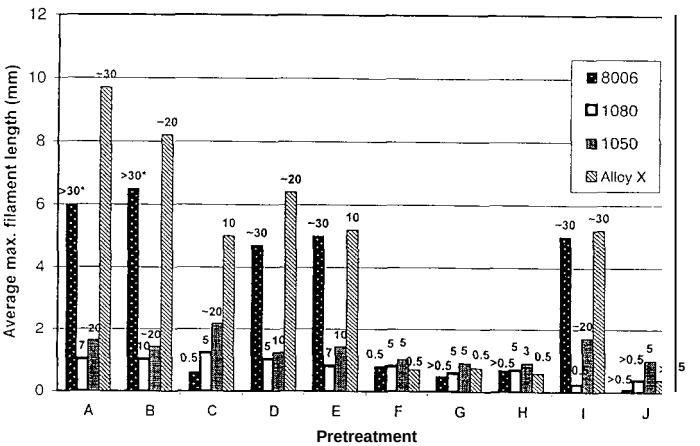


Fig. 14-2. Average max. filament length (the average of three longest filaments) and filament density as a function of pretreatment method on as-fabricated substrates after 1150 h exposure to FFC test.'

* Area along scribe completely delaminated by FFC. Key to pretreatment: (A) No pretreatment, (B) phosphoric acid degreased, (C) etched in NaOH and desmutted, (D) AC anodized, (E) B+D, (F) C+D, (G) B followed by DC anodizing, (H) C+G, (I) B followed by yellow chromating, (J) C+I.
(Alloy X contains small amounts of Mn, Fe and Si).

However although correctly operated chromate pretreatment processes gave good filiform corrosion resistance there could be problems. Exposure tests at the Hook of Holland suggested that the green chromate phosphate coating gave better results than the yellow hexavalent chromium coatings,[14] and the tendency of the latter to give powdery surfaces might be a cause of this.[15] Interestingly the green coatings were almost universally used in the UK where there were generally fewer problems with filiform corrosion.

Extensive studies by Pietschmann and Pfeifer'' and by workers at Cranfield University[17] showed that alternative chrome-free chemical systems gave no improvement over conventional chromating, and many gave inferior results, but there was promise in electrochemical anodizing systems.[16] This quickly became the focus of attention as Pietschmann and Pfeifer showed that sulphuric acid anodizing under closely defined conditions could give filiform corrosion resistance six times higher than that given by yellow chromate coatings. They recommended d.c. anodizing in a 180-200 g/l sulphuric acid electrolyte at 25-30°C to give a minimum film thickness of 3 microns, and preferably 6 microns. In order to reduce the anodizing time they recommended use of a current density of 3 A/dm^2. Such a film was not sealed, but was thoroughly rinsed and dried before painting. Such anodizing conditions give a rather more open porous structure than conventional architectural anodizing, in order to give

better adhesion of the organic coating. They also looked at the effect of chromic acid and phosphoric acid anodizing, but concluded that sulphuric acid was the most practical electrolyte.

The practicality of sulphuric acid anodizing was considered by workers in Italy.[18] They saw anodizing as a higher cost pretreatment process and economic considerations as the main limitation for its introduction. They recoininended a spray anodizing system to make the process more compatible with conventional paint pretreatments and concluded that with such a system anodizing could be used economically.

The findings on anodizing were taken up by the quality labelling authorities (GSB in Germany and Qualicoat in Europe as a whole), and anodizing was accepted as an alternative to chromating in their specifications. For example, the GSB specifications[19] recommend the use of an anodizing pretreatment for work that will be exposed in marine climates with relatively high humidity levels. A thickness of 3-8 microns is allowed, produced essentially under the conditions described above. Degreasing, alkaline etching and desmutting is required before anodizing. This process is now being used in a number of plants in Europe in order to minimise filiform corrosion effects.

Filiform corrosion as a problem with painted finishes is not restricted to architectural applications, but occurs in other situations, notably on body panels used in automotive applications. It has been widely recognised as a problem with painted steel finishes, and with the increasing use of aluminium automotive panels evaluation of filiform corrosion resistance is required for these also, and Powers"' has reported work in this field. Alloys in the 2000 and 6000 series were considered in this work, and he concluded that 2008 alloy gave the best combination of formability and filiform corrosion resistance, with 6009 as the second choice.

2. PAINT SYSTEMS

The technology of modern paint systems is an exceedingly complex subject which must be considered as being outside the scope of the present book. There is a very wide range in the basic types of organic coating but these can also be used in various combinations and permutations to provide a virtually infinite variety of properties. The following is a brief list of the principal types of finishes used.

Air drying coatings

***Alkyd** based finishes.* These are more widely used than any other type of organic coating; they are economical, easy to apply, have good properties and good appearance. Air drying alkyds can be regarded as drying oils modified chemically by reacting with a hard resin such as glyceryl phthalate to reduce drying time and increase toughness. They can also be blended with other resins.

Chlorinated rubber resins. These are made by reacting a rubber latex with chlorine to give a hard brittle resin of outstanding chemical resistance. It is combined in use with suitable modifiers such as hydrocarbons to give fast drying coatings. They may also be added to certain alkyd resins.

Cellulosics. A group of high polymer resins which form coatings by evaporation of the solvent in which they are dissolved. They include the familiar cellulose nitrate originally used in high speed car body finishing, cellulose acetate, cellulose acetate-butyrate (of reduced flammability) and ethyl cellulose with good low temperature flexibility. The low solids content of about 10% is a limitation.

Vinyl and acrylic polymers are high viscosity lacquers with low solids content but giving good properties although with relatively high cost.

Solution-type vinyl resins are copolymers of vinyl chloride and vinyl acetate. They have good chemical and abrasion resistance but poor heat resistance.

Pigmented vinyls have good weather resistance. Some are compatible with certain alkyds to give vinyl-alkyd coatings.

Acrylics. Air drying acrylic resins are similar to vinyls but with much better heat resistance and generally a rather lower chemical resistance. Their exterior durability is excellent, even when unpigmented, the natural colour being white.

Catalysed air drying coatings are organic resin systems to which a suitable catalyst is added to form a high polymer coating, and in this way there is very little solvent loss and practically the whole of the applied coating can constitute the final dried film with properties not unlike the stoved finishes. Epoxy resins, polyurethanes and polyesters can form the basis of catalysed systems.

Stoving finishes

Alkyd-amines. These are alkyd resins combined with urea or melamine-formaldehyde resins and are similar in properties to the modified alkyd air drying coatings. They are widely used, economical and easily applied with good hardness, chemical resistance and resistance to abrasion.

Epoxy-ester resins. These are oil-modified hard resins, usually a polymer of bisphenol and epichlorohydrin. The epoxy-ester resins are normally used in combination with amino resins; they have rather better chemical resistance than alkyd-amines.

Solution type epoxy resins are polymers of epichlorohydrin and bisphenol A. There is a series of these with varying properties which, for stoving, are cross-linked with urea-formaldehyde, melamine-formaldehyde or phenolic resins. Baked epoxy films have superior properties in most ways, having excellent resistance to chemicals and solvents, good hardness and good flexibility while adhesion is

excellent even to bare metals. Gloss retention in exterior exposure is not good, however.

Vinyl resins. Some of these may be cross-linked with amino resins to give strong finishing of better hardness, adhesion and solvent resistance than air-dried vinyls.

Plastisols. Vinyl resins dispersed in a non-volatile liquid or 'plasticizer' is referred to as a plastisol.

Organosols. Vinyl resins dispersed in a volatile solvent. High solids content is possible with these dispersions to give very thick coatings.

Thermosetting acrylics. These can be made with a range of properties according to wish. In general they have very good colour and gloss retention at temperatures up to 200°C; they have good resistance to grease, detergents and good exterior durability. They are generally superior to alkyd-amines but have higher cost. They are the most widely used wet paint system, particularly on coil.

Polyester coatings. These are similar in properties to stoved acrylics and may have better hardness combined with flexibility. They are widely used as the basis for powder coatings.

Silicone coatings. The outstanding property of silicone coatings is excellent heat resistance combined with durability, but their cost is very high and their curing cycle of at least 60 minutes at 230°C is an embarrassment. They will, however, withstand continuous service at temperatures as high at 300°C, and at over 500°C for aluminium-pigmented coatings. It is also possible to form combined systems of silicone-alkyds or silicone-polyesters of intermediate price and properties.

Polyamide-imide polymers. These coatings have good heat resistance (up to 400°C) and also give good hardness, adhesion and chemical resistance, and are non-toxic. They are therefore used particularly in the finishing of cooking utensils.

Fluoropolymers. These represent the most recently available class of paint coatings. They are based on polyvinyl fluoride or polyvinylidene fluoride, and have good flexibility and excellent outdoor weathering performance. Polyvinyl fluoride is applied as a laminated film so is normally only applied to sheet, but polyvinylidene fluoride may be applied in conventional ways and is used as a finish for sheet and extrusions. Both finishes are, however, very expensive and tend to have a more limited colour and gloss range.

A general indication of the relative properties and cost of a range of coatings applied to aluminium extrusions has been provided by Ross,?' and his conclusions are shown in Table 14-1. The excellent properties of the polyvinylidene fluoride coatings stand out in this table, but this is achieved at a cost about 5 times that for an acrylic coating, and with the need to use a primer before applying the PVF_2 coating." Coatings for continuous coil lines have been similarly summarised by Bates.??

TABLE 14-1

Relative properties of various finishes at a typical film thickness of 20-25 μm[21]

Coating type	*Ease of application*	*Stoving conditions*	*Flexibility*	*Abrasion resistance*	*Solvent resistance*	*General chemical resistance*	*Chalking resistance*	*Corrosion protection*	*Dirt retention*	*Cost*
Acrylic	1	2	3	3	2	2	3	2	2	low
Silicone acrylic	1	2	3	3	2	2	2	2	3	med
Exterior alkyd	1	2	4	3	2	3	3	2	3	low
Polyester	3	2	2	3	2	2	3	2	2	low
Silicone polyester[2]	2	3	3	2	2	2	2	2	5	med
Polyvinylidene fluoride[1]	1	4	1	1	1	1	1	1	2	very high

1 = Best 5 = Worst

[1] Usually used with an epoxy primer;

[2] May be used over a primer

3. METHODS OF APPLYING ORGANIC COATINGS

The methods employed for applying paint to aluminium do not differ from those generally used for all metals. They include: brushing, spraying, manual, automatic or the more recent electrostatic processes, dip coating, roller coating, flow coating and electrophoresis. Such coating systems have been reviewed by Cowley.[23,24] The comparative use of different coating systems in Europe is shown for a range of industries in Table 14-2.[24]

TABLE 14-2

European data showing application method and industry[24]

Industry	*Spray*	*Roller coating*	*Electro deposition*	*Dip*	*Flow*	*Brush*	*Curtain*	*Other*
Wood	132	74		15			198	
Structural	12					149		7
Refinish	142							5
Metal packaging	33						27	
Marine	200	71				27		
Coil		40						
Heavy transport	41	70						
Machinery	32		4					
Agriculture	22			8	2			
Drum	24			7				
Wire		1						
Building	14							23
Domestic appliances	11			2				
Aerospace	5							
Storage	6							3
Other	727		5	120				
TOTALS	1401	256	13	152	2	176	198	38

Brushing

Painting by brush is not economical in production except for specialized work or for touching-up damaged surfaces, but it is the dominant process in structural applications.

Spray painting

This is the most important method of applying organic finishes for the mass production of finished components, and it usually provides the best finish. As the process readily lends itself to mechanization, labour costs can be reduced to a minimum. The spray gun consists essentially of a cup from which the paint is atomized and projected by means of a constant stream of cleansed, compressed air.

In hand spraying, the work is usually placed on wire screens supported on rotary tables which are turned as required to provide uniform paint coverage. This is also assisted by spraying in two directions, i.e., at right angles to each other. Paint spraying is carried out in spray booths. Both in order to prevent dirt or dust settling on the work and to avoid the escape of volatile solvents into the shop, the booth is fitted with extraction fans. Absolute cleanliness is essential. The work must not be handled without gloves as a finger mark might prevent paint from adhering to the metal. Dust which might stick to the surface of the paint must also be rigorously excluded.

Automatic equipment

The application of organic finishes by mechanized spraying plant is to be highly recommended for mass production of similar components. Its advantages are threefold: (1) labour costs are reduced to a minimum; (2) rejects for peeling or blistering are reduced by eliminating handling and conducting the operation in a totally enclosed space away from dust; (3) automatic control allows the paint to be distributed more uniformly.

For many components, automatic plant incorporates a horizontal mesh conveyor belt which carries the work through to the drying oven. The paint is applied from one or more spray guns travelling backwards and forwards across the work. **A** battery of guns placed vertically above each other at each spraying station may be employed where the work stands upright on the conveyor. Batteries of spray guns may be fed from a common paint tank maintained at a constant pressure, e.g., 1-1.4 bar (15-20 lbs/sq inch).

As an alternative to the conveyor system, semi-automatic plant may be installed in which the normal hand spray booth is used while only the movement of the gun across the work is mechanized. By this means it is possible to use unskilled labour, as the only manual operation is loading the trays and moving them off the turntable. Further, the space requirements are those of fully-automatic plant and less waste is caused by over-spray.

As is the case in many automatic processing units, mechanization brings with it two disadvantages: (a) the comparative inflexibility of the plant which must be adjusted to suit differently shaped articles; and (b) stoppage in a gun or due to a faulty mechanism may produce a pile of rejects before the fault is noticed. To eliminate this fault, electronic detection devices may be used to sound an alarm at

any deviation from the correct spraying conditions, but such equipment is necessarily expensive and is practicable only in very large installations.

Electrostatic spraying

Wet coating

One of the most serious drawbacks to spray painting is the waste of paint in over-spray. In ordinary hand spraying, this will normally be 20-30% of the total consumption. In automatic plant, the figure may be much higher, depending upon the shape and spacing of the work.

A widely used method to avoid over-spray is to pass the atomized paint particles through a high-potential electrostatic field. In the zone of this field, the particles become positively charged at approximately 100,000 volts and are attracted to the work which is cathodic and is earthed on the conveyor. In this process the paint spraying pressure is substantially lower and the aim is to produce a 'fog' around the work which is then coated uniformly. Although a high voltage is required, the electric power consumption is low as the current drawn is only a few milliamperes. This method of spray painting has become extremely popular for mass production painting, particularly in the appliance industry where the top coat is often sprayed in a mechanized electrostatic spray line on top of chromated aluminium, frequently after dip painting (e.g., with epoxy primers).[25] It is also used for painting complex extruded shapes, for example **for** architectural applications.[21,26] On these lines, reciprocating disc spray units are often used, and the sections may be hung vertically or horizontally. Large vertical lines are common in the USA, and are now becoming more common in Europe. They are most suitable for high volume production (1400-1600 kg/h)[27] with few colourchanges (each colour change may require as much as 4 hours downtime), and are therefore mainly used for producing white finishes on extrusions. These lines are claimed to be more labour efficient and to have reduced chemical and paint consumption.[28] With vertical jigging the work can be indexed to present all faces to the reciprocating discs to obtain good coverage, but horizontal work is passed between electrostatic bells on both sides of the conveyor, with the most critical surfaces facing the sprays. To obtain the best coverage with an electrostatic material, it is important to have the electrical resistance of the paint correct, and in order to maintain good durability, this is usually adjusted by modifying the solvent balance. Modern vertical lines now incorporate the possibilities of both wet-spray and powder coating, and the layout of one such line designed in Italy is shown in Fig. 14-3.[27] Also from Italy comes a so-called 'compact plant' which is designed for small lots of mixed products with frequent colour changes.[27] It gives maximum exploitation of floor space (not more than 90 m^2) by locating the curing oven over the painting booth and the racking/unracking area, and it is again mainly designed for powder coating. The general layout and travelling powder coating booth are shown in Fig. 14-4.

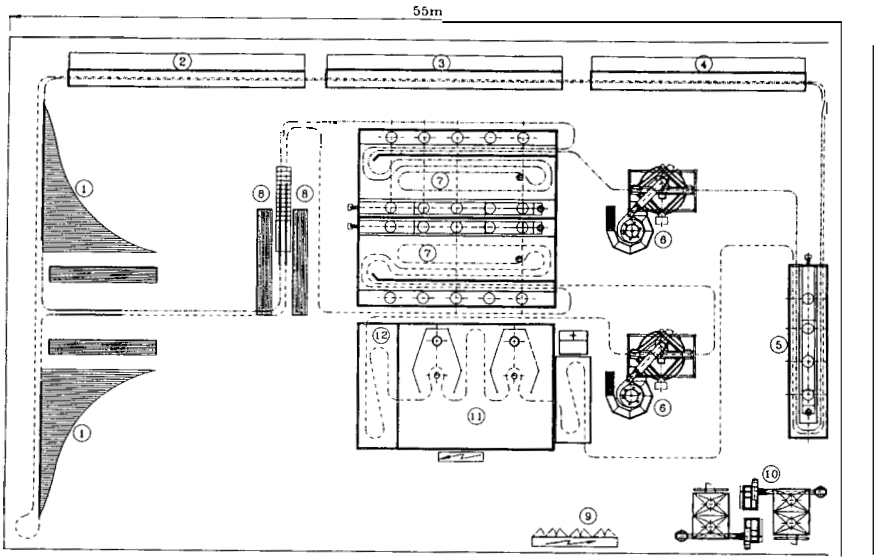


Fig. 14-3. Typical layout of a Trevisan MFV line:
1) Loading: 2) Degreasing; 3) Desrnutting; 4) Chromating;
5) Dryer; 6) Powder Booth; 7) Curing oven; 8) Unloading;
9) Control panel; 10) Final filter; 11) Wet paint booth; 12) Flash-off[28]

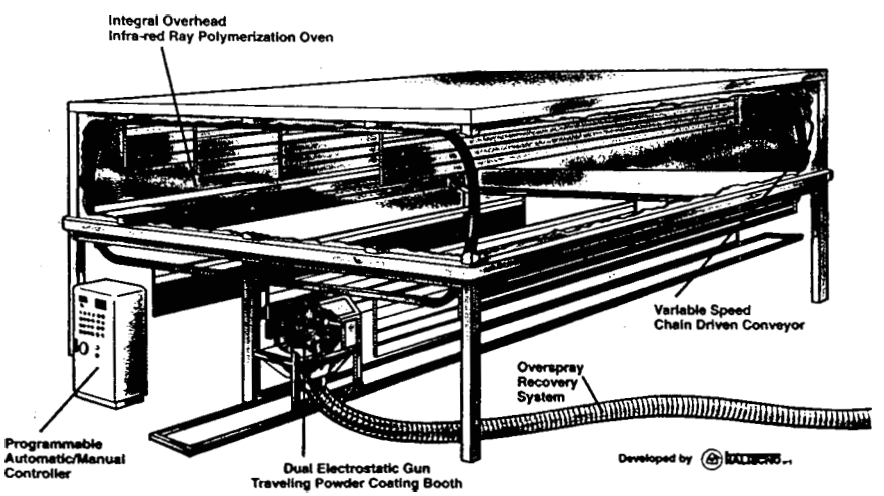


Fig. 14-4. The compact unit, patented by Italtecno S.r.l., Italy, features an infra-red oven. powder coating booth and controller.[27]

Powder coating

A major use of the electrostatic spraying system is now in the application of powder coatings to metal surfaces. This technique has rapidly become the most widely used method of batch painting sheet and extruded aluminium components. It is attractive because no solvents are involved, and this both reduces the paint cost and eliminates the problems of solvent handling and recovery.

The powder coating process has been described by Rankin.[29] Conventional paints consist of resins (which form a continuous film when dry), pigments (which provide the colour and opacity), small amounts of various additives, and solvents. The latter only dissolve the resin in order to allow application of the paint, and do not contribute to the performance or properties of the dry film. The powders used for painting are thermosetting and contain the same basic constituents, but are completely solvent free. These powders flow freely at room temperature and, after application, fuse into a continuous film during the stoving process. Although different resins are available in powder form, including epoxies, epoxy-polyesters, polyurethanes, acrylics and polyesters, it is only the polyesters that are widely used for coating aluminium. These give good toughness, flexibility and adhesion, and have excellent resistance to impact, scratch, abrasion and handling damage. They also have good exterior durability and this is said to be improved further using silicone modified polyesters.[30] Much work is still going on to develop improved powder coatings, particularly for architectural applications of aluminium. Some of this is concerned with improved gloss retention in severe exposure conditions such as Florida, and some is more involved with the health hazards of powders.[31,32,33,34,35] The main chemical components used to form the paint film are based on carboxy functional polyester resins cured with triglycidyl isocyanurate (TGJC). This use of a very low molecular weight epoxy functional co-reactant allows a relatively high proportion of UV resistant polyester to be included in the formulation. TGIC reacts with the carboxyl groups on the polyester to form an ester linkage. However TGIC has been found to be potentially hazardous to health, and though quite safe when good handling and powder application are observed, manufacturers have recently developed alternative TGIC free systems. In many of these the TGIC is replaced by a β-hydroxyalkylamide which, with specially adapted polymers, gives no potentially dangerous volatile components.'' In practice these new coatings have also provided other improvements, particularly in powder application characteristics.

Powder coatings are applied using electrostatic spray guns and a typical powder application process is shown in Fig. 14-5. The powder, usually contained in a hopper adjacent to the application booth, is delivered *to* the electrostatic guns, which can be manual or automatic. The voltage which is applied at the nozzle of the powder spray gun produces an ionisation area. As the powder particles pass through this area they become electrically charged, and are then attracted to the earthed article. The electrostatic forces of attraction hold the particles in place until the coated article passes into the oven, where it melts, flows out and cures to

a tough, smooth film. Curing is carried out for 5-30 minutes at 140-200°C depending on the powder being used and the articles being coated.

The spray booth is usually sealed to prevent loss of powder, and excess powder is sucked from the bottom of the booth into a cyclone recovery chamber, with the air being exhausted to atmosphere via a bag filter arrangement (Fig. 14-5). The recovered powder can then be processed through sieves and blended in the correct proportion with the unused powder. The problems of powder recovery have been discussed by Craine.[36] He saw the main problems as large losses of powder with low efficiency cyclones and residual powder in the system at times of colour change. Using multiple smaller cyclones and avoiding cartridge filters reduced these problems.

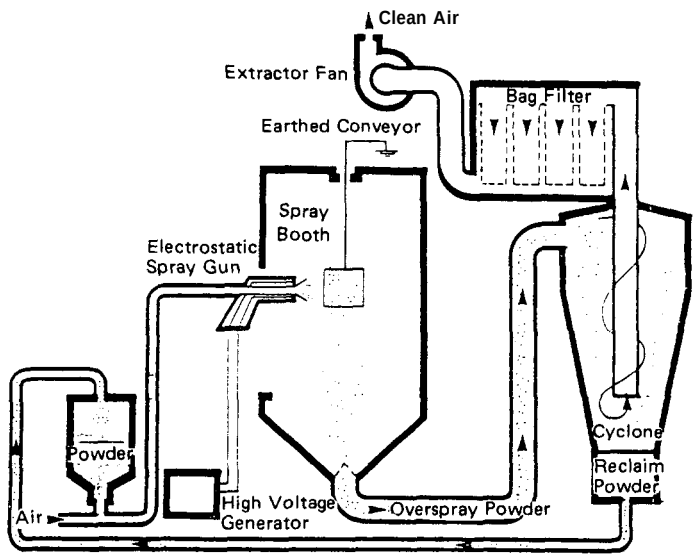


Fig. 14-5. Powder application and recovery

A limitation of powder coating is that very thick coatings (40-150 μm) are applied by the normal powder process. Whilst this gives excellent surface protection, the build-up can be irregular and this will interfere with engineering tolerances on mating sections. Much work has been carried out to reduce the film thickness variation, and coatings in the range of 60-80 microns have been produced by careful control.[29]

Much work is being carried out to further improve powder coatings and to extend the range of powders applied. Smaller components are now coated with

thermoplastic powders such as polyamides and nylons," and some inorganic materials such as vitreous enamels are being applied in powder form. A line for powder coil coating of aluminium has been reported from Italy,[38] and a powder coating line for precut metal sheet, which is then postformed, has been described from the USA.[39] Glover has described various ways of electrostatically charging the powder,[40] and Gokemre and Dennis[41] have investigated the effect of powder storage conditions on the performance of thermosetting powder coatings.

The problems that can occur in powder coating processes, both with the equipment and in coating appearance and properties, have been described by Brace *et al.*[42] Examples in process terms include the supply of clean, dry, oil-free air for fluidizing and transporting the powder, lack of proper fluidization or over-fluidization of the powder bed, and poor powder adhesion to the work. **A** major problem with powders is the very wide film thickness spread that occurs over the work surfaces. On complex sections this is not helped by the fact that partially closed areas are shielded by a 'Faraday Cage' effect.[43] The electrostatic force is dominant near the workpiece surface, and powder deposits in the direction of the lines of force in the electrostatic field as shown in Fig. 14-6. This has the advantage of giving a wrap-round effect on the back surface of the section, but areas such as the corners in Fig. 14-6 receive much less powder. Brace recommends that the width of the gap between two faces should be a minimum of 1.5 times the height of the gap. Reducing the amount of fluidizing air to the gun, reducing electrostatic voltage at the gun tip, and preheating the component so the powder melts when it reaches the surface, all help to minimise the Faraday Cage effect. The implications of different powder charging systems such as corona charging, tribo-charging, and contact charging, have been described by Reddy.[44] Tribo-charging, which is increasingly used, largely eliminates Faraday Cage effects, but also gives poor wraparound, so more guns are needed to cover all the significant surfaces, and not all powders are suitable for tribo-gun application.

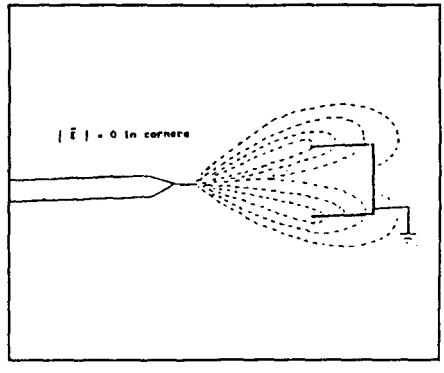


Fig. 14-6. The 'Faraday Cage' effect"

Unacceptable film thickness variation is one of the factors covered in a consideration of powder application and cure problems described by Bridges,[45] and illustrated in Tables 14-3 and 14-4. Cowley[46] has looked at quality control of an industrial powder coating plant using FMECA (Failure Mode Effect and Criticality Analysis) techniques. He concludes that this method can be very effective, but significant changes in management attitude and training are required.

Special powder coatings for use in particular applications or industries have also been described. Workers in the USA[47] have compared high heat resistant powder coatings, obtained by the addition of silicone to the powders, to vitreous enamel and liquid silicone-modified polyester coatings. They concluded that the powder coatings were a viable alternative. Similarly Burke[48] has investigated chemical resistant powder coatings for military applications.

TABLE 14-3

Powder coating problems, application[45]

Symptom	*Possible causes*	*Remedies*
Poor attraction of powder to component	a) Incorrect voltage at gun	Clean gun. Check voltage *or* replace gun.
	b) Poor earthing	Clean earthing points and jigs.
	c) Excessive build up of cured powder on jigs	Clean jigs.
	d) Excessive forward air pressure	Reduce forward air pressure.
	e) Incorrectly positioned guns	Reposition offending guns.
	f) Poor jig design	Re-design jigs to reduce shielding
Low film thickness on component	a) Powder delivery too low	Set correct powder feed pressure. Check powder venturi is correct size, is clean and is set correctly.
	b) Insufficient coating time	Increase time of component in front of guns by slowing track speed. Increase number of spray guns. Slowing down reciprocator speed.
	c) Faraday cage effect	Adjust voltage. Adjust forward air. Reposition guns.
	d) Surface area of jig too large compared to surface area workpiece	Minimise jig size.
	e) Damp powder	Remove powder and replace. Ensure all powder **is** kept sealed until in use.
Film weight on component too high	**a)** Excessive powder delivery	Reduce powder feed to gun. Increase distance of gun to component.
	b) Gun voltage too low	Reset voltage.
	c) Excessive coating time	Reduce time of component in front of gun by: Increasing track speed. Increasing reciprocator speed.
	d) Excessive preheating temperature (if used)	Reduce preheat cycle.

TABLE 14-3 *(continued)*

Symptom	*Possible causes*	*Remedies*
Variable emission from gun (Surging and spitting)	a) Damp air supply	Check de-watering chambers. Install or check air refrigeration unit.
	b) Variable air supply	Check compressor not overloaded.
	c) Damp powder	Remove powder; clean plant; replace powder. Ensure powder is kept in sealed bags until in use. Keep minimum of powder in plant overnight.
	d) Powder too fine	Check ratio of recovered to virgin powder. Adjust if necessary. Check with supplier that particle size of virgin powder is within specification.
'Back Tracking' (Metallic powders)	a) Excessive metallic content	Contact supplier.
	b) Free metal present	Contact supplier.
Uneven broken appearance before curing	a) 'Back ionisation'	Reduce deposition rate and film thickness

TABLE 14-4

Powder coating problems, curing/appearance[45]

Symptom	*Possible causes*	*Remedies*
Low gloss	a) Oven temperature too high	Reduce air temperature. Check metal temperature with oven recorder.
	b) Time in oven too high	Increase track speed. Check time/metal temperature ratio with oven recorder.
	c) Contamination with incompatible powder	Clean all equipment thoroughly. Dumping contaminated powder.
	d) Contamination with chlorinated solvent vapour	Check proximity and operating efficiency of chlorinated degreasing plant.
Even discoloration	a) Cure temperature too high	Reduce temperature. Check metal temperature with recorder.
Patchy discoloration	a) Inadequate pretreatment	Check and rectify.
	b) Corrosion products on surface	Clean off with chemical pretreatment
Gloss too high	a) Cure temperature too low	Increase oven air temperature. Check metal temperature with oven recorder.
	b) Oven cycle too short	Decrease track speed. Check time/metal temperature ratio with oven recorder.
Poor flow	a) Heat up rate to temperature too slow	Check heat up profile with oven recorder.

TABLE 14-4 *(continued)*

Symptom	*Possible causes*	*Remedies*
Poor hammer/texture pattern	a) Heat up rate too slow	Check heat up profile with oven recorder.
	b) Too much reclaimed powder being added to virgin powder	Reduce ratio of reclaim to virgin powder. Ensure generation of reclaim powder kept to minimum
Colour contamination	a) Poor housekeeping when changing colour	Keep colour changes to minimum Ensure thorough cleaning after colour changes.
	b) Cross contamination during manufacture	Contact supplier.
Foreign matter in film	a) Inadequate cleaning	Clean gun, booth and recovery equipment.
	b) Unsieved recovered powder	Sieve all reclaim powder.
	c) Sieve for recovered powder too coarse	Reduce size of sieve mesh.
	d) Virgin powder 'bitty'	Contact supplier
Poor adhesion	a) Undercured film	Check cure cycle with oven recorder.
	b) Poor pretreatment	Check and rectify.
Pinholes/Cissing in film	a) Silicone contamination from hammer powders or polishes	Locate and remove source of contamination.
	b) Oil in air supply	Check oil separators.
	c) Water in air supply	Check or install refrigeration unit.

Hot and airless spraying

In hot spraying, economies are affected by using an appreciably higher paint-to-solvent ratio, made possible by heating the paint *to* reduce the viscosity. Airless spraying is a further development in which the use of compressed air is eliminated and the hot paint, which is substantially free from solvent, is pumped at high pressure to the spray-gun. More recent spray-gun developments include air-assisted airless spraying, and high velocity low pressure (HVLP) spraying. Both of these systems are designed to reduce overspraying. For details of these and the preceding methods the reader is referred *to* the literature.[43,49,50]

Dip coating

Dipping the work into a tank containing the paint is a relatively cheap and simple method of application. The main disadvantage is that the coating thickness is difficult to control. It is also necessary to achieve adequate draining or

de-tearing on withdrawing the component, and open paint tanks are subject to evaporation losses arid in some cases fire risks. On the other hand, the plant is easily mechanized and is often extreinely cheap to run, while for articles which, because of their shape, are difficult or impossible to spray, dip coating may be the only convenient method of paint application.

The paint should be continuously agitated by means of a rotating screw or paddle fitted into the bottom of the tank.

Slow, controlled withdrawal is required to avoid tears or drops adhering to the edges. Special equipment for this purpose is on the market although, of course, large installations must be individually designed. Electrostatic de-tearing, utilizing equipment similar to that employed for electrostatic spraying, also helps in this process.

Barrel and centrifugal coating methods

Very small components may be treated by contact with the paint in rotating barrels. This method is used particularly for gilt, bronze or similar finishes.

During recent years, some use has also been made of a centrifugal lacquering machine, in which the excess lacquer is removed from the work by centrifugal force. However, due to faults at points of contact, only a second-class finish is obtained with this type of equipment.

Roller coating

This process is employed for sheet and coil material only. The equipment is similar to that used in a large printing press and consists of a number of rollers. A typical coater configuration is shown in Fig. 14-7. The paint is picked up from a reservoir by the first or 'pick-up' roller which travels in an anti-clockwise direction. Above it and travelling in the reverse direction is the 'applicator' roll, which picks up the paint from the 'pick-up' roll and applies it to the sheet which is passing over a much larger 'back-up' roll. A second coating unit applies paint to the reverse side of the sheet. Other roll configurations are possible and 3-roll applicator systems are also used.

Roller coating is the standard method of applying paint on continuous strip lines mainly due to three advantages:

1. It gives a particularly uniform paint coating.
2. Paint wastage is limited to between 2 and 5% compared with about 10% for flow coating and 30% for spraying.
3. It is easily brought under automatic quality control.

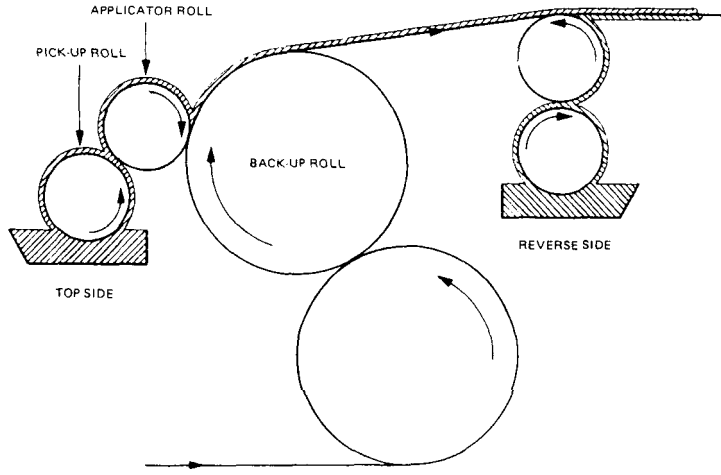


Fig. 14-7. '2-roll reverse' coater configuration

The rollers are driven from gearing and adjusted so that there is just sufficient space between them to allow the passage of the paint, while only the scraper roller presses on to the sheet. The paint must be of controlled viscosity, and is formulated specially for the purpose. There is little waste as excess paint runs off from the scraper into a container and is pumped back to the reservoir.

A novel coating system involving an extrusion head located just above the metal surface, and extruding a layer of paint onto the aluminium strip, has been described by Alcan.[51] This coater is computer controlled and is capable of applying controlled, virtually non-repetitive patterns and of precisely metering the paint application. It can be used for applying many different types of coating and can give excellent simulation of wood-grain for siding applications.

One or both sides of the sheet may be coated, and the process is used for coating foil for applications such as milk bottle caps, chocolate wrapping and other packaging uses, and for coating sheet, for example, for architectural and caravan applications, where the sheet is often formed after painting. Such coil lines are described in a later section of this Chapter.

Flow coating

Very large or intricately-shaped parts are coated by this process, in which the work is suspended over the tank, while the paint is pumped up and distributed by a hose.

Electrophoresis

Application of paint and other organic materials by electrophoretic deposition onto various metallic substrates has been practised for a number of years, but the commercial application to aluminium has been slower than to other materials because of greater difficulty in getting defect-free deposits; this has been attributed by some of the presence of an oxide film.[52] Thus Berry[53] obtained sandy finishes and localised heavy deposits of paint during anodic electrodeposition of a phenolic-alkyd paint. Fink and Feinlib[54] used anodic depolarizing agents in an attempt to overcome gassing problems at aluminium anodes when depositing synthetic polymer lattices, to improve on the porous nature of the deposits which earlier workers had reported.[55,56] The formation of successful electrodeposited paint films was claimed by Ito and Shibuya[57,58] in 1966, and a plant for the electrocoating of aluminium extrusions was commissioned in the U.S.A.[59]

The formation on aluminium in some paint systems of an anodic oxide layer which inhibited electrodeposition was noted by Ito and Shibuya,[57,60] and Broughton[61] observed that by working at a constant current density of 0.107 A/dm^2 (1 A/ft^2) with an unpigmented alkyl-melamine resin, he required a continuously rising voltage, and was able to measure the weight of oxide formed on the anode at 1 minute intervals. Fig. 14-8 shows that the oxide film formed is proportional to the terminal voltage and that if the thickness of this oxide film is calculated, assuming a density of 3.0, it corresponds to 12 Å/volt which is the same as for barrier layer formation during normal anodic processes (Chapter 6). Most of the voltage drop is therefore across this oxide film. The gain of weight of the anode is in contrast to the behaviour of most other metals which lose weight during electrophoresis.[57]

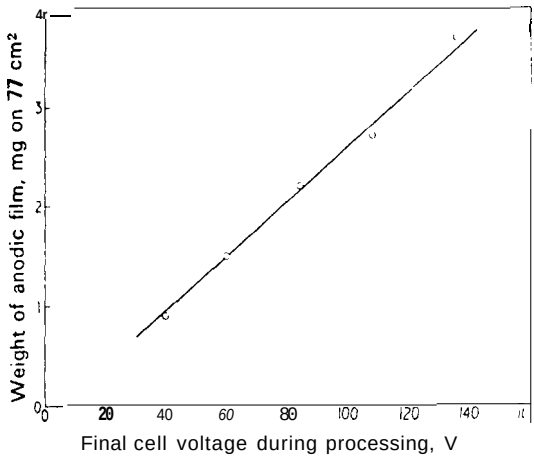


Fig. 14-8. Relationship between oxide film weight and cell voltage during deposition of the unpigmented alkyd-melamine resin (10% solids at 14°C) onto etch degreased 99.0% purity aluminium[61]

Broughton noticed that at constant current density operation the initial voltage rise was rapid but very little paint deposit formed during this period (Table 14-5), a very thin paint film forming at 60 seconds which subsequently became microporous. This induction period suggests that the electrocoagulation of paint does not occur as a result of aluminium cations produced at the metal surface but supports the views of Bruce[62] and of Tawn and Berry[63] that localised acid conditions which develop in the anolyte as electrocoating proceeds are responsible for much of the paint deposits which form on metal surfaces. Ito and Shibuya[64] investigated the effects of adding chloride ions to a water-soluble alkyd primer and noted an initial increase in the rate of paint deposition because of prevention of passivity of the anode, but the rate was subsequently reduced because the corrosion products led to an increase in the film resistance. The physical and chemical properties of the coated film were not affected by additions of chloride in the range 0 to 70 ppm.

TABLE 14-5

Visual examination of uncured unpigmented alkyd-melamine resin obtained at various stages of electrodeposition onto aluminium-1¼% manganese alloy at constant current density (1 A/ft²)

Deposition time, seconds	*Cell voltage, V*	*Appearance of the panels after electrodeposition*
15	11	No adherent paint film on specimen surface
30	15	
45	**23**	
60	40	Extremely thin adherent paint film
90	**42**	Paint film with fine porous structure
120	*50*	Paint film with fine porous structure

Broughton[61] noted that some resin systems are more easily applied to aluminium substrates than others. For example, paints based on a phenolic alkyd resin were only applied in the defect-free condition to aluminium surfaces when certain batches of resin were used and also where the formulation of the paint, pretreatment of the metal and the electrical conditions which prevailed during deposition were closely controlled. Other resin systems, such as the alkyd-melamine and the oxidizing alkyd resins, produced paint systems which were far more easily applied to a variety of aluminium substrates (Fig. 14-9). With these paint systems the metal pretreatment and electrodeposition conditions could be varied considerably whilst still maintaining the integrity of the final paint coating. The greater flexibility of processing conditions which could be tolerated by the alkyd and the alkyd-

melamine paint systems was apparently related to the mobility of these films in the electrodeposited state either before or during curing. Where the uncured paint films retain a certain amount of mobility, then defect-free paint films can be readily obtained. Under conditions where this mobility is too restricted, by the use, for example, of too much thickening agent, defects can easily be introduced into the paint films. Mobility must be controlled, however, to avoid paint retraction from sharp corners and edges.

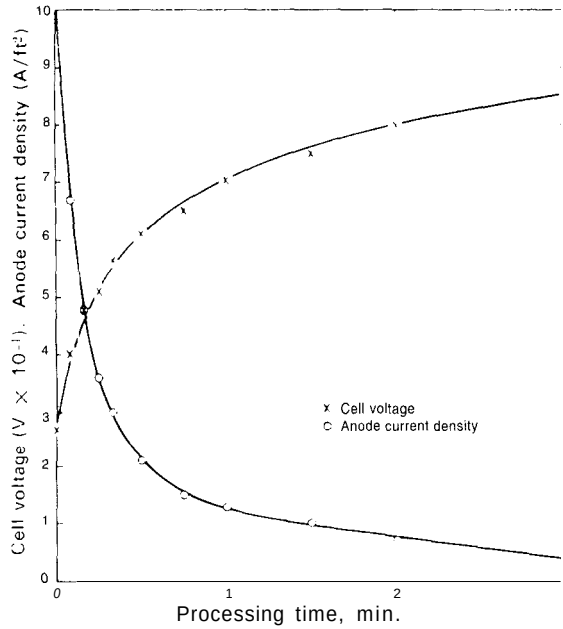


Fig. 14-9. Typical voltage-time and current density-time relationship during deposition of the unpigmented alkyd-melamine resin (10% solids at 24°C) onto etch degreased 99.0% purity aluminium[28]
1 A/ft² ≈ (0.1 A/dm²)

The pretreatments examined by Broughton before electrophoresis included vapour degreasing, etch degreasing, Alocroin 100, zinc immersion deposits, Bondal, acid pickling to DTD 915B, and anodizing in sulphuric acid to 1 μm and to 5 μm (0.04 mil and 0.2 mil), both sealed and not sealed. The best paint deposits were obtained in all cases when the pretreatment was Alocrom 100 with a film

weight of about 10 mg/dm^2, and localised heavy deposits were obtained on anodized or untreated substrates. Defects noted by Broughton included heavy porous deposits, cissing and pinholing (Fig. 14-10), and the procedure was successfully applied to heat exchanger units consisting of aluminium fins mounted with very close spacing on copper tubes where coating by any other technique would have been extremely difficult.

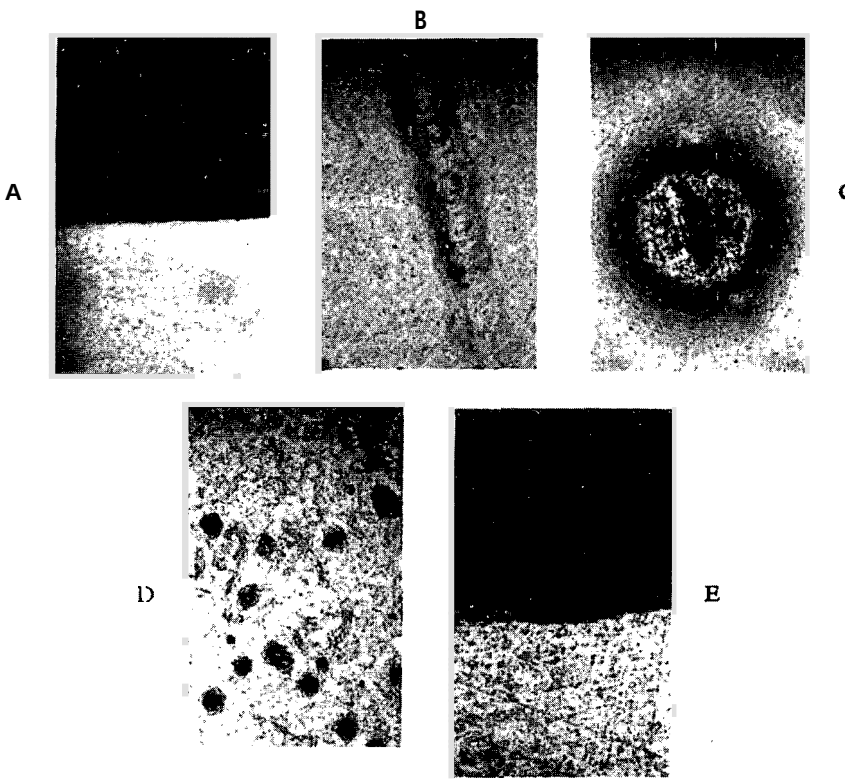


Fig. 14-10. Defects in electrodeposited paint films[61]

(A) Cross section through localized porous heavy paint deposit (x 40)

(B) Surface photograph of porous ridge of heavy paint deposit associated with the rolling direction **of** the substrate metal (x 40)

(C) Surface photograph of cissing defect in which the basis metal is clearly visible (x 40)

(D) Surface photograph showing pin hole defects in electrodeposited paint film (x 40)

(E) *Cross* section through pin hole defect (x 350)

Since then the electrophoretic deposition of clear acrylic lacquer coatings on anodized aluminium extrusions has become the major method of sealing such finishes in Japan, and these processes are described in Chapter 8 and 11. The mechanism of such processes has been investigated by Sato[65] and by Ashida and Ueda,[66] and they too have shown that barrier layer growth occurs in the anodic electrocoating process. The adhesion of such films to anodic coatings has been studied by Omata *et al.*,[67] who concluded that this depends on penetration of the polymer into the anodic coating. With sulphuric acid anodized coatings, the resin particles are too large for this to happen to any significant extent, but films produced in phosphoric acid show greater incorporation of resin. Similar application of acrylic resins on .sheet has been indicated by Baker,[68] who showed that the blister defects often seen were due to residual phosphate from the chromate-phosphate pretreatment. Ellinger[69] has discussed the formulation and manufacture of paints suitable for electrophoresis, and many Japanese patents describe suitable electrophoretic lacquer compositions.

In the U.K., the interest has been with the application of paint rather than lacquer coatings, and particularly the anodic electrodeposition of white paints on extrusions. This type of electrophoretic process was developed in the U.S.A., though now it is little used there, and became the standard finish for many domestic window and door frames in Britain in the 1970's and early 1980's, but since then the market has been taken over by powder coatings. The process used has been described by Phillips.[70] The extrusions were pretreated by a conventional alkaline cleaning and etching operation and were then thoroughly rinsed before being placed in the electrophoretic painting tank. This contained a water-soluble acrylic-based paint, the resin being rendered soluble by the addition of suitable amines such as melamine. When current was passed through such a solution the resin and pigment migrated to the anode whilst the amine was discharged at the cathode. In effect, therefore, as the resin was deposited the level of amine in the solution increased and this caused serious bath instability if allowed to continue. Methods of removal of excess amine were therefore developed, and the most usual process used was ultrafiltration.

The ultrafiltration system made use of membranes of a defined pore size range, which were designed to allow the smaller water and solubilising agent (amine) molecules through, but prevented passage of the larger pigment and resin particles. The mixture allowed through the membrane was called the ultrafiltrate, and, by discharging a small amount of this to drain, excess amine build-up could be prevented. The ultrafiltrate had a second use in that it could be used for rinsing the work coming out of the paint tank, so allowing the re-use of the paint solids removed. Such a closed loop ultrafiltration system is shown diagrammatically in Figure 14-11.

The electropaint was continuously circulated to avoid settling of the paint solids, and heat resulting from the pumping process as well as from the passage of electric current, needed to be extracted in order to maintain the desired temperature. Dry coating thicknesses of the order of 25 microns were normally applied, using a

voltage of 150-170 V for a time of 1-2 minutes. After painting, the work was rinsed as already described, before stoving conventionally at temperatures of 180-200°C for 20-25 minutes.

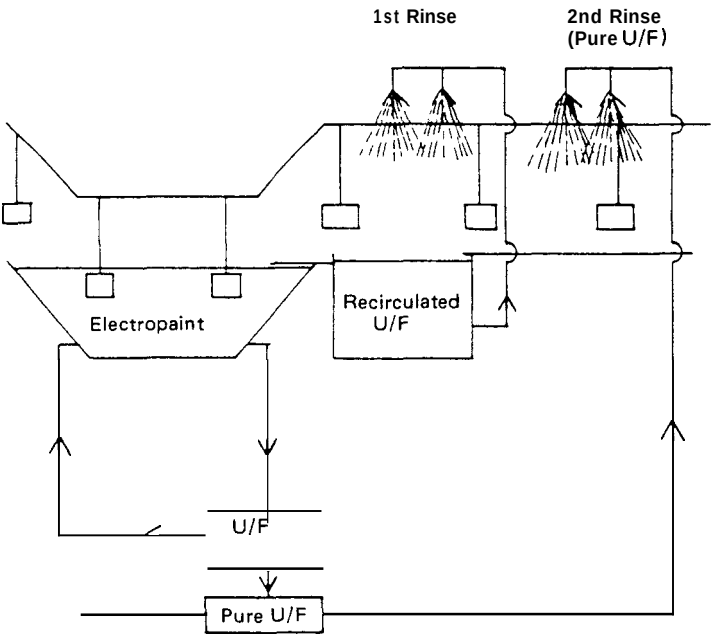


Fig. 14-11. Closed loop ultrafiltration

As with other electrophoretic coating processes a barrier layer of oxide was generated on the aluminium during the early stages of the coating process, and this was thought to be responsible for the good adhesion of this type of coating. It is also the reason that the conversion coating type of pretreatment normally used with powder or strip painting processes, could not be used, as this was damaged or disrupted during the electrophoretic process.

Many plants of this type existed in the U.K., all of which were producing white finishes,[70,71,72] and some, such as that at Alcan Extrusions, were fully automatic,[73] but they have since all closed or been replaced by powder painting facilities.

The Epla process

Winkler has described the Epla process[74,75] for electrochemical deposition of plastics onto aluminium and other non-ferrous metals, which was patented by ECM-Gesellschaft fur Electrochemische Materialbeschichtung in Germany. It has been applied to a wide variety of aluminium alloys in the rolled, extruded, drawn and cast forms.

The Epla bath consists of an aqueous suspension of solid comminuted thermoplastic materials with stabilizers, plasticizers and/or inorganic salts. For colourless, transparent coatings the bath consists of a suspension concentrate and a solution which confers electrical conductivity. The coating may be coloured by incorporating dyestuffs into the electrolyte, or made opaque by including pigments or titanium dioxide. Suitable plastics for the process are polystyrene co-polymers and polyacrylates, which are 'plasticized' by co-polymerizing with butadiene or by incorporation of a plasticizer from the large range which is available. The bath contains no low boiling organic solvents.

Anion surface active emulsifiers, which are in part co-polymerized with the plastics and in part adsorbed upon it, confer on the plastics particles an anodic charge which facilitates mobility of the particles in the applied electric field and their deposition upon the workpiece connected to the anode.

The pH of the bath is between 7 and 10, preferably 9, and is adjusted by addition of ammonium hydroxide. The ability of the suspension to carry a high loading of pigment facilitates the introduction of a high proportion of electrochemically-inert extenders, such as PTFE, polyethylene or polyamide. After stoving, these components are firmly embedded in the plastic base and in this way confer upon it outstanding antifriction properties and/or a further increase in its already very good corrosion resistance.

A bath suspension ready for use has a content of solids between 5 and 32%. The ratio of pigment to plastics binder is from 1:2 to 1:20 in suspensions yielding opaque coatings, and 1:60 for those giving transparent coatings. The latter bath will have a typical density of 1.018 g/ml and a specific electrical conductivity of 10,000 $\mu S.cm^{-1}$, while baths giving opaque coatings will have a density of 1.033-1.060and a conductivity of about 6000 $\mu S.cm^{-1}$ when suitable for application to aluminium basis materials.

The deposition voltage may lie between 30 and 120 V and the optimum temperature is between 15 and 35°C. The initial anode current density is from 1 to 8 A/dm^2, falling rapidly to as low as one tenth of this in only 2-10 seconds. The total deposition time is 5-120 seconds and generally is less than 45 seconds.

One characteristic of the process is that for set deposition conditions the anodic current will fall very abruptly when a particular film thickness has been applied. This thickness, which can therefore be predetermined, is attributed by Winkler to a Joule heating effect which sinters the particles of the thermoplastics materials. Pretreatments can include degreasing, etching in alkaline or acid solutions and also anodizing in sulphuric acid for 1-5 minutes at 18-21"C.

After electrocoating, the work is rinsed in deionized water and stoved at 160-200°C for 3-10 minutes at the appropriate temperature. The thickness of coating is generally from 2-25 μm (0.08-1 mil) but can be made thicker.

The specific advantages claimed for the Epla process are very short deposition times and stoving cycles, and in comparison with electrodeposited lacquers (see Table 14-6), there are better throwing power, lower voltages, no low boiling point solvents so that steady conditions can be maintained with less fire hazard, and no polymerisation reactions in the bath. The process has been used for hot water radiators, curtain rails, curtain walling and decorative components.

4. PAINT CURING SYSTEMS

Most of the paint systems described are normally heat cured and a conventional oven is used. With conveyor-type extrusion painting lines, the sections may pass between banks of infra-red heaters, or hot air ovens may be used. Ovens are designed to cope with the maximum throughput of the line, with some degree of flexibility in the speed of the conveyor and in oven temperature. Ovens have warm-up, main curing and exit zones, all of which need to be monitored, to make sure that they are achieving the correct temperature or temperature gradients. Heavy sections or thick components such as castings will require more heat input to get them up to temperature, so it may be necessary to slow the line down when curing such components. It should be remembered that it takes twice the amount of heat to raise aluminium through 100°C compared with steel, which means that the oven requires a higher heat input or a slower line speed. Continuous strip painting lines have complex oven systems, which include a fume incinerator and a heat recovery system. Both a drying and a curing section are usually included, with the drying section slowly raising the temperature of the strip to prevent solvent boiling in the coating, and hence damaging it. Modern paint lines use flotation ovens constructed with individual zones which are each independent in terms of temperature and atmospheric composition. High circulation volumes are used to give good temperature control, and close control of the solvent level in the drying oven is maintained. Excess solvent is fed to the incinerator and burnt there to provide heat for the ovens. Alternative emission control options have been described by Carthew.[76]

Whilst heat curing presents the normal method of curing, special types of organic coating are also cured by ultraviolet radiation or by electron beams. These systems are of greatest interest in the packaging and canning industries, where very fast curing systems are often required. Phillips[77] has reported work on reflector materials for U.V. curing systems and Levinson[78] has described electron beam curing. The latter paper compares both electron beam and U.V. curing with normal oven curing, and a summary of the relative merits and problems is shown in Table 14-7.[78]

TABLE 14-6

Basic differences between anodic coatings of plastic and electro-dip lacquering[74]

Points compared	*Epla anodic coating*	*Electro-dip lacquering*
Bath dispersion	Suspension of fine solid plastics particles. No content of low boiling point solvents.	Solution or emulsion of dissolved or drop-form polymer in water, with compound of low-boiling point organic solvents.
Type of polymei	Fully-cured thermoplastics based on polystyrene co-polymer or polyacrylate with, if desired, additions of PTFE, polyethylene or polyamide.	Polycondensates of poly-adducts with polymerization process not completed which, under influence of heat. undergo adequate cross-linkage.
Charge on polymer	Anodic due to co-polymerized and adsorbed anion-active emulsifiers.	Anodic due to dissociation of hydrophilic polymer groups, Brownian motion and adsorbed anions.
pH value of dispersion	7-10, preferably 9. Suspension and deposition process are non-sensitive to variations within this range.	6-11. pH value of solution or emulsion must be held constant within a maximum of ±0.5 pH unit of the optimum pH value for the given polymer system.
Specific electrical conductivity of the dispersion (at 20°C)	5000-12,000 $\mu S.cm^{-1}$	400-5000 $\mu S.cm^{-1}$
Deposition potential	30-120 V	Usually 90-500 V
Initial anode current density	1-8 A/dm^2	0.1-2.5 A/dm^2
Coating time	2-120 sec, usually not above 45 seconds.	30-200 seconds
Coating thickness	Usually 2-25 µm under certain circumstances	5-40 µm.

In Australia a novel curing system called 'Vapocure' has been developed.[79] This system is described as an energyless, non-polluting process for the drying of paint, printing inks and coatings. It works, in conjunction with specially formulated urethane paints, by introducing molecules of a specific catalyst into the turbulent air stream in the curing booth. This reduces the energy threshold needed for the curing reaction to take place and curing is effected in a few minutes at room temperature.

TABLE 14-7

Process comparison of curing methods[78]

	Electrocure	*U.V.*	*Oven*
Capital cost	High	Low	Medium
Curing equipment length (ft.)	10-30	10-30	90-300
On-off operation	Yes	Yes	No
Inert atmosphere	Yes	No	No
Cure temperature °F	Ambient	100-120	130+
Cure time	1 sec or less	Seconds	Minutes
Cure pigmented coatings	Yes	No	Yes
Catalyst required	No	Yes	Sometimes
Coating solids (volume %)	90-100	90-100	20-65
Coating coverage sq ft/mil dry	1000-1400	1000-1400	400-500
Coating cost	High	High	Low
Cost/mil sq ft	Low-medium	Low	Medium
Hazards	X-rays	U.V.	Explosion
Operating energy requirements (relative)	1	10	100

5. PRE-PAINTED ALUMINIUM STRIP

Pre-painted strip is now produced on large volume lines for many different applications. In the U.S.A., and increasingly in European countries, such strip has become available with a large variety of coatings including alkyd, acrylic, vinyl, epoxy, epoxy-phenolic, polyester, silicone polyester, polyvinyl fluoride and polyvinylidene fluoride type finishes. Painted aluminium strip is used for caravans, residential and industrial sidings, awnings, garage doors and wall

panels; thermosetting acrylic finishes, which have good durability and will withstand forming operations well, are considered one of the most suitable for these purposes. Plastic coated strip is also available and includes P.V.C. laminated material, which is coated with thermosetting adhesives and has established itself in the aircraft, furniture and other industries. Polyvinyl fluoride is similarly applied and is mainly used for architectural applications, as are the conventionally applied polyvinylidene fluoride coatings which are generally considered the most durable in exterior applications.

Continuous strip painting lines are now large, complicated and expensive installations. They operate at high speeds and are very versatile in the types and forms of coating that they can apply. A typical paint line of this type is installed at Alcan Aluminiumwerke: Goettingen and has been described by Limbach[80] and by Tolke (Fig. 14-12).[81] This line is designed to process aluminium strip 800-1650 mm wide and 0.2-2.0 mm thick at line speeds up to 200 m/min. The overall length of the line is about 200 m and the threaded strip is some 600 m long. The line is shown diagrammatically in Fig. 14-12 and includes decoilers, a strip joining unit, a tension leveler, entry and exit accumulators, a wet pretreatment section, coaters for primers and topcoats, a laminator, primer and topcoat ovens and recoilers. The pretreatment section includes spray degreasing and then either spray application of a conversion coating or roll-coat application of a no-rinse type coating. A general view of the entry section of the line is shown in Fig. 14-13, and the coater house with primer and topcoat coating units is shown in Fig. 14-14. The hot section of the line **has** ovens for drying and curing the coatings and is shown in Fig. 14-15. This section includes a fume incinerator and a heat recovery system, and these are balanced so that the energy requirements of the drying zones and the incinerator are matched to the total quantity of solvent extracted from the coating. Essential stoving requirements[''] are that:

1. The rise in temperature in the drying section must be sufficiently gradual to prevent solvent boil in the coating.

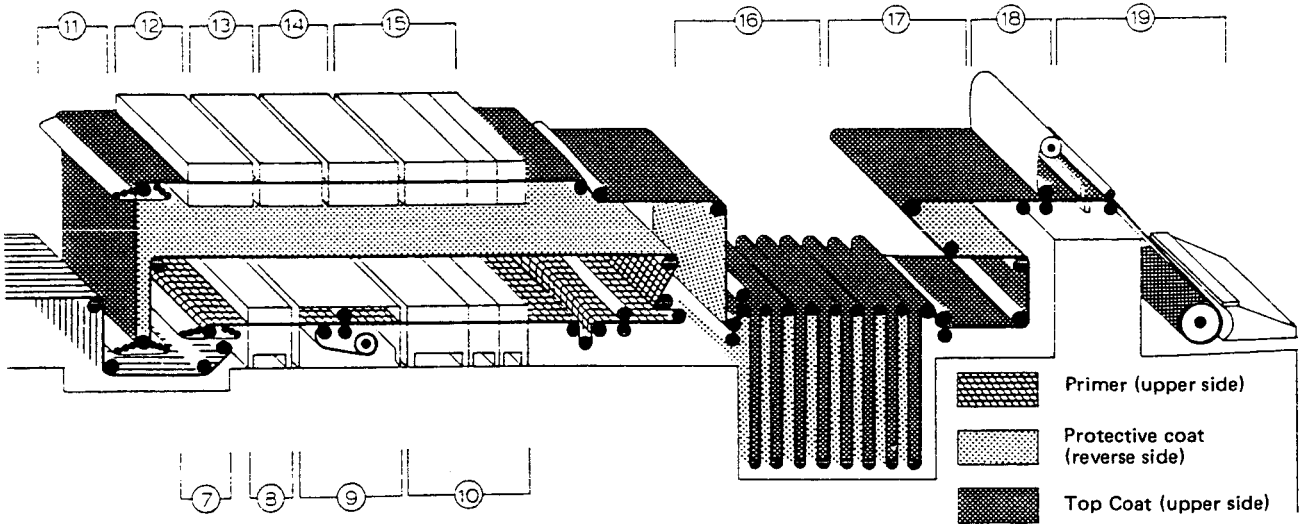
2. The rise in temperature in the curing section must be sufficiently gradual to prevent distortion of the strip.

3. A specific peak metal temperature must be reached for satisfactory curing of the coating.

4. Temperature differences across the strip width must be minimal (3°C) to avoid coating colour variations or impairment of strip flatness.

The requirements are best met using flotation ovens which can be controlled.

1 Uncoilers with strip joiner
2 Tension leveller
3 Entry accumulator
4 Degreasing
5 Pretreatment
6 Identity coding unit



7 Prime coater
8 Primer oven
9 Laminator for decorative film etc.
10 Primer cooling
11 Top coaters

12 Top coat oven
13 Precooling oven
14 Spare zone
15 Top coat cooling
16 Exit accumulator
17 Inspection zone
18 Laminator for prot[illegible]
19 Recoilers

Fig. 14-12. Layout of [illegible] int line

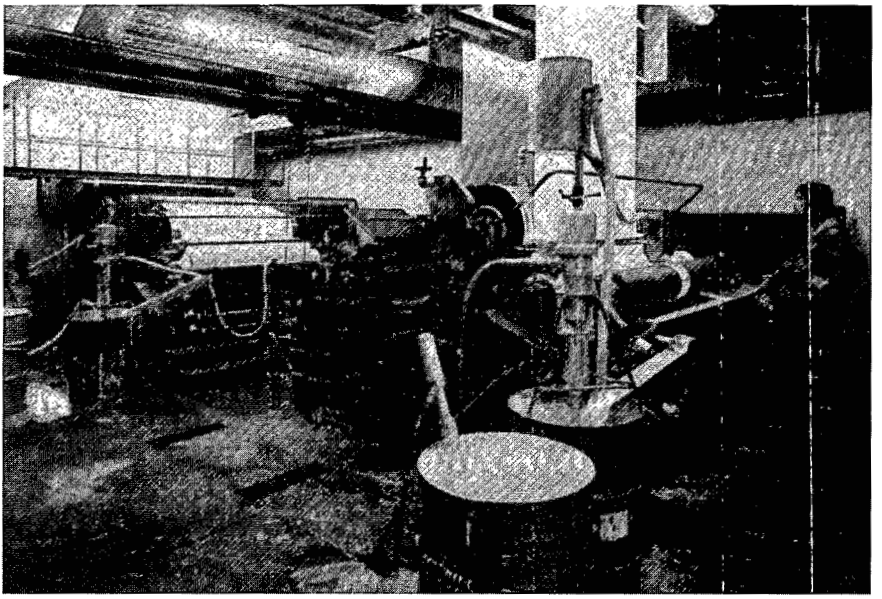


Fig. 14-13. General view of the entry area of the Alcan Aluminiumwerke paint line

Fig. 14-14. Coater house on the Alcan Aluminiumwerke paint line

Fig. 14-15. Drying and stoving sections of the Alcan Aluminiumwerke paint line

An indication of the capacity of such a line is given by Tölke,[81] who quotes the potential production as 36 million m^2/year or 39,000 tonnes of 1500 mm x 0.4 mm aluminium strip.

A similar type of line taking strip up to 1524 mm wide has been installed by Euromax[82] and is claimed to have high versatility. Use of quick-change coaters means that a colour or material change can be made without slowing the strip and with minimum wastage of material.

Many other such lines have been described[83,84,85,86,87,88,89] including the installation of Cégédur at Issoire[85] which applies paint to anodized strip; the large 135 ft (41 m) coil coating line of Kaiser[86] at Scarborough, Ontario, which coats 18 inch (46 cm) wide strip at 120 ft/minute (36.6 m/min); the coil coating line of Freuhof Corporation[87] at Alabama used for aluminium truck bodies; and the large coating line at Jackson, Tennessee, of Consolidated Aluminum Corporation[88,89] operating at a speed of 200 ft/minute (61 m/min) and which can turn out 75,000 ft^2/h (7,000 m^2/h) of painted strip. More recent lines in the U.S.A. reflect the need for flexibility, both in terms of coil size and metal, and many operate with both steel and aluminium.[90] Fast coil changeover and fast colour change are other important considerations.

Most of the lines described are generally capable of roll or spray coating both primers and topcoats, but a line described by Baker[91] at Kaiser Aluminum: Toledo is unique in coating the primer electrophoretically. The prime reason for using the electrocoat system in the Kaiser line seems to have been the necessity of converting a single coat line into a 2-coat system within the space already available. An anodic electrocoat system, similar to that used for painting extrusions, is employed. Contact to the strip is made via a polished, chromium plated contact roll and stainless steel cathodes are used in the vertical electropaint tank. The applied voltage is between 50 and 150 volts and the treatment time is 2-6 seconds. A thin (2.5-5 μm) primer coating is applied, and this has been found suitable for a range of topcoats, particularly for the siding and architectural markets. In quite a different direction Schultz has described an experimental line at Alcoa[92] which is used for the development of coil coating processes. It incorporates the possibilities of cleaning, brightening, electropolishing, conversion coating and anodizing with spraying, electrocoating, roll-coating or powder coating.

Moves in the U.S.A. and other countries to increasingly limit solvent emissions from paint lines have forced consideration of paints with reduced solvent contents. Waterborne coatings have received much consideration and are now widely used particularly in North America. Early water-based formulations suffered from poor flow, tended to foam, dried too fast, did not have good adhesion to metal, and were susceptible to water absorption and softening when exposed to the atmosphere.[93] However these problems have been overcome by appropriate formulation, and 2-coat systems which are considered to have equivalent performance to 2-coat solvent-based paints are available. These systems are not solvent free, as up to 20% solvent may be present as rheology modifiers, coalescing agents, etc., but in some cases they enable a line to be operated without solvent incineration. With the lower solvent content, the amounts of make-up air brought into the oven can be reduced, as this volume is dictated by the volume required to remove the solvent expelled from the coating. Heating this make-up air is very expensive and the use of water-based coatings can reduce the energy required to $^1/_3$rd of that used for solvent-based systems.[93] The lower curing temperature of the water-based coatings is also claimed to give significant savings.[94]

Another approach to solvent reduction and energy saving is the use of paints with a high solids content, and the type of coater developed by Alcan[51] makes application of such coatings on coil lines easier. The principles of high solids coatings have been described by Miller,[95] who points out that they are similar to solvent based coatings but using resins of lower molecular weight, and this has effects on factors such as viscosity, flow, volatility and reactivity. Both water-based[96] and high solids paints[97] are also applied in the extrusion finishing field, and Bertsch and Powers[98] have calculated the relative energy costs for applying a range of water-based and high solids coatings in comparison with a solvent-based acrylic. These are shown in Table 14-8. They conclude that significant energy savings can be made with most water-based and high solids coatings, particularly by the use of low temperature curing systems, but other factors such as anti-pollution requirements must also be taken into account.

TABLE 14-8

Energy costs[98]

Coating		*Cost of gas $/hr* *	*cost of electricity $/hr* **	*Total cost $/hr*
Acrylic		3.24	1.52	4.76
Ultra-high-solids polyester (95%)	**(Hi-bake)**	2.07	1.50	3.57
	(Lo **bake)**	1.21	1.50	2.71
High-solids polyester (80%)	**(Hi bake)**	2.20	1.50	3.70
	(Lo **bake)**	1.29	1.50	2.79
Medium-solids polyester	**(Hi bake)**	2.47	1.50	3.97
	(Lo **bake)**	1.39	1.50	2.89
High-solids urethane		0.76	1.49	2.25
Medium-solids **urethane**	(Hi **bake)**	1.60	1.50	3.10
	(Lo **bake)**	1.61	1.50	2.17
Epoxy powder	**(Hi bake)**	1.86	1.50	3.36
	(Lo **bake)**	1.39	1.50	2.89
Polyester powder	(Hi **bake)**	2.02	1.50	3.52
	(Lo **bake)**	1.73	1.50	3.23
80 20 **waterborne**	**(Hi exhaust)**	2.31	1.53	3.90
	(Lo **exhaust)**	2.00	1.53	3.53
80 20 **'catalyzed' waterborne**	**(Hi exhaust)**	1.04	1.51	2.55
	(Lo **exhaust)**	0.84	1.51	2.35
Electrodeposition waterborne	(Hi **bake)**	1.93	1.49	3.42
	(Lo **bake)**	1.38	1.49	2.87

* **Based on natural** gas **at** $1.50 1,000 ft^3

** **Based** on 50.04 kW hr.

A recent European Coil Coating Association Congress[99] reported that, in 1998, over 2 million m^2 of coil coated aluminium were produced, with 71% going to the building industry and 13% to the automotive industry. Volumes in the USA are also very high, so coil coating of aluminium represents an important field.

6. PAINT STRIPPING

As with all finishes, problems can arise during the application or cure of the paints, and methods of removal of the paint and reprocessing of the part may be necessary. In some industries, such as the aircraft industry, abrasive methods may be used, but wet-sprayed or powder coated extrusions present a particular problem.

The standard way in the past of removing paint from such sections was to immerse them in a methylene chloride solution, but the fire and health and safety hazards of this material have caused other solutions to be investigated. Hot alkaline stripping solutions, based on sodium hydroxide, have also been used, and Gammage[100] describes a rotary stripping system that simplifies and speeds up this and other immersion processes. The aluminium extrusions are carried from tank to tank in the rotary device, and it is placed in each stripping solution and rotated. The working action created by the system as it rotates is said to speed **up** the stripping process, allowing a full load to be stripped in about 20 minutes. This system also reduces the problems of waste paint build-up at the bottom of the tank, which can impede effective stripping in **a** dip system.

This apparatus is also said to work well with the low temperature, methylene chloride free paint strippers that have been developed, and the operation of one such solution is described by Pulido.[101] She looked at both aluminium and steel substrates and, with aluminium, compared the new stripper with hot alkaline and methylene chloride systems, with the benefits shown in Table 14-9.

TABLE 14-9

Time required for complete stripping of 75 micron (3 mil) coatings of powder paint on an aluminium substrate

Stripper	*Temp* °C	*Stripping Time*			
		Polyester	*Hybrid*	*Polyurethane*	*Epoxy*
Hot alkaline	60	1 hr	approx. 1 hr	1.5 hr	approx. 4 hr
Hot alkaline	70	–	–	–	1.5 hr
Methylene chloride	Room	1.5 hr	approx. 1 hr	approx. 3 hr	approx. 4 hr
New stripper	60	15 min	10 min	5 min	15 min
New stripper	70	6 min	5 min	3 min	6 min

This system is a two-phase one involving both solvent action and alkalinity, and it is clearly effective. It needs to be circulated to involve the action of both phases, and the greater the circulation the shorter the stripping times.

Much work is being carried out on this sort of development, but stripping is always a messy operation and is best avoided, wherever possible, by producing the finish correctly the first time round.

Paint stripping in the aircraft industry has been discussed by Hans,[102] and again the trend has been to avoid methylene chloride and move to less toxic chemicals. The products used are based on benzyl alcohol which has very low toxicity. Both acid and alkaline activated systems have been used, but all take significantly longer for the stripping process than methylene chloride.

7. PRIMERS

Much of the earlier discussion in this Chapter has been concerned with application of organic coatings to aluminium under factory conditions. but site painting of aluminium is also required, for example in structural applications, and specially formulated primers are usually used.

The application of a first or primer coat is essential for all structural aluminium except that to be used under only mildly corrosive conditions. The primer is a bonding coat and its main properties are good adhesion and flexibility. It invariably contains metallic inhibitive pigments. The most common vehicles used for primers on aluminium were oil-modified alkyd resins, vinyl resins, and/or phenolic resins, but over the years the primers have followed the same sort of development as the finishing coats, and high performance primers now include such resins as epoxy-polyamides, polysulphides, urethanes and acrylics.

Pigments

Zinc chromate is by far the most popular pigment. For less severe conditions, red iron oxide may be employed, while strontium, barium and calcium chromates are also useful in admixture with zinc chromate. Other compounds which have been used include zinc tetroxychromate $ZnCrO_4 \cdot 4Zn(OH)_2$, ferrous ammonium phosphate, aluminium powder, zinc oxide and titanium dioxide. Lead-containing pigments must not be used on aluminium as they accelerate the appearance of pitting corrosion, probably due to the reduction of the pigment to metallic lead with resulting electrolytic action in the presence of moisture.

Although going back many years an important contribution to our knowledge of the relative merits of primers on light alloys was the series of corrosion tests carried out by Rigg and Skerrey at the British Aluminium Co. Ltd.[103] These authors applied four pigments, zinc chromate, zinc tetroxychromate, iron oxide and red lead, in a phenolic-linseed stand oil-oiticica oil varnish medium to panels of aluminium and Al-Cu-Mg-Mn alloy as well as to three magnesium alloys and steel, and exposed the panels to marine, industrial, urban and rural atmospheres. The results after 3½ years are given in Tables 14-lo and 14-1 1.

In marine atmospheres, red lead coatings suffered by chalking and erosion, while if covered with a top coat the paint film as a whole tended to crumble. Corrosion was marked on aluminium and magnesium. Iron oxide primers on the other hand maintained their colour, though they too suffered from chalking. The latter was here prevented, however, by a top coat. The magnesium alloys were not protected to the same extent as aluminium. As expected, both the zinc chromates gave rather more protection to all the light metals. Of the two, the tetroxychromate suffered more from erosion in the absence of a top coat, and seemed less satisfactory on the less corrosion-resistant alloys.

The results quoted show that the oil-base top coat to D.T.D.260A gave better adhesion than the cellulose medium to D.T.D.63A which suffered from erosion, though all the panels showed flaking between the primer and the top coat.

TABLE 14-10

Protective value of various primer and top coat systems on aluminium and steel[103]

Corrosive environment:		*Marine (Dungeness)*			*Accelerated tests*			*Industrial (Widnes)*			Rural *(Frodsham)*		
Paint system:		Al (99.5%)	B.S. L70	Steel	Al (99.5%)	B.S. L70	Steel	Al (995%)	B.S. L70	Steel	Al (99.5%)	B.S. L70	Steel
Primer	Top coat	*Approximate time required for panels to suffer slight corrosion (years)*											
Zinc chromate	–	3%	3½	½	3½	3%	½	3%	3%	½	3%	3%	½
Zinc chromate	DTD63A	3%	3½	1%	3%	3%	1½	3%	3%	1½	3%	3%	2
Zinc chromate	DTD260A	3%	3½	2	3%	3½	1½	3½	3%	1½	3%	3½	3%
Zinc tetroxy chromate	–	3%	3%	½	3½	3%	½	3%	3	1	3%	3%	1%
Zinc tetroxy chromate	DTD63A	3%	3½	1½	3%	3½	½	3½	3	1	3%	3%	1%
Zinc tetroxy chromate	DTD260A	3%	3%	1%	3%	3½	1½	3%	3%	1½	3%	3%	3%
Red lead	–	¼	¼	½	¼	¼	½	2	½	¼	1	½	½
Red lead	DTD63A	1	1	1%	1	½	1	2%	2%	1	3%	3%	1%
Red lead	DTD260A	1	1	1%	1	½	1½	3%	3%	1	3%	3%	3%
Iron oxide	–	3%	3%	¼	3%	2%	½	3	1½	¼	3%	3½	½
Iron oxide	DTD63A	3%	3%	1	3%	2%	1	3%	3%	1	3%	3%	1½
Iron oxide	DTD260A	3%	3%	1	3%	2%	1	3½	3½	1	3½	3%	2½
Plain metal, untreated		1%	½	¼	½	1	¼	1	1	¼	1%	½	¼
Plain metal, chromated or **pickled**		1%	½	¼	1%	1	¼	1	1	¼	1½	½	¼

TABLE 14-11

Summery of results for Dungeness (marine tests)

Specimens: Aluminium (99.5%) and B.S. L70 (Al-Cu-Mg-Mn) 3%-years' exposure[103]

Paint System		*Main Paint Failures and Corrosion on*	
Primer	*Top* ***Coat***	***Aluminium***	***B.S.*** *L70*
Zinc chromate	–	Trace of flaking	Trace of flaking
Zinc chromate	DTD63A	Slight flaking	Moderate flaking, slight pitting and trace of corrosion at scratch, very slight local corrosion
Zinc chromate	DTD260A	Very slight flaking	Moderate flaking
Zinc tetroxy chromate	–	Moderate erosion	Slight erosion and trace of pitting
Zinc tetroxy chromate	DTD63A	Slight flaking	Slight flaking
Zinc tetroxy chromate	DTD260A	Very slight flaking	Considerable flaking
Red lead	–	Considerable chalking, moderate local corrosion, moderate pitting, and corrosion at scratch	Considerable chalking, considerable local corrosion, moderate pitting and severe corrosion at scratch
Red lead	DTD63A	Trace of crumbling, moderate local corrosion, moderate pitting, considerable corrosion **at** scratch	Trace of crumbling, considerable local corrosion, moderate pitting, very severe corrosion at scratch
Red lead	DTD260A	Trace of crumbling, slight local corrosion, moderate pitting and considerable corrosion at scratch	Trace of crumbling, considerable local corrosion, moderate pitting, very severe corrosion at scratch
Iron oxide	–	Slight chalking, very slight local corrosion, and very slight corrosion at scratch	Moderate chalking, slight local corrosion, trace of pitting, and very slight corrosion at scratch
Iron oxide	DTD63A	Slight flaking, very slight local corrosion, and very slight corrosion at scratch	Considerable flaking, slight local corrosion, trace of pitting. and very **slight** corrosion at scratch
Iron oxide	DTD260A	Slight flaking, very slight local corrosion and trace of corrosion at scratch	Considerable flaking, very slight local corrosion, trace of pitting, and very slight corrosion at scratch
Plain (untreated) metal	–	Slight to moderate general corrosion and trace of pitting	Moderate general corrosion and trace of pitting
Plain metal (chromated or pickled)	–	Slight to moderate general corrosion and trace of pitting	Moderate general corrosion and trace of pitting

The results were on the whole similar for industrial exposure, though the time until failure occurred was markedly extended. As long as the top coating was adequately maintained, lead primers did not increase the corrosion rate on aluminium, but these panels were inferior to any of the three others.

The colour and gloss of red iron oxide primers were maintained for 12 months and the rate of attack on the aluminium was retarded as long as the coating was undamaged. Again, however, the two zinc chromates were markedly superior and gave good protection to the light alloys for three years in the absence of a finishing coat. After this time, the zinc tetroxychromate failed by erosion, though the primer continued to inhibit corrosion for a further six months. Little difference was observed between the two chromates under top coatings, and though there was a tendency to flaking, both gave good results. Again, flaking took place above the primer, and was least in the case of the oil media.

Results in rural exposures followed the same general pattern, though the general corrosion rate was reduced. Here, however, iron oxide and a top coat gave excellent protection to aluminium, though flaking was in evidence on the magnesium. Zinc chromate again was the best, zinc tetroxychromate was a little inferior, as it failed by erosion after three years. There was no sign of corrosion, however.

The results of exposure after 10 years confirmed the earlier findings, some of the paint systems based on zinc chromate or zinc tetroxychroinate primers requiring only cleaning. Iron oxide primers appeared suitable for rural sites while red lead-based primers were again unsatisfactory. The chromate primers also proved very satisfactory on mixed assemblies of aluminium and steel. Of the top coats, the oil-base material to D.T.D.260A proved more satisfactory than the cellulose medium (D.T.D.63A).

More recent work for the American Navy[104] has looked at a range of corrosion inhibitors in alkyd and epoxy based primers. Mechanistic studies suggested that incorporation of either phosphate or silicate into a chromate containing primer could result in improved corrosion resistance, and best results were obtained with a cadmium phosphate chromate salt with an empirical formula of $6CdO \cdot 4CrO_3 \cdot 2P_20_5 \cdot K_2O$. The feasibility of using organic materials as inhibitive pigments was also investigated, and those capable of forming insoluble aluminium compounds, such as alizarin, were found to be the most promising.

As in other areas of pretreatment development, the pressure to use chromate-free systems has increased, and Foster *et al.*,[105] in Canada, have developed chromate-free primers for use in Canadian military applications. The currently approved chromate-containing primer is covered by Canadian General Standard Board specification 1-GP-132, and the formulation of this primer is shown in Table 14-12. The special features of this primer are a short drying time and high gasoline resistance, and it was formulated specifically for aluminium.

TABLE 14-12

GP-132 Formulation

Ingredient	*Weight(%)*
Part 1	
Zinc chromate	28.09
Magnesium silicate	4.08
Alkyd resin, 60% solids	6.84 *
Maleic anhydride	0.10
Aluminum stearate gel	3.72
Xylene	14.38
Part 2	
Xylene	4.12
Alkyd resin, 60% solids	28.37
UCAR CKU 2266, 50% solids	8.98
Lead drier	0.40
Cobalt drier	0.10
Antiskinning agent	0.10
Total	100.00

(*) Aroplaz 1365-X (NL Industries) or equivalent

The new primers had to retain these properties, and two successful formulations are reported, one based on an oil-modified alkyd with an oil modified, highly heat-polymerised phenol-aldehyde resin dispersion, and the other on a short oil and a medium oil alkyd mixture. The anti-corrosion pigment used was a mixture of phosphate and borate (40:60) and the pigment mix is shown below:–

Anti-corrosion pigment	26.70% (vol)
Yellow iron oxide	25.34
Magnesium silicate	21.74
Barium sulphate	9.11
Titanium dioxide	17.11

The final resin and pigment formulation is shown in Table 14-13.

TABLE 14-13

Detail wt% formulation for chromate-free primer

Ingredient	*Formula* A	*Formula B*
Pigment mix	37.91	38.45
Beckosol 12079 (50%)	39.91	–
Beckosol 12006 (50%)	–	16.58
Beckosol AA 200 (60%)	–	13.82
Paraplex RG-10 (100%)	1.79	–
CKU 2266	–	7.34
Bentone SD-1[a]	0.39	0.79
Lead drier	0.311	0.316
Cobalt drier	0.079	0.079
Xylene	17.13	20.14
n-Butanol	2.10	2.13
Duomeen TDO[b]	0.23	0.24
Exkin #2[c]	0.12	0.12

(a) NL Chemicals Ltd.

(b) Armak Chemicals Ltd.

(c) Nuodex Canada Ltd.

Effect of alloy composition

Table 14-10 summarizes the results obtained by Rigg and Skerrey[103] in tests on various combinations of primer and top coat on aluminium and the Duralumin-type alloy B.S. L70, and shows, incidentally, that the influence of alloy composition, which was considerable, particularly in marine and rural exposure on the unpainted metal, was for the most part completely masked by the application of any of the finishing coats. Alloy composition, however, begins to affect the corrosion properties markedly once the paint coating is penetrated, as is seen from Table 14-11. Table 14-14 shows results obtained by Edwards[106] on alloys of different composition and structure tested after the application of an oil-modified glyptal composition to which a little melamine-formaldehyde resin had been added. The results were obtained on panels which had been deformed by producing a dome 1.25 and 2.5 mm (0.05 or 0.1 inch) in depth, and scratched to remove the varnish, in order to simulate penetration of the coating. (Table 14-15).

TABLE 14-14

Salt spray corrosion tests on painted aluminium[106]

Specimen		*Loss* in *weight (8 weeks salt spray)* (g/ft^2)	(mg/dm^2)	*Spread of corrosion from domes* (mm)	*Spread of corrosion from scratch* (mm)	*General appearance*
A	NS3-0 (3103)	–	–	3	14	Corrosion in streaks following rolling marks; no heavy deposit of corrosion product
B	NS3-H4 (3103)	–	–	Nil	Nil	Good
C	4% Cu, 2% Mg	–	–	Nil	Trace	Good
D	NS4-H3 (5251)	–	–	Nil	Trace	Good
E	NS5-0 (5154A)	–	–	Trace	Trace	Good
F	NS5-H2 (5154A)	–	–	Nil	Trace	Good
G	HS30-M (6082)	0.005	0.54	Nil	Nil	Good
H	HS30-TB (6082)	–	–	Nil	Nil	Good
J	HS30-TF (6082)	0.005	0.54	Trace	8	Corrosion not severe and confined to a few areas near points of damage
K	AA7178-TB*	0.100	10.8	Trace	10	Corrosion deposit fairly heavy, but almost entirely originating at damaged points
L	DTD683-TF	0.355	38.2	4	4	As for K
M	HS15-TB (2014A)	0.235	25.3	Trace	Trace	Generally good, but a few isolated nodules of corrosion product
N	HC15-TF† (2014A)	0.120	12.9	13	9	Corrosion heavy, confined to areas near points of damage
Q (steel)	Bright mild steel	7.185	773	10	8	Severe rusting spreading from scratch and edges, also many isolated rust spots
R	HS15-TF (2014A)	0.485	52.2	Trace	Trace	Small nodular corrosion points, some of which do not originate at damaged points
S	AA7178-TF	0.705	75.9	3	7	Fairly heavy corrosion deposit, but almost entirely originating at damaged points

* With 0.95% Cr. † Clad specimens

In exposing a variety of bare and painted aluminium alloys in a chemical factory, Clark"" found that while an alloy containing 4% copper behaved the worst, others, including aluminium-magnesium, aluminium-magnesium-silicon and aluminium-manganese alloys, were in general indistinguishable from 99.5% aluminium with respect to corrosion resistance. Zinc chromate in linseed oil proved the best primer while top coats had relatively little effect on the life of the system. Pretreatments, such as anodizing and chromate treatment, improved the corrosion resistance almost equally. Under the same conditions, the under side of aluminium sheet members underwent much more severe attack than the upper surface.

TABLE 14-15

Adhesion tests of exposed specimens (see Table 14-14)[106]

Good, no cracking, no flaking	*Fair, cracking but no flaking*	*Poor, both flaking and cracking*
B	A	F
C	D	G
M	E	K
N	H	L
P	J	R
Q (steel)	–	S

Etch primers

A type of primer that is now universally popular is the etch (or wash) primer, based mainly on oil-free synthetic thermosetting resins of, e.g., the vinyl-butyral or ethoxyline type.[108] These contain phosphoric acid and are very suitable for light alloys. Before applying these coatings, vapour degreasing is usually sufficient.

The function of etch primers[109] is to eliminate the need for pretreatment of the aluminium, and their widest use is probably in the light engineering industries. They arc extensively used on electrical equipment, telephone and radio components, instruments, scales, etc. They are usually 'universal' in that they can be used on aluminium as well as on zinc, brass and ferrous metals, and although individual etch primers may vary greatly in their applicability to other metals, the majority will give good results on aluminium and its alloys.

Mazia[110] has summarised a range of U.S. primers covered by general government (G.S.A.) and military specifications as follows:–

TT-P-1757 Primer Coating, Zinc Chromate, Low Moisture Sensitivity – resin-modified, medium-oil phthalic alkyd.

TT-P-618 Primer, Zinc Chromate in Styrene-Butadiene Resin Carrier – very fast drying.

TT-P-645 Primer, Paint, Zinc Chromate – an alkyd resin system often used without topcoats, as a protection during shipping.

MIL-P-15930 Primer, Vinyl-Zinc Chromate – used specifically for total vinyl systems.

High performance primers used on military aircraft under aliphatic polyurethane topcoats"' are:–

MIL-P-23377 Primer Coating, Epoxy-Polyamide, Chemical and Solvent Resistant, with Strontium Chromate Inhibitive Figment.

MIL-P-87112 (USAF) Primer Coating, Elastomeric, Polysulphide, Corrosion Inhibiting, Strontium Chromate Inhibited.

Clearly these specifications cover a range of chromated primers from inexpensive alkyds to high-performance epoxy-polyamides and polysulphides.

Two-pack primers

A typical primer of the formulation known as the WP-I type is shown in Table 14-16.

TABLE 14-16

Farmulation of typical two-pack primer[112]

Base grind	*% (wt)*	
Vinylite resin (XYHL)	*1.2*	
Basic zinc chromate	6.9	
Talc	1.1	
Isopropyl alcohol (99%) or ethyl alcohol (95%)	48.7	
Butyl alcohol	16.1	
		80.0%
Acid diluent		
Phosphoric acid	3.6	
Water	3.2	
Isopropyl alcohol or ethyl alcohol	13.2	
		20.0%

Most etch primers have a similar formulation, though the resins used may vary. The disadvantage of the two pack primers (or reactive-type) is that they must be mixed immediately before application. They are mainly sprayed but may also be applied by dipping and are usually stoved at temperatures varying from 177-316°C, when the metal reacts with the phosphoric acid.

One important advantage of etch primers is that they are very suitable for on-site spraying, particularly in marine applications where they have given good results[106,113] because, as distinct from other paint systems, American work tends to show that such primers can be applied during damp conditions. It may perhaps be commented, however that British trials have not been quite so successful.

For this **type** of work the following composition has been patented.[114]

phosphoric acid (85%)	2.24 pt (wt)
polyvinyl alcohol	8.96
zinc tetroxychromate	8.54
silica	1.42
carbon black	0.08
butyl alcohol	102.24

After application of this coating, a further coating of the same composition, but without the phosphoric acid, is applied.

American military specification MIL-P-15328 covers a two-part primer of this type, with one component being the polyvinyl-butyral resin, pigmented with tetroxychromate, and the other being an alcoholic solution of ortho-phosphoric acid.

One-pack primers

This type of etch primer is also known as the 'reacted stable' primer. The main difference in formulation is that the zinc chromate is replaced by chromic acid. As the primer need not be specially mixed before each application it is easier and rather cheaper in use, but the adhesion and protective values are not as high as are those of the two-pack WP-1 type.

A typical composition for a one-pack primer is:[112]

chromic acid solution (33%)	1.40% (wt)
polyvinyl butyral	10.95
10% phosphoric acid (85%) in acetone	10.95
ethyl alcohol (95%)	62.20
butyl alcohol	14.50

In making up this primer, the chromic acid and acetone-phosphoric acid solution are first stirred together and poured with stirring into a solution of the

resin in the ethyl alcohol which has been warmed to 45°C. After 20 minutes the butyl alcohol is added. Again a one-pack wash primer of this type is covered by an American military specification (MIL-C-85 14).

Factors affecting etch primers

Using two-pack etch primers formulated according to DEF 1408 and DTD 5555A, Walker[115] carried out tests on the effects of mixing ratio and 'pot life' on the adhesion and corrosion resistance conferred by the primer coat and complete multi-coat systems, using both L16 (5% Si, 1-1.5% Cu, 0.5% Mg) aluminium and mild steel panels. The etch primer was applied by spraying to a dry film weight of 10-17 g/m^2 (0.3-0.5 oz/yd^2) and cured for 14 days at room temperature before testing: the ratio of base to catalyst (phosphoric acid) was varied from 35:65 to 65:35.

The base:acid ratio was found to affect the degree of rusting of steel panels, the highest base content of 65% providing the best results, and although no corrosion of aluminium was observed the best coating properties were again obtained with the higher base contents; this is rather at variance with the recommendations of the standards to use a ratio of 50:50. When using a primer according to DEF 1408 there was checking, cracking and flaking of the film below 50% base, and checking at 50:50, but a good coating when the base was greater than 50%. With a primer according to DTD 5555A there was improvement up to 60:40% (base:acid) with this ratio being better than 50:50%. The DTD coating was better than the DEF 1408 coating.

In earlier initial tests Dennis and Walker[116] had shown that adhesion as measured by a pull-off test was not affected by the method of mixing the primer, the mixing ratio or the environmental humidity, but that the adhesion of a finishing coat is adversely affected if the primer is not adequately cured before the latter is applied. In later tests which took into account also the effects of weathering, Walker[115] used, as a measure of adhesion, a torque spanner test to remove from the surface a hexagonal rod bonded to it with an epoxy resin. He found that whereas in the case of steel the effect of weathering for 1 year was to impair the adhesion progressively by as much as 40%, in the case of aluminium panels there was an apparent increase in adhesion of from 1-20% according to the mixture used: this apparent increase was due to a change in the nature of failure from cohesive to adhesive. The transfer of the site of failure from the primer itself to the primer/metal interface was explained as being due to an increase in the cohesive strength of the primer in the course of weathering. However, at the high base-to-acid ratios which, as noted above, gave the best results, the primers of both types continued to exhibit cohesive failure after exposure to weather, indicating that these ratios are the optimum.

Most values obtained for the adhesive strength were in the range 200-330 bar (3-5000 p.s.i.) and there were no values below 87 bar (1300 p.s.i.). In general the effect of exposure to both natural weathering and continuous salt spray was to change the site of failure from cohesional failure in the primer layer to apparently clean adhesion failures in the substrate. Corrosion of the aluminium was not observed in these tests and there was not, therefore, any correlation of loss of adhesion with low corrosion resistance, but it was noted that the greatest incidence of failures occurred in those specimens which showed advanced checking and cracking of the paint layer, that is, those which had contained the larger amounts of the acid component.

With regard to 'pot life' after mixing of the two-pack primers, Walker recommended that this should be a maximum of 8 hours for DTD 5555A, which is a phenolic resin-modified type, and 16 hours for the DEF 1408 primer.

An important feature of primers for aluminium is a low lead content in order to ensure the best resistance to corrosion, and neither lead nor lead compounds should be present in the dried film in excess of 0.3% expressed as metallic lead content. This provision also occurred in DEF 1115A dealing with the protection of aluminium or aluminium alloys under marine conditions, and related in particular to internal protection where the primer was followed by a fire retardant coating in accordance with DEF 1114. The primer in this case consisted of a good quality resin varnish medium pigmented with zinc chromate together with suitable mineral fillers and suspending agents. The medium was a phenolic resin varnish or a phenolic alkyd mixed with linseed or tung oil, and the zinc chromate **(BS** 389) should not be less than 40% of the total amount of pigment in the paint. The lead content should be less than 0.3% of the dried film and the paint should not contain barium carbonate.

Chemistry of etch primers

The chemistry of the etch primers and their mechanism has been discussed by Rosenbloom[117] and Marsh.[118] The reactions taking place between the constituents of the etch primer appear to be complex. In the two-pack primer, the zinc tetroxychromate in the presence of phosphoric acid probably forms chromic acid which is reduced by the organic solvent present to trivalent chromium. At the same time, the phosphoric acid reacts with the polyvinyl butyral to give a chromium phosphate complex which, when attached to the polyvinyl butyl chain, forms cross linkages between the chain, or polymerizes with similar groups. An inorganic film is also believed to be formed and this may influence adhesion to some extent. The adhesion is a direct function of the phosphoric acid content and, as is seen in Fig. 14-16, the type of curve obtained is largely independent of the basis metal.

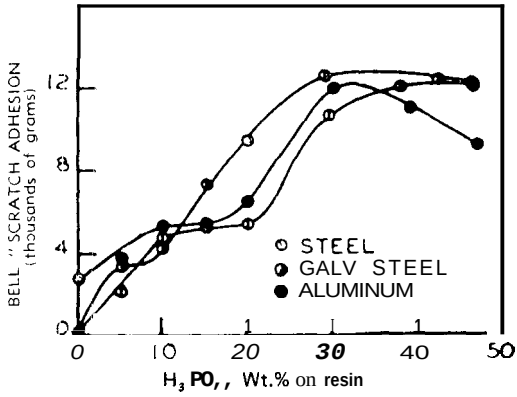


Fig. 14-16. 'Demonstrating that etch-primer adhesion increases with increasing acid content (after Rosenbloom)[117]

In the one-pack primer the reaction between the constituents takes place in the initial make-up. According to Marsh,[118] etch primers of the two-pack type have very good adhesion to bare aluminium as well as to aluminium that has been anodized or chromate pickled, while the adhesion of the single pack primer is only a little inferior. In practice, spray application is usually more economical than dip application. This is obviously the case with the two-pack primer which must usually be discarded 6-8 hours after it has been mixed.

Etch primer coatings are highly flexible, and have been bent through 180 degrees or elongated 2¼% without damage. Clear, pigmented or coloured finishes are obtainable and most finishing coatings can be applied over the self-etching primer.

More recent studies of the mechanism of chromate inhibitors in a rage of resin carriers has been reported from the U.S.A.[104] They conclude that paint failure occurs as a result of damage or weakness in the oxide film on the aluminium giving cathodic sites where hydrogen can be evolved, resulting in rapid corrosion and blistering. The effect of the chromates is to interfere with this reaction and block the cathodic sites, A buffering action takes place with zinc or cadmium chromate primers, because of hydroxide precipitation as the pH rises, but this does not take place with strontium chromate. Alkyd primers are susceptible to attack by hydroxyl ions, which are neutralised by the buffering type of pigment. This explains the fact that, while all three pigments are effective in epoxy primers, zinc and cadmium are significantly superior to strontium in alkyd primers.

Primers for adhesive bonding

Increasingly in the aircraft industry a surface may need to be prepared for adhesive bonding rather than painting, and it is in this area that the definition of

'priming' becomes much less clear, as it may be the pretreatment coating that is the 'primer' in this case. There are numerous publications on this subject, and some have been referred to in Chapter 4 (page 219) and Chapter 7 (page 515).

The field is reviewed in books such as that of Kinloch.[119] Many different pretreatments are used including chromate-containing and chromate-free conversion coatings, and chromic acid or phosphoric acid anodizing, and these processes have been described in earlier chapters. However in this field they are usually coated after pretreatment with a thin primer coating, more to preserve the pretreated surface and prevent any deterioration, than to give any additional adhesion in the bonding operation. In this regard silanes are often used as an alternative to more conventional **primers** and have been widely studied.[120,121,122,123]

An interesting application in this field is the use of primers in the repair of adhesively bonded aircraft, and this has been studied by Chabot and Brascia.[124] These tests were on 2024-T3 sheet, and two γ-glycidoxy-propyl-trimethoxy-silanes and an air-drying epoxy-phenolic were used, in comparison with a standard heat-cured expoxy primer. The adhesive used was an epoxy structural film adhesive. These workers found that none of the repair systems were equal to the phosphoric acid anodized and heat-cured epoxy primer used as a control, but, of the repair systems, the silanes provided the best combination of adhesion and durability.

Primers for architectural paint repair

One of the problems that is encountered with paint finishes on buildings is that of repair to damaged or deteriorating surfaces, and some companies have specialised in this area. One such company[125] renovates both powder coated and anodized surfaces and they use a range of primers according to the substrate and the required topcoat. Most are two-pack products, with general use of a chromate-free etch primer, and a zinc phosphate acrylic/urethane copolymer primer used specifically on anodized aluminium. Surface sanding and solvent degreasing are generally used prior to application of the primer.

8. PAINT SPECIFICATIONS

As the amount of painted aluminium increased, particularly in architectural markets, in the 1960s and 1970s, specifications covering the properties and performance of paint finishes were required. In the U.S.A. the Architectural Aluminum Manufacturers Association (AAMA) produced a comprehensive document in association with the National Aluminum Council.[21] Their specifications cover all aspects of paint performance testing and exist in two forms – AAMA 603.8: 1992 for windows and doors,[126] and AAMA 6052: 1992 for higher performance on building exteriors.[127] The former specification covers appearance, hardness, dry and

wet adhesion, impact resistance, chemical (acid), mortar and detergent resistance, humidity and salt spray resistance, and accelerated and outdoor weathering. The same ground is covered by 605.1 but a greater degree of resistance, for example in salt spray and humidity, is required. Additionally there are abrasion and erosion tests and extra acid resistance requirements, and cleaning and chromate or chromate/phosphate pretreatment of the aluminium are mandatory.

In the U.K. a British Standard (BS 4842) was produced in 1972 to cover stoving organic finishes on extrusions for external architectural applications.[128] Although generally similar to the AAMA specifications, the British Standard concentrated the testing on test panels produced with the work, and, apart from appearance, gloss, thickness and cure, only cross-hatch adhesion tests and a 72 hour sulphur dioxide test were required on the extrusions. A completely revised version of BS 4842 appeared in 1984.[129] This took account of the many developments in organic coatings in this period, particularly the increased use of electrophoretic and powder painting. It was decided that powder coatings could not be covered in BS 4842, and a new standard (BS 6496) was produced to cover these.[130] A much greater emphasis on correct pretreatment was evident in the 1984 version of BS 4842, and a chromate or chromate-phosphate conversion coating, applied after adequate acid or alkaline cleaning, was made mandatory. The only exception was with coatings applied by anodic electrophoresis., where only thorough alkaline or acid cleaning before painting was required. In order to test the quality of the pretreatment, a 2-hour pressure cooker test for the coated product was included.

Both BS 4842: 1984 and BS 6496: 1984 are divided into four sections, the first dealing with the scope and general definitions of the standard. The second section is concerned with the performance and other requirements for the liquid paint coating, and is intended to be carried out by or on behalf of the supplier or manufacturer of the paint. It covers colour, gloss, adhesion, scratch resistance, mortar resistance, solvent cure tests, acetic acid salt spray resistance, weathering tests, humidity resistance, SO, resistance, permeability and storage properties, all assessed by means of test panels. Satisfactory experience of the results of 1 year's exposure in Florida is required for all the systems used.

The third section is concerned with the performance and other requirements for the finish on the aluminium component, and is intended to be carried out by or on behalf of the applicator of the paint. This section covers the material pretreatment and performance requirements (preferably measured on test pieces) for surface appearance, colour, gloss, thickness, adhesion, scratch resistance, solvent cure test and pretreatment quality. In the case of thickness the two standards, of course, differ considerably, as BS 4842 requires a thickness of not less than 20 μm, and BS 6496 specifies a minimum thickness of 40 μm and a maximum thickness of 120 μm. It is pointed out that control of thickness is technically difficult with powder coatings and it may not always be possible to achieve a specified maximum thickness whilst maintaining a minimum thickness of 40 μm.

The fourth section is concerned with the methods of test used for evaluating paint finishes, and mortar tests, acidified salt spray tests and permeability tests are

detailed in each standard. In addition BS 6496 includes a falling cylinder impact test, and BS 4842 covers solvent resistance. Finally both standards give recommendations for the care and maintenance of the painted products. The finishes should be washed with water containing a mild detergent, and harsh scrubbing or the use of abrasive cleaners should be avoided. In general cleaning should be carried out at 3-monthly intervals in industrial or marine sites, and at 6-monthly intervals in rural situations.

These new specifications were strongly influenced by another specification[131] produced by the Aluminium Window Association in 1976 for Stoved Organic Finishes on Aluminium Window Products, which was a considerable advance on **BS** 4842: 1972. **As** with the later specifications, this required conversion coating pretreatment and included a water resistance test, as well as giving advice on care and maintenance.

The proposed European Standards, which are still in draft form, follow very much the same lines as the British Standards. They are again in two parts, one concerned with powder coatings (prEN 12206-1), and the other with liquid organic coatings (prEN 12206-2). They propose to widen the allowed pretreatments to cover chromate-free and electrolytic processes such as anodizing, but only if they have been successfully tested with paint coatings exposed for at least five years in marine and industrial conditions. The increase in filiform corrosion under paint finishes, described earlier in this chapter, has led to the proposed inclusion of a filiform corrosion test in the standards.

The widespread use of paint finishes in architectural applications has led to a need for quality certification schemes of the type developed for anodizing by Qualanod, and a similar Qualicoat scheme was established in 1986. The specifications produced[132] cover powder, liquid and electrophoretic paint coatings, and many changes have taken place since the original specification was produced.

A similar scheme has been operated in Germany for many years by GSB International, and their equivalent specification is GSB RAL RG-631. **A** comparison of the requirements of this specification for powder coatings with those of the Qualicoat specification and BS 6496: 1984, is shown in Table 14-17.[133] As can be seen from this Table, the requirements are generally similar. Comparison of these with the American specifications in certain properties such as thickness, corrosion resistance and exposure performance is shown in Table 14-18. However factors such as thickness requirements are more difficult to compare here, as the European standards refer only to powder coatings and the AAMA standards are more concerned with liquid organic coatings. Since the data in Table 14-17 was produced the Qualicoat and GSB specifications have been more closely aligned, and requirements for properties such as cupping, hardness indentation, bending and mortar resistance are the same in both. Both now allow anodizing as an alternative to chromate pretreatment, and the Machu test has been included as a requirement. This involves 48 hours immersion of a cross-hatched sample in a sodium chloride (50 g/l), glacial acetic acid (10 ml/l), hydrogen peroxide (5 ml/l) mixture at a pH of 3.0-3.3 and a temperature of 37°C.

TABLE 14-17

Comparative requirements of European paint standards[133]

	Qualicoat Spec. 5th. ed. 1990	*British Standard B.S. 6496-I984*	*GSB RAL RG-631*
1. Gloss level (at a 60° angle)	0-30 ± 5 30-70 ± 5 70-100 ± 10 ISO 2813	Sp. Val. ± 5 BS 3900 D5	DIN 67530
2. Film thickness (microns)	minimum 60 ISO 2360	40-120 BS 3900 C5	50-80
3. Adhesion Cross cut: 1-2 mm spacing	Gt0 ISO 2409	Gt0 BS 3900 E6	Gt0 DIN 53I56
4. Cupping test (Erichsen)	6 mm ISO 1520	6 mm BS 3900 C16	5 mm DIN 53156
5. Impact resistance	2.5 Nm ECCA 75	2.3 Nm BS 6496 C16	20 inch/pounds ASTM D 2794
6. Hardness * Bucholtz Indentation	90 ISO 2815		80 DIN53151 ISO 2815
* Scratch Hardness		4000 grams BS 3900 E2	
7. Bending Test	6 mm ISO 1519		5 mm DIN 53152
8. Sawing, Milling, Drilling	No break or separation		No break or separation
9. Mortar Resistance (24 h.)		No loss adh. BS 6496 C16	No loss adh. ASTM C207
10. Salt Spray/Acetic Acid (1000 h)	Acetic acid ISO 3769	Acetic acid BS 6496 C15	Salt spray DIN 50021
11. Kesternich Sulphur dioxide	24 cycles ISO 3231	240 h BS 3900 C8	30 cycles DIN 500I8
12. Humidity Test		1000 h BS 3900 F2	1000 h DIN 50017
13. Boiling Water Pressure Cooker	2 h	2 h or 2 h BS 3900 F3	2 h
14. Colour Stability	7 DIN 54004		7 DIN 54004
15. Accelerated Weathering Test	1000 h SUNTEST DIN 53387 and ISO 4892	2000 h MARR CABINET BS 3900 F3	1000 h SUNTEST DIN 53387
16. Natural Weathering (Florida 45° South)	12 months ISO 2810	12 months	12 months

TABLE 14-18

Comparative requirements of European and U.S. paint standards[133]

	EUROPE			U.S.A.	
	GSB	BS	Qualicoat	AAMA	
	RAL RG-631	6496/84	5th. ed. 90	603.8	605.2
1. Film thickness (microns)	min. 50/	min. 40/ max. 120	min. 60 max. 120	20	30
2. Mechanical properties:	very similar requirements				
3. Salt spray resistance (hours)	1000	1000	1000	1000	1000
4. Humidity test (hours)	1000	1000	1000	1000	1000
5. Florida exposure (years)	1	1	1	1	5

9. SPECIFIC FINISHES AND APPLICATIONS OF PAINTED ALUMINIUM

Architecture

One of the biggest applications of painted aluminium is in architecture, and in this field it is taking over some of the traditional anodizing markets. Painted coil has long been used for industrial roofing and siding and, particularly in North America, also for residential siding. Panels are formed after painting, so flexible coatings with good adhesion are required. In many cases acrylic coatings are used, but polyvinylidene fluoride coatings are specified in the most severe environments. Painted extrusions are very extensively used for windows and doors, and spray-applied and electrophoretically applied acrylics were most usual, but powder coated polyesters now dominate in the European market. White finishes are predominant in the domestic window field, but the wide range of colours available is making paint finishes attractive to architects. The good performance and ready availability of powder coatings means that this type of coating is most widely used, particularly in Europe, and they are now being used for curtain walling and sheet panelling on buildings, as well as on extruded products.

The high use in America of thermosetting acrylic paints has been recorded by Nusbaum,[134] and Phillips[135] has described the use of wet acrylics and polyester powders for windows. Cox[136] has indicated many applications of coil-coated products, and Skerrey[137] has described the development of painted aluminium cladding for the building market. In this latter case an alkyd amino paint is applied to the chromate-phosphate conversion coated sheet after

forming, and this has been preferred to the more common practice of forming after painting. Up to 17 years experience on buildings in marine, industrial, urban and rural environments is reported, and relatively little surface deterioration has been seen. The painted sheet suffered loss of gloss, slight to moderate chalking, very slow erosion and a very slight colour shift in this period. The visible changes were very uniform and gradual over an initial exposure period of 2-4 years, with very little further change in the subsequent period. No adhesion defects at edges, profiles or fixings were seen. Good performance of an alkyd melamine paint system has been reported by Bishop.[138] He has evaluated coil-coated paints on a range of substrates including cold rolled steel, galvanized steel and aluminium in railway architectural applications. He concludes that pre-coated aluminium has given the best performance, with the alkyd melamine still in excellent condition after 19 years. Street[139] has described a range of applications of coil-coated aluminium, including many different architectural uses, and he indicates the wide range of coatings that can be produced on modern coil lines.

The need for very durable finishes in the architectural market has led to much development work by the major paint companies. Work on powder coatings by Courtaulds in this area has been described by Osmond,[140,141] and in ICI by Heath[132] and Codecasa.[142] A particular concern has been the need to improve gloss retention with powder coatings, in order to meet the 5-year Florida exposure requirement of AAMA 605.2-92 (Table 14-18). This standard was based on the performance of polyvinylidene difluoride (PVDF) wet paint ***coatings,*** and traditional polyester powders could not give comparative performance. However new, so-called 'super durable' powders now give similar results as shown in Fig. 14-17. In a different direction the development of wet paint system:; based on acrylic siloxane formulations, which compare in performance with PVDF coatings but are more VOC compatible, has been reported in America.[143] The comparative technologies of polyester powders and fluorocarbon wet paints have been described by Tomes *et al.*[144] This work indicates the higher coating cost of the PVDF coatings and the need for multicoat systems, but accepts that the powder systems can give lower gloss retention. Deterioration of the coating as a result of UV light exposure is in the form of surface chalking, and methods for evaluating the degree of chalking have been studied by Riva and Boi.[145] These tests generally involve taping the surface and evaluating the amount of chalk retained on the tape surface after removal. Quantitative evaluation using a 60° Glossmeter according to ECCA T14 was considered the best method.

An interesting study of the weathering of painted aluminium by workers in Germany[146] compared the onset of filiform corrosion during outdoor exposure at marine and industrial sites with results in laboratory filiform corrosion tests. This showed that exposure at the Hook of Holland, with a combination of marine and industrial pollution, was most severe, and that only the results of the HCl accelerated filiform corrosion test correlated with this. Results with the

NaCl accelerated test showed that, over a 2-year period, corrosion in the laboratory was less than that at the exposure site, making it unsuitable as an accelerated test.

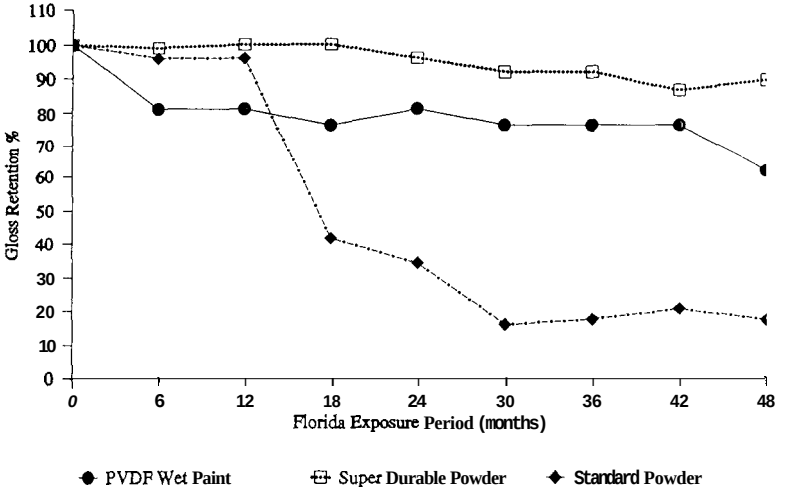


Fig. 14-17. Gloss retention curves for various coating systems from actual Florida exposure[""]

Coil-coated aluminium sheet is increasingly used in architectural applications in the form of composite panels, which are complex combinations of insulating and sound-deadening materials with external and internal facing panels. The Alusuisse range of Alucobond panels is an example of this.

Caravans

The caravan industry (Fig. 14-18) offers what is probably the best available example of an ideal market for prepainted aluminium sheet. Light weight is an essential feature of the vehicle, and an attractive durable finish is required. Painted aluminium is almost invariably used, and fabrication is relatively easy. Sheet can be hammered around corners with no precautions other than the use of wooden tools and plastic headed hammers, and fixing nails and screws can be covered by trim, or prepainted in matching colours.[136] Acrylic paints are the most common in this application, and single colours were normally used, but the ability of modern coil paint lines to apply stripes or

bands of another colour, or to produce more complex patterns, is widening the scope of such finishes.

Fig. 14-18. Typical caravan produced from prepainted aluminium sheet

Air- and space-craft

Very rigorous conditions apply to aircraft finishes. Frequently 7.5 μm (0.3 mil) zinc chromate primers are applied over phosphated or anodized aluminium aircraft sheets and are followed by nitrocellulose lacquer-based top coats or, more recently, by acrylic resin-modified nitrocellulose which has good resistance to diester lubricants. Alternatives are alkyds or acrylic lacquers, epoxy-based amine-cured enamels and polyurethane coatings. The last two are particularly useful when decorative effects are required on commercial aircraft; polyurethane coatings have been found to have good resistance to hydraulic and to polyglycol fluids.

Epoxy primer-acrylic or nitrocellulose-acrylic lacquer systems have been used on helicopter parts, and the sequence for applying such systems, which incorporate two 7.5-10 μm (0.3-0.4 mil) primer coats, has been described by Howard.[147]

Polyurethanes, fused epoxies, epoxy-polysulphide blends and fluoroelastomer coatings are reported to give the best resistance to heat and abrasion on aluminium subjected *to* the critical conditions encountered in rocket blasts.[148]

The special problems of aircraft paint and painting have been discussed in considerable detail by Hoey[149] who has described the various hazards and how the various primers and finishes stand up to them. They do a tolerably good job up to speeds of Mach 2.2, but beyond this with flight at Mach 3, the temperatures reach 400-500°C and coatings are based on inorganic systems using polyphosphates, silicates and ceramic dispersions.

Schmitt[150] has described current protective coatings used for the U.S. Air Force, and he indicates that aliphatic polyurethanes form the basis for protective coatings for general surface protection, camouflage, thermal flash resistance and corrosion protection. Elastomeric polyurethane and fluorocarbon coatings are used for aircraft radomes and antenna covers where the coating must possess combinations of rain erosion resistance, dielectric transmission properties, conductivity for antistatic protection, thermal flash resistance and camouflage colours. **A** comparison of such rain erosion resistant coatings is shown in Table **14-19.**

TABLE 14-19

Comparison of available rain erosion coatings[150]

Property	*MIL-C-7439B Neoprene*	*MIL-C-83231 Black Polyurethane*	*MIL-C-83445 White Polyurethane*	*AF-C-VBW -15-15*** White Fluorocarbon*
*Erosion resistance Minutes at 500 MPH/Lin/Hr rain	**40**	160	***15***	110
Dielectric transmission	Excellent	Excellent	Excellent	Excellent
Service life	< 6 months.	> 3 yrs.	> 2 yrs.	> **5** yrs.
Temperature limit	93.3°C	**149°C**	149°C	260°C
Ease of application (all spray applied)	Difficult	Moderate	Moderate	Moderate
Special requirements	Low humidity	**40%** R.H.	40% R.H.	None (< 80% R.H.)
Strippability	Easy	Easy	Easy	Fair
cost	Low	Moderate (competitive on coverate basis)	Moderate	High
**Thermal flash resistance Cal/cm^2 total fluence	–	–	20 (one pulse)	80 (and multiple pulses)

* AFML rotating arm apparatus
** AFML aerodynamic quartz lamp facility
*** Note: Coloured fluorocarbon coatings would exhibit similar properties except for thermal flash resistance.

The U.S. Air Force Wright Aeronautical Laboratory (AFWAL) is also developing high solids and waterborne coatings to ease application problems, and to include encapsulated corrosion inhibitors and develop readily cleanable coatings.[150] Removal of aircraft coatings is also a necessary feature to be considered.

Aerospace coatings present different problems as they are exposed to extremes of temperature and radiation, but silicone resins are used with specially treated zinc oxide pigments.

Domestic appliances

For appliances such as washing machines and refrigerators, acrylic finishing coats are the most popular. Polyamide-imide coatings are used on cooking utensils.

Automotive applications

The increasing use of aluminium in automotive applications, including now structures and external body panels, has meant that the paint shops in the car industry have to cope with mixtures of aluminium and steel. The greatest implication of this is in the pretreatment stages of the process, with modifications required in the cleaning and phosphating baths[151,152,153] as described in Chapter 5, and, in general, no significant changes are necessary in the actual painting procedures. Early aspects of the finishing of aluminium body panels were discussed by Alcoa.[154] Much of this work is concerned with the mechanical aspects of aluminium in body panel applications, but it points out the importance of adequate phosphating of the aluminium surface to ensure a similar deposition of primer on both steel and aluminium surfaces in the electropainting stage. Work by Alcan[155,156] questions the need for an electrocoat primer with an all-aluminium body structure and suggests this as a significant cost saving, and further work examines the use of preprimed sheet in external body panels.[157] Townsend has reported the comparative performance of painted steel and aluminium sheet in automotive corrosion tests,[158] and Dietz[159] has provided very useful recommendations on the corrosion protection measures necessary on an all-aluminium car body.

Aluminium has been used for car bumpers for many years and traditionally these were bright anodized, but the desire to match the bumper colour to that of the vehicle has led to the use of paint finishes. The production of Volvo 760 bumpers has been described,[160] and in this case the aluminium bumper has a plastic overlay pressed over it. The bumpers are sprayed in two colours, the lower section being painted the same colour as the car bodywork, often with metallic paints, and the upper section being coaled in graphite grey.

Containers

The internal protection against corrosion of aluminium containers is another problem of increasing importance since this is a rapidly expanding market

consuming large tonnages of aluminium. There is no single or simple solution to the many requirements and each problem must be tackled on first principles. Thus, epoxy/phenolic finishes adhere well to aluminium without pretreatment; the epoxy/amines have a better colour but are not so resistant to chemicals. Vinyl resins give no undesirable taste to foodstuffs but in this case the metal surface requires pretreatment. Copolymers may not be taste-free but they are suitable for pigmentation with titanium dioxide. Polybutadiene and acrylate resins are recommended for many purposes. Stoving finishes are formulated so that curing can be effected in a short time at 260-300°C, and in the case of some heat-treatable alloys which might be used for reasons of strength, there may be more severe restrictions on time and temperature to avoid any loss of mechanical properties. For deep-drawn containers a very thin oxide layer is formed on the aluminium and this is overcoated with a highly elastic protective finish. Where the contents have a pH of 5 to 7 epoxy/phenolics are recommended, but for acidic fruit juices then thick vinyl coatings are best applied as organosols or plastisols.

Application by electrophoresis is of importance for container interiors.[161] Beer barrels present quite a challenging problem because of the requirements of considerable mechanical rigidity, a welded construction, very precise dimensions, inserts of other metals, a corrosive situation if the contents hold traces of copper salts and the necessity for the protective coating to withstand rough usage including denting of the surface. Internal anodizing is one of the solutions to this problem.

Marine conditions

Water-resistant paints for sea water present a special problem, more particularly as sodium chloride has been found to hydrolyse in paint coatings to give sodium hydroxide which attacks aluminium fairly rapidly. Alkali-resistant coatings are therefore useful.

Tests carried out by Edwards[106] showed that alkyd-melamine and urea-formaldehyde stoving enamels, ready-mixed oil paints to B.S. 295 and most oleoresinous hard gloss paints, chlorinated rubber, and a vinyl resin-base etch primer alone or followed by hard gloss paint or cellulose lacquer, were all suitable. A number of small corrosion areas were found beneath the film in the case of polystyrene lacquers, whilst considerable peeling occurred with a high-temperature black stoving enamel, black cellulose lacquer and a tung oil/phenol-formaldehyde resin varnish. The vinyl resin-base etch primer gave good results compared with zinc chromate primers, which showed a stronger tendency to flake.

Some marine primer formulations for aluminium are extremely complex, for example:[162]

Zinc oxide	6 pt (wt)
zinc chromate	21
titanium dioxide	5
talc	46

Malaga rouge	2
alkyd resin	40.5
white spirit	14
dipentene	3.5
butyl alcohol	2
lead naphthenate	1.2
manganese naphthenate	0.1
cobalt naphthenate	0.1

A series of 10 year exposure tests at a site at Beaumaris, Anglesey, reported by Harper[163] compares the effects of (alternatively) anodizing, priming with zinc chromate or painting with a normal marine paint system, on a number of aluminium sand and gravity diecastings. The results in Table 14-20 show that, in all cases, both the anodized specimens and those which had merely received one coat of zinc primer stood up quite well. While the fully-painted specimens, not unexpectedly, suffered the least loss of metal, they frequently suffered significant losses of paint; indeed, after 5 years, most of the paints had softened and ceased to give much protectioti.

TABLE 14-20

Weight loss of variously-protected aluminium castings after 10 years natural exposure (mg/cm²)[162]

Casting alloy *		*Unprotected*	*Anodized* †	*Zinc chromate primed*	***Fully** painted* §	
					Paint loss	*Metal loss*
LM1	M	3.2	0.7	–	2.2	0.04
LM4	M	1.3	0.7	1.0	2.6	0.1
LM4	W	1.4	0.6	1.1	3.1	0.22
LM5	M	0.4	0.7	1.2	4.9	0.22
LM6	M	0.9	0.3	1.3	3.1	0.13
LM8	M	0.8	0.7	1.6	3.6	0.16
LM8	P	1.0	0.7	1.8	3.8	0.24
LM8	W	0.8	0.7	1.5	5.3	0.27
LM8	WP	1.0	0.6	1.3	3.2	0.13
LM10	W	0.8	1.8	–	18.4	0.53
LM14	WP	1.9	0.4	1.3	7.3	0.36
LM23	P	1.7	0.5	1.6	2.5	–

M as cast, W solution heat treated, P precipitation heat treated.
† Anodized in 15% sulphuric acid, 13-17°C, 15 V, 30 minutes, then sealed in boiling water.
§ Zinc chromate primer + undercoat + finish coat.

Anti-fouling paints

The problem of anti-fouling paints to prevent marine attachment is not easy. Zinc oxide pigments have a mild anti-fouling action and are often preferred to mercury or copper which, though they prevent attachment better, tend to impair the corrosion resistance of the aluminium. If no undercoating is used, or to guard against breakdown of this type of paint system, organic compounds such as 10-chloro-5:10-dihydroxyphenanthrene have sometimes been incorporated into anti-fouling paints, though again they are usually only mildly toxic and not completely satisfactory.

The heavy metals may, however, often be used with safety over a zinc chromate primer, with a barrier film of chlorinated rubber or plastic paint, and the latter is the common practice in America.

According to Kingcome,[164] an anti-fouling paint for use on aluminium should have the following properties: (a) it should give complete protection for at least six months; (b) it should be tough enough to resist erosion; (c) it should be smooth and flexible; and (d) it should be easy to apply.

Early work in America tended to be almost exclusively concerned with systems consisting of a two-pack etch primer followed by a polyvinyl chloride-acetate copolymer undercoating (like the etch primer pigmented with zinc tetroxychromate) followed by an anti-fouling paint of similar composition but pigmented with cuprous oxide. The film thickness was 150 μm (6 mil) for etch primer and undercoat and 75 μm (3 mil) for the anti-fouling paint.

Similar good results were obtained in British tests[165] in which essentially the same system was used, with the exception of the undercoatings which were (1) vinylite coatings pigmented with red lead and (2) a linseed oil phenol-formaldehyde varnish pigmented with white lead, basic lead sulphate and iron oxide.

Interesting results were obtained with anti-fouling paints in France.[166] In these tests, an aluminium-magnesium alloy A-G5 was coated with three paints containing (a) copper and mercury; (b) zinc-iron-copper-arsenic-phosphorus; and (c) organic toxic material. In some cases these were applied without an undercoating, while in the others a zinc chromate primer was used. The results showed that provided a primer was used, immersion in sea-water up to 18 months had little or no effect on the mechanical properties. In the absence of a primer, rapid deterioration in mechanical properties occurred in the case of alloys coated with paints containing copper and mercury. The primer appeared to be much less important when the other types of anti-fouling materials were employed.

At one time mercuric oxide was frequently used to augment the cuprous oxide in anti-fouling paints, but experience showed that the high cost of the mercury compounds is not justified in terms of performance, and their use has been discontinued.[50,167]

Organo-metallic compounds have also been used in antifouling compositions, and the organo-tin compounds have been found particularly effective.[168,169] They tended to replace copper compounds with paints on aluminium, and

copolymerisation of organo-tin compounds with polymers gives excellent anti-fouling properties[168] (for example tributyl-tin methacrylate with acrylic and styrene polymers). All of these anti-fouling compositions work by releasing materials which are toxic *to* marine growths such as barnacles, mussels and seaweeds. The leaching rate is important and must be kept above a critical value. For copper this has been found to be 10 μm/cm^2/24 h to prevent barnacle growth, but results suggest that tin is some ten times more effective.[170]

The paints are based on a solution of resin and oleoresinous medium, and function by slow dissolution of the acidic resin in the slightly alkaline seawater, so that fresh toxic material is continuously exposed.'" The solution rate is controlled by inclusion of water insoluble substances such as pitch, tar or wax.

Clear lacquers

Although clear lacquers have been useful on a small scale for many years to protect polished aluminium, they have not been competitive with anodic finishes for this application, partly because of the loss of reflectivity and the yellowing of most formulations on exposure, and partly because of their relatively poor resistance to abrasion and to detergents and cleaning compositions. Added to this is the fact that there is usually no significant financial saving in using lacquers as compared with anodizing when the aluminium is electro- or chemically polished, as in this case the two wet processes fit into one complementary sequence.

With the improvement of clear organic lacquers, the value of such coatings *as* replacements for anodic oxide finishes for bright aluminium surfaces has been re-examined. On the face of it such coatings, apart from their relatively inexpensive application costs, have the advantage that they can be used for alloys which cannot be bright anodized. One prerequisite for their use, however, is adequate cleaning and particularly the removal of any traces of alkali from cleaning solutions or even of lime from the mechanical polishing operation, which is not removed by vapour degreasing. Such alkali may in time react with the resin of the lacquer to form soaps which cause cloudiness or peeling in service.

Alkyds, vinyls, acrylics and epoxies have all been used for clear lacquers on aluminium, although Gaynes[171,172] points out that all these have their own disadvantages, and that adequate pretreatment and rigid control of curing conditions are essential for success. Best of these are probably the acrylics, which will stand up for periods varying from *2-5* years in outdoor exposure on anodized aluminium without deterioration. The normal thickness of such coatings is between 12 and 20 μm (0.5 and 0.8 mil), and they have been widely used to protect anodized aluminium window frames against alkaline plaster or mortar.[173] Non-yellowing lacquers are essential, and methyl methacrylate or cellulose acetate butyrate lacquers are used. At one time these lacquers were thought to be suitable as protective coatings in their own right in external architectural applications, but Guminski and Meredith[5] have shown that filiform corrosion occurs under the

lacquer film. The speed with which this occurs depends on the pretreatment used, conversion coatings or thin anodic coating pretreatments giving the longest life in any particular environment, but even with the best pretreatment only about 2 years satisfactory appearance may be expected.

The use of electrophoretically deposited lacquer coatings as a sealing system for anodized aluminium, which has become so widely practised in Japan, has already been described in Chapter 11, but Dow Chemical Co. have described the electrophoretic application of a clear polymer to cleaned aluminium surfaces.[174] A similar process has been developed under the name of the Edeca process by Sumitomo in Japan.[175,176] A clear acrylic based coating is applied after cleaning and chromate-phosphate conversion coating the aluminium (thin coating of 15-25 mg/m^2 coating weight). Coloured coatings are also produced using waterborne pigments or chromogen bonded polymers.

Specialised applications of organic coatings to aluminium include those involved in foil conversion processes, where a range of polymer films, adhesives, coatings and printing inks is applied for decoration and functional requirements. Most are concerned with packaging applications. Carr[177] has described the use of coloured stoving lacquers to simulate other materials such as bronze, brass and copper.

PTFE coatings

The application to aluminium of the fluorocarbon polymer polytetrafluoroethylene, better known as PTFE or by its trade names such as Fluon, Teflon or Tefal, is one which presents a unique set of problems, because the essential nature of the material is that it sticks to virtually nothing and is attacked chemically by scarcely anything. It is an extremely useful coating because of its extraordinarily low coefficient of friction, which is little different from that of dry ice, great chemical inertness to practically every known material and ability to withstand temperatures in excess of 300°C. Its popular culinary use on the non-stick frying pan needs no further comment except perhaps to observe that nothing is ever perfect. The invention of the coating in France is attributed to Marc Gregoire.[178]

The coating is applied to metal surfaces in the form of an aqueous slurry of fine particles by either dipping, spraying or painting and is first dried at about 110°C to remove water, before finally sintering by a short treatment at about 400°C to form a continuous coating. The coating in this form is microporous[179] and does not offer adequate protection against corrosion, its application being mainly industrial for non-stick, slippery surfaces, particularly for handling foodstuffs and on non-stick cooking utensils.

Adhesion of PTFE to metal surfaces can be effected by the use of a primer coating which is a similar aqueous suspension of PTFE particles containing acid additives, the most effective being chromic acid or a mixture of chromic and phosphoric acids. These coatings are usually undercured at about 315°C to give a

dry coating thickness of 0.05-0.075 mm, so that good bonding will be achieved with the top-coat of pure dispersion which is sintered at the higher temperature.[180] In the case of domestic utensils however there is objection to the use of coatings containing chromium because of toxic hazards, and although primers based on phosphoric acid only have been developed,[181] there is still a suspicion that the coatings may decompose to release fluorine-containing compounds at lower temperatures than the pure coating. In the case of cooking utensils, therefore, it is customary to dispense with the use of a primer coat and to secure adhesion mechanically by either sandblasting to give a rough surface with re-entrant cavities, or by deeply etching in hydrochloric acid to give a deeply-pitted surface (Fig. 14-19). The etching techniques for PTFE adhesion have been discussed in Chapter 4, page 193, with reference to the various patents covering these procedures.

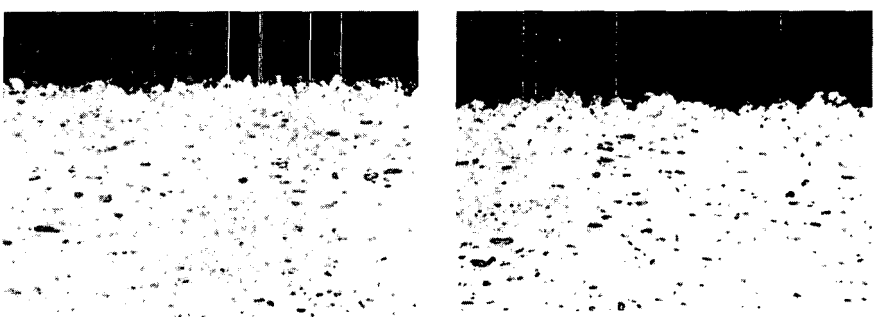


Fig. 14-19. Cross sections of pure aluminium after etching and before (left hand photograph) and alter (right hand photograph) coating with PTFE (x 125)

It should be noted that the sintering temperatures used for PTFE are in the range where complete recrystallization of the aluminium can take place, leaving the metal in the annealed condition. Most holloware has been coated in the form of flat circles which are: subsequently spun or flow-formed so that the soft condition is required, but in other respects the high sintering temperature is a disadvantage. This effect can be minimised by rapid radiant heating for short periods or by the use of an electric arc.[182]

PTFE coatings have very poor wear resistance and this situation has been improved in the domestic field by employing rough substrates which in effect are islands or peaks of metal protruding from a surrounding sea of PTFE, so that any wear or abrasion is carried by these peaks, while they are too small in area to affect the non-stick properties significantly. This situation can be brought about by flame spraying the aluminium with aluminium powder; thus Westinghouse[183,184] have proposed the use of 100-200 U.S. mesh powder to produce a layer of 0.07-0.15 mm (2.8-6 mil) thickness of 10-60% porosity which is subsequently PTFE coated and shot peened to promote better adhesion. In the Armourcote[185] process a 'hard crystalline layer of stainless steel' bonded *to* the aluminium was used and this was claimed to increase the life of the article by at least five times. Flame sprayed cermet layers of aluminium powder and Al_2O_3 have also been proposed for PTFE-coated holloware, and these also give a greatly extended life.[186,187]

Additions have been made to the PTFE dispersions in order to obtain reinforced coatings of greater wear resistance, to give greater cohesive strength or to obtain other improved properties. The use of an initial coating, where the PTFE dispersion contains Al_2O_3 particles in suspension, to be followed by a second PTFE coating has been proposed[188] and Tefal have obtained non-staining layers for holloware by incorporating into the coating powder spangles or platelets of gold, nickel or chromium.[189] Société Tefal have also ingeniously incorporated a non-toxic thermal indicator into the coating in the form of cadmium sulpho-selenide or other thermal sensitive material which changes colour when a particular temperature has been attained.[190] At the United States Naval Research Laboratory[191] the cohesive strength of PTFE coatings has been improved by the addition of a small amount of synthetic colloidal boehmite (Baymal). The amount added is only from 0.1-0.4% and the alumina is adsorbed onto the Teflon, the electrostatic forces producing a large increase in strength. In aqueous dispersions coagulation is reduced and the storage life improved and a thixotropic effect is produced which enables moulding direct from dispersions. There is also a large improvement in the durability of lubricating coatings by the promotion of self-healing properties. Farbwerke Hoechst[192] have prepared PTFE dispersions suitable for electrodeposition of the polymer onto metals, by adding a fluorinated surface active agent such as perfluorocaprylic acid to the dispersion. The use of silicone coupling agents is increasingly suggested to improve adhesion,[193,194] and, in further attempts to improve coating hardness, anodizing treatments[195,196] and a special high silicon (14-25%) alloy[197] are claimed.

The direct bonding of PTFE in sheet form to aluminium is less common, but in one process a 3 mil (0.075 mm) sheet of PTFE was bonded to Duralumin by etching in 10%hydrofluoric acid at 70°C, applying an intermediate layer of PTFE powder and pressing the two sheets together between platens at 65°C and a pressure of 200 lb/in^2 (13.3 bar).[198]

Temporary protective coatings

It is frequently required to apply a temporary protective coating to aluminium sheets or extrusions immediately after production for either physical protection or protection against corrosion during transit or storage until they are used by the customer. Although there is no serious corrosion hazard in general, the freshly produced aluminium surface which has not acquired the full protective value of its oxide film can sometimes develop minute pits which become visible after etching and anodizing and can impair the appearance. The greatest risk is with structural alloys in the extruded form where a virgin surface unprotected with any lubricant or oil is exposed, and when this is subjected to cycling temperatures in a damp atmosphere containing traces of chloride. Sheet materials have normally a lubricant present but in this case it is generally the bright rolled mirror surfaces of reflectors or nameplates which require protection for handling or fabricating.

Meier[199] has outlined the requirements of such protectives as:

Simple in application
No disturbing reactions with the metal
Physiologically unobjectionable
Uniform coverage of the surface
Penetration into fine pores and fissures
Displacement of moisture already present on the surface
Long continuing effectiveness
Usable over a wide temperature range
No interference with subsequent treatments
Simple to remove from the surface
Economical in use.

It is the custom to coat materials by spray or roller coating processes with either a transparent or coloured lacquer which can easily be removed when necessary by stripping it off by hand, or occasionally in a trichloroethylene vapour plant. The coating must be uniform in thickness if the material is to be formed, blanked or pierced, and free from any small thick lumps which would cause the surface of tightly wound coils to dent.

In the case of extrusions, dilute solutions are applied by spraying or dipping. The requirement here is that the protective can be readily removed during the normal treatment sequence uniformly and without causing any contamination of the treatment tanks. Proprietary formulations have been devised with these requirements in mind but in the absence of these, a light oil application or lanoline is of great help. A further desirable requirement would be a protective system satisfactory in other ways which could be applied to extrusions as

produced before cooling and which could remain in place during ageing heat treatments which might involve 6 hours or so at 200°C. The ideal temporary protective in this respect is not yet available.

Temporary protection of architectural finishes is also required, in this case as a protection against mechanical damage or mortar and cement splashes. Anodized finishes are particularly prone to the latter form of damage and taping of products before shipment to site is frequently recommended. However choice of tape is important, as it may be in place for many months and must remain removable, without leaving residues of tape or adhesive, after long periods of weathering. Clear lacquer coatings which are left to weather away naturally are an alternative. Recommendations for protection of paint finishes are less consistent, as tapes can adhere so strongly to the organic coating that it is damaged when the tape is removed. Some manufacturers recommend certain low-tack tapes, but the standards generally recommend against their use.[129,130,131]

Sealing compounds

Special sealing compounds are often used in joints between different parts of an assembly, particularly for the treatment of dissimilar metals. These are usually barium chromate compounds (60-98%), or impregnated tapes or pastes containing aluminium. Tapes should preferably have a fabric base and may be obtained to various dimensions. Neoprene tape coated with zinc chromate has also been employed.

Sealants and mastics used with aluminium architectural components must be compatible with the finishes concerned, and specifications recommend that the sealant supplier and the fabricator should ensure that adequate adhesion to the finish will be obtained.[126,127] General guidance on the use of mastics and sealants is provided by the Aluminium Window Association,[200] and their general classification of mastics and sealants, with an indication of their expected life, is shown in Table 14-21.

TABLE 14-21 Classification of mastics and sealants used in architecture[200]

Material	*Category*	*Use in window installation*	**Max. movement capability in tension/compression*	*Life expectancy of material*	*Comments*
Oil based bedding mastics	Plastic	General purpose bedding in enclosed compression joints	Negligible	5-10 years	1. Exposed surfaces require painting. Durability is dependent on volume of material and area exposed to atmosphere.
Oil based painting mastics	Plastic	General purpose painting	± 3% of joint width	5-10 years	1. Painting exposed surfaces increases life of material.
Extruded tapes	Plastic	Compression joints	Not applicable	10-15 years	1. A vast range available with varying properties. 2. Requires application under compression to obtain adhesion.
Butyl gun grade mastics	Plastic/ Elastic	Concealed lap joints subject to little movement	± 6% of joint width	10-15 years	1. Should not be exposed to direct weather as material is affected by U.V. light. 2. Adequate volume must be used.
Acrylic sealants	Plastic/ Elastic	Perimeter pointing	± 10%-± 15% of joint width dependent on type	15-20 years	1. Can be hot or cold applied. Hot applied materials require special heating equipment. 2. Some acrylic sealants have high adhesion quality and seldom require primers.
Acrylic and nitrile small joint sealants	Plastic/ Elastic	Remedial work	None	15-20 years	1. Most acrylic sealants are subject to shrinkage on solvent release.
Polysulphide one-part sealants	Plastic/ Elastic	Perimeter pointing	± 10% of joint width	15-20 years	1. Priming necessary for certain aluminium finishes. Sealers for porous substrates. 2. BS 5215 specifies quality standard.
Polysulphide two-part sealants	Plastid Elastic	Perimeter pointing	± 12% of joint width	15-20 years	1. Sealers necessary for porous substrates. 2. BS 4254 specifies quality standard. 3. If dynamic movement is anticipated, design for ± 5% movement of joint width.
Polyurethane sealants (can be one-part or two-part)	Elastic	Perimeter pointing Expansion joints	± 10% of joint width for one-part ± 12% of joint width for two-part	15-20 years	1. Priming usually necessary for all substrates. 2. Not yet in general use in U.K.
Silicone sealants (one-part)	Elastic	Perimeter pointing, expansion joints, where dynamic movement is anticipated	± 12% of joint width (higher for recently introduced low modulus materials)	20 years	1. Sealer to masonry essential. 2. Priming of some aluminium finishes may be necessary.

* Percentages stated may vary depending on manufacturer

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CHAPTER 15

Vitreous Enamelling

1. INTRODUCTION

Owing to the continuous development of the organic finishes described in the previous Chapter, the vitreous enamelling of aluminium is now very limited, and this has essentially become an historical account of its development and demise. It is still used in some specialised applications, but the expansion of the industry predicted in the 1960's for the architectural and holloware fields has never taken place.

Vitreous or porcelain enamels consist of a mixture of inorganic oxides which are fused into high-melting-point glass. The basic materials may include borax, quartz, fluorspar, felspar as well as various metallic nitrates and carbonates and the oxides of heavy metals such as lead, nickel, cobalt, antimony, tin, or manganese.

Vitreous enamels are prepared by mixing the ingredients in powder form, heating the mixture to above its melting point, and pouring the liquid into cold water. The resulting splintered glass is known as the frit, which is then ground in a ball mill and is macle into a liquid slip with water and the addition of floating agents, opacifiers and pigments ready for applying to the metal surface. After coating the metal uniformly, the enamel is fused and the volatile constituents are driven off. The metal is then allowed to cool, with the result that the enamel forms a smooth glassy coating which is inert and extremely resistant to atmospheric corrosion, acids and alkalis, as well as being of good abrasion and impact resistance.

The normal type of enamel of the composition described melts at 700-1000°C and is suitable for application to iron and steel, and copper and its alloys. Aluminium alloys, however, melt at 570-660°C, depending on their composition and cannot, in general, be heated above 550°C, so special enamels or methods of application were required.

Enamels for use on aluminium and its alloys were available as early as 1917[1] and McGinnis[2] made reference to the vitreous enamelling of cast aluminium architectural panels in 1929. However, it was not until the immediate post-war period (1945) that vitreous enamelling of aluminium was developed and that special enamels[3] were made commercially available. The shortage of iron and steel during the late 1940s stimulated the extension of the use of vitreous enamel on the more readily available aluminium for holloware, bathroom and kitchen fittings, refrigerator linings, lighting fittings, etc. With the expanding building programme, both in the U.S.A. and in Great Britain, vitreous enamelled aluminium was also used for architectural panels and road signs. Not all the early applications of vitreous enamelled aluminium were successful and in Great Britain its architectural use was very limited. It is likely that this lack of success was in part associated with the use of the same equipment and processing control techniques normally employed when vitreous enamelling steel and cast iron. The need for the individual treatment of aluminium was recognised, however, and holloware manufacturers, in both Great Britain and the U.S.A., introduced production lines designed and used exclusively for the treatment of aluminium.[4,5] In the U.S.A. the use of vitreous enamelled architectural panels was generally accepted and one major manufacturer stated that up to 1968 over 5 million square feet (about half million m^2) had been erected on buildings in various parts of the country.[6] However the rapid development of highly durable organic coatings limited the further expansion of the aluminium enamelling industry.

In addition to its low melting point, another difficulty encountered in the enamelling of aluminium was its high coefficient of linear expansion which, at 20 to 24 x 10^{-6} per "C, was more than twice that of the enamels normally used for ferrous metals.'

Enamels having expansion characteristics nearer to that of aluminium were therefore required if the development of excessive stress-strain values at the metal/enamel interface, with the resultant chipping or crazing of the enamel, was to be avoided. Since all enamels are relatively weak in tension but strong in compression, it was usual for them to be formulated to produce expansion values slightly less than that of the basis metal (Table 15-1).

The better adhesion properties of enamels to aluminium, together with the thinner coatings required to give adequate coverage, reduce the possibility of incipient chipping or spalling and permit the use of larger differences of expansion than would be permissible with other metals.

TABLE 15-1

Typical expansion values of various metals and suitable enamels[8]

Metal	*Range of coefficient of cubic expansion* x 10^{-6} per °C*	
	Metal	*Practical modern enamels*
Cementitic and pearlitic cast iron	34-36	28-31
Pearlitic-ferritic cast iron	36-38	30-33
Low carbon sheet iron	40-41.5	26-31
Pure aluminium (Al 99.7%+)	66	39-45
Low alloy aluminium (99% Al)	67-72	41-47
Stainless steel (18% Cr:8% Ni type)	46-54	32-44

*cubic expansion = linear expansion x 3

A favourable factor in the treatment of aluminium, on the other hand, is the presence of the natural oxide film. The mechanism by which enamels adhere to the metal is not completely understood, but seems to depend upon the bond of the metal and the coating with the oxide of the metal. In the case of copper this has been demonstrated by Carter and King[9] to be cuprous oxide, while on ferrous metals there is evidence that cobalt and nickel oxides formed in firing the enamel contribute to adhesion.[10] On aluminium, the bond is between the enamel and the slightly porous hydrated aluminium oxide film which partially dissolves in the strongly alkaline fused enamel." The adhesion of vitreous enamel to 6063 extrusions has been studied by Baker.[12] She found that good adhesion and spall resistance required a diffusion of aluminium or aluminium oxide into the enamel without the formation of reaction products, and the resulting wide diffusion zone was not subject to chemical degradation and was mechanically stronger than the enamel. On the other hand this satisfactory adhesion was adversely affected by preferential diffusion of magnesium, and a high level of magnesium and other reactive products could be identified in the diffusion layer with a spalled product. Similar work was reported by Howlett[13] on the effects of magnesium in aluminium alloys on vitreous enamelling, and, like other workers, he stressed the importance of having the magnesium present in the form of second phase particles. He also indicated the importance of selectively removing the magnesium containing compounds from the surface in the deoxidising treatment, and recommended use of an acid chromate deoxidiser followed by an alkaline chromate conversion coating for Al-Mg-Si alloys. This chromate-rich layer prevents further diffusion of magnesium to the metal surface during firing. Howlett saw the mechanism of

bonding of the enamel depending on the aluminium oxide and aluminium surface dissolving into the vitreous enamel during firing, and reported that, under normal conditions, up to 5000 Å of oxide could be dissolved into the enamel. This supported the idea that the glass near the interface must be reasonably saturated with the oxide of the metal to which it is to bond, before adhesion of the glass to the metal substrate could occur.

In the enamels used on aluminium, the melting point of the material was reduced by the addition of lead and/or alkali metals, the latter having the additional property of increasing the coefficient of expansion.

The formulation and manufacture of enamels for use on aluminium and its alloys have been described in the U.S.A. by Andrews[14] and in Russia by Vargin.[15]

2. LEAD-BEARING ENAMELS

If lead oxide or silicate is added to the frit, the melting point of the enamel may be greatly reduced. Table 15-2[7,16] shows some of the eutectics of oxide mixtures used in enamels.

TABLE 15-2

Eutectics of oxide mixtures used in low-melting-point enamels

Oxides	*Eutectic. °C*
$K_2O.SiO_2$-$Na_2O.SiO_2$	745
K_2OSiO2-$Na_2O.2SiO_2$	705
$Na_2O.2SiO_2$-$Li_2O.2SiO_2$	637
$Li_2O.B_2O_3$-$Na_2O.B_2O_3$	650
$K_2O.PbO.4SiO_2$	757
$PbO.Na_2O.SiO_2$-$PbO.SiO_2$	620
$PbO.Na_2O.SiO_2$-$PbO.SiO_2$	590
$PbO.Na_2O.SiO_2$-$Na_2O.SiO_2$	580
$3PbO.SiO_2$-$Na_2O.SiO_2$	620
$3PbO.SiO_2$-$Na_2O.SiO_2$	590
$2PbO.SiO_2$-$PbO.2B_2O_3$	525

The compositions of some of the frits used are shown in Figs. 15-1 and 15-2.

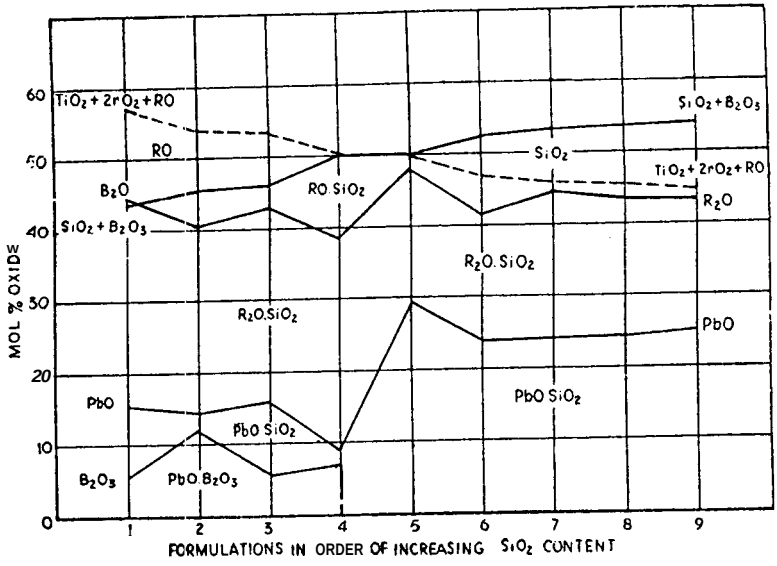

Fig 15-1 Composition of U S frits (du Pont)

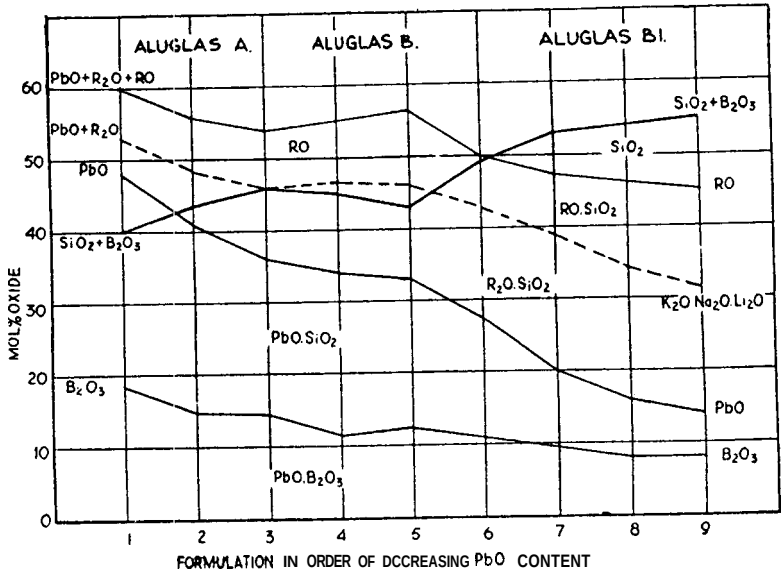

Fig. IS-2. Composition of Aluglas frits

In these, the molar percentages of acidic and basic oxides are plotted against the enamel composition in order of increasing acidity or SiO_2 content. Such diagrams are useful in order to obtain a picture of the composition and properties of the enamel.

The ratio of the percentages of basic oxides, e.g., PbO, R_2O, RO (where R is an alkali or alkaline earth metal) to acidic oxides such as SiO_2, shows the balance of composition. The approximate molar percentages of some of these enamels is shown in Table 15-3. Aluglas was the trade name of frits which were developed by the Amalgamated Research and Development Co. Ltd.

As can be seen from Table 15-3, the American enamels" differed from their British counterparts mainly by their lithium and titanium contents, the former being added as an opacifier, often in combination with antimony in order to prevent the formation of a yellowish colour which tended to result from the use of lithium oxide by itself.

A Russian formulation[18] was described which contained 13% TiO_2 and 43.5% PbO, to which were added various colouring materials, while Vargin[15] referred to the use of lithium oxide and antimony oxide in lead-bearing enamels developed at the Leningrad Institute of Technology.

TABLE 15-3

Approximate molar percentages in lead-bearing enamels suitable for application to aluminium[19]

Oxide		*U.S. frits (du Pont)*	*British frits (Aluglas)*	
			B	*B.I.*
Lead oxide	PbO	10-18	25-35	10-20
Silica	SiO_2	38-56	30-40	40-50
Lithium oxide	Li_2O	5-12	0-3	0-3
Other alkalis	R_2O	0-42	9-12	12-16
Titanium oxide	TiO_2	0-11	–	–
Boric oxide	B_2O_3	–	10-15	8-10
Aluminium oxide	Al_2O_3	–	1-3	2-4

Neither titanium nor lithium could be used in the early British enamels due to patent protection and their high cost.' Instead they contained heavier concentrations (40-50%) of lead oxide (e.g., Aluglas A). Such frits were later replaced by enamels such as Aluglas B and B.I whose lower lead content gave the coating somewhat greater resistance to chemical attack.

In the British enamels, molybdates were used as opacifiers, ammonium molybdate being added to the batch, while further additions of sodium or calcium molybdate, together with zircon, were added in the mill. Molybdates, which are thought to give a precipitate of MoO_3 during the final firing,[7] also increased the fluidity of the enamel. **A** typical white enamel formulation containing molybdenum trioxide has been described as follows:'"

Na_2O	=	5.72%
K_2O	=	6.92%
LiO_2	=	1.32%
PbO	=	39.68%
Al_2O_3	=	I 1.27%
B_2O_3	=	6.87%
P_2O_5	=	26.62%
SiO_2	=	0.94%
MoO_3	=	0.66%

The molybdenum trioxide was added to the frit during the final milling operation.

Pigmented borax frits[21] have also been used for enamelling aluminium building components as well as holloware. These were usually sprayed onto the etched surface and fired for 4-I0 minutes at closely controlled temperatures.

Depending on the amount of lead present, the enamels could be fired at temperatures as low as 450°C though 500°C was more usual. The enamels were, however-, comparatively soft and of poor corrosion resistance compared with those used on ferrous metals and could be toxic in contact with foodstuffs, an important consideration for their application in kitchen ware. Particularly in the case of higher lead contents (above $PbO{\cdot}2SiO_2$ composition), strict safety regulations were in force also in the application of the enamels and this was certainly a limiting factor in their use.

3. LEAD-FREE ENAMELS

The possible health hazards associated with the use of lead-containing enamels'' helped to promote the development of a range of lead-free compositions using alkaline earth metals, with the addition of oxides of boron and sodium orpotassium. The reduced acid resistance of these coatings was improved by the addition of lithium, either as carbonate or silicate, to the frit.[23] Frazer and Cianchi[24] described a range of enamels which, while being free from lead, were still considered toxic because of the high proportion of barium oxide added to reduce the melting point.

A typical composition of an early British lead-free enamel known commercially as Aluglas D was as follows:[24]

Barium oxide (with or without oxides of zinc, calcium or strontium)	17-30%
Silica	18-36%
Sodium and potassium oxides (with or without lithium oxide)	21-36%
Boric oxide	8-13%
Alumina	0-4%
Titanium oxide	0-15%
Zirconium oxide	0-5%
Tin oxide	0-5%
$TiO_2 + ZrO_2 + SnO_2$	0-15%
Firing temperature (°C)	500-580

Donahoy[25] described the use of oxides of cobalt, copper, nickel and cadmium in a fluoro-phosphate enamel for which the following compositional details have been given:[26,27]

P_2O_5	20-32%
Al_2O_3	15-23%
Li_2O	5-15%
Na_2O	15-33%
CuO, CaO, NiO, SbO	3-12%
B_2O_3	2-15%
F	2-15%
Firing temperature (°C)	480-540

Enamels based on the above formulation had good acid resistance and were found to be suitable for application to a number of aluminium alloys.

The ratio of acidic to basic oxides already referred to was of importance in determining the chemical properties of the enamel coating. For the purpose of this classification, tri- and tetravalent oxides of general formula R_2O_3 and RO_2 were considered as acidic oxides and contained such compounds as silica as well as the oxides of aluminium, boron, and titanium. Basic oxides were those of the monovalent alkali metals and divalent alkaline-earth metals of general formulæ R_2O and RO. A ratio of

$$\frac{RO_2 + R_2O_3}{R_2O + RO}$$

was, therefore, frequently employed, expressed as the molecular percentages of the oxides concerned. Generally speaking, the higher the ratio, i.e., the higher the proportion of acidic oxides, the higher was the acid resistance of the enamel, but also the higher its melting point. In Aluglas D,[24] this ratio was usually maintained between 0.3 and 1.40,' and it was possible to obtain a Moh's hardness value of 6 by this means.

A leadless enamel of a different type has been described by Carrol. The frit contained:[28]

Phosphorus pentoxide	44%
Aluminium oxide	21%
Boric oxide	8%
Zinc oxide	7%
Sodium oxide	6%
Potassium oxide	6%

It had rather a high firing temperature of 540°C and required an undercoat of copper in order to prevent attack of the aluminium by the frit. Such undercoats could be applied by simple immersion in copper sulphate solution. Titanium oxide was added as opacifier and the enamel was reported to have good resistance to boiling water.

An alkali metal aluminium phosphate enamel[29] containing small amounts of TiO_2 and ZrO_2 was claimed to have an improved resistance to acid and alkali attack, while a Russian source[30] described an enamel containing 10%NaF_2 which was resistant to boiling water and to a 4% solution of acetic acid. Another Russian patent[31] claimed improved chemical resistance from a 36-39% SiO_2, 9-11% TiO_2, 6-8% B_2O_3, 2-4% Na_2O, 5-7% K_2O, 3-5% Li_2O and 2-4% CdO containing enamel. Along similar lines partial replacement of SiO_2 in a conventional enamel with 4.5% Li_2O and 2% Al_2O_3 was said to lower the firing temperature and give enamels with increased thermal shock resistance.)' Approximately equal amounts of SiO_2 and TiO_2 (18-23%) were included in another Russian formulation.[33]

During the firing of a lead-free enamel containing essentially 22-35% TiO_2, 14-29% SiO_2, 17-26% Na_2O and 1-3% LiO_2, surface corrosion of the aluminium was noted which caused slight unevenness of the coated surface. It was discivered that the corrosion could be reduced by the addition to the frit of I-11% of antimony oxide (SbO_3).[34]

A lead-free enamel for aluminium patented in the U.S.S.R.[35] contained SiO_2 17.14%, TiO_2 16.28%, Na_2O 17.59%, K_2O 12.70%, SnO 6.51%, B_2O_3 6.76%, Li_2O 4.34%, CdO 4.34%, Al_2O_3 2.17% and P_2O_5 2.17%.

Matt finishes were produced in vitreous enamels by the inclusion in the frit of finely divided polytetrafluoroethylene (Fluon) which formed a gas when heated and caused roughening of the surface.[36] Enamels containing phosphorescent pigments have been described by Strongin and Goldman.[37]

Colouring oxides such as MnO_2, NiO, CoO, Fe_2O_3, Cr_2O_3 and CuO have been studied by Sroczynskii[38] in a lead-based enamel. He found that MnO_2, CoO, Cr_2O_3, CuO and NiO yielded a wide range of coloured enamels when colouring was performed during the melt, and the acid resistance of the resulting enamels was better than when colouring agents were added during milling. CuO and Cr_2O_3 were found to improve the chipping resistance of the enamels. The effect of metal oxides on the intermediate layer has been studied by Russian workers.[39]

4. ALLOY SELECTION

Of the large number of commercially available aluminium alloys, only a few were suitable for vitreous enamelling, and some required a chemical pretreatment to ensure maximum enamel-to-metal adhesion. Some of the alloying constituents in aluminium alloys could have a detrimental effect on the adhesion of the enamel, either during firing or after ageing in a corrosive atmosphere.

In general, it was found that the purer the grade of aluminium used, the easier it was to produce a durable vitreous enamel finish. The firing temperature for the enamel was higher than the annealing temperature of aluminium alloys and it was necessary to select the alloy which gave the minimum permissible distortion on firing. The alloy also had to be chosen to give the required mechanical properties after firing. Table 15-4 shows the effect of firing on the mechanical properties of three aluminium alloys used for vitreous enamelling.

TABLE 15-4

Properties of aluminium sheet after enamelling[40]

	0.1% proof stress		*U.T.S.*		*elongation on*	***Vickers***
Alloy	*ton/in²*	*N/mm²*	*ton/in²*	*N/mm²*	*2"* (%)	***hardness***
1100 unfired	9.25	143	11.7	181	4.5	48
1100 fired	1.5	22	5.55	86	41	23
3003 unfired	12.5	193	14.6	225	5.5	62
3003 fired	2.3	36	7.2	111	31	33
6061 unfired	17.6	212	20.2	312	11	106
6061 fired	7.35	114	13.95	216	17.5	70

The 99% aluminium purity (1100) was used for applications where the mechanical weakening of the metal which occurred on firing was acceptable. The

1¼% manganese alloy (3003) was used when slightly higher mechanical properties after firing were required. This alloy hardened during cold working but annealing took place during the enamel firing operation.

The heat-treatable magnesium-silicide type alloys, e.g. 6061, 6062 and 6063, did not show such a large reduction in mechanical properties but were not as readily enamelled as the purer grades. Enamel spalling was the main problem associated with the use of these alloys. It is suggested that this was caused by incipient melting of the metal associated with the presence of magnesium which was not in the combined form of Mg_2Si. The addition of 0.5-2.5% silicon in excess of that required to combine with the magnesium present was said to give better enamel adhesion, and this has been covered in a British patent.[41] Hubbell[42] also claimed that alloys with a Mg:Si ratio of less than 1.73 (i.e. with excess silicon) could sometiines be enamelled without any pretreatment other than an adequate cleaning.

An aluminium-zinc-magnesium extrusion alloy, X7014, with good enamelling properties and improved mechanical properties after room temperature ageing was described by Church.[43] A chromate metal pretreatment was recommended for the aluminium-zinc-magnesium and the magnesium-silicide alloys.[44,45]

A number of clad alloys in sheet form were developed, mainly for architectural purposes.[46,47,48] These sheet products had *a* core of heat treatable alloy which imparted good mechanical properties, and *a* cladding of an aluminium alloy to which the enamel had a high level of adhesion, without the necessity of a chromate pretreatment. Naturally ageing Al-Zn-Mg alloys, clad with commercial purity aluminium, were developed for holloware use, and these have been described by Frankel[49] and Achenbach.[50] Such alloys could recover up to 90% of their pre-enamelling strength, without the need for artificial ageing.

Permanent mould (gravity) and sand castings in alloys LM6, LM8, and LMI 8 (AA 43, 344, 356) could be satisfactorily enamelled provided they were sound and had a good surface finish." Pressure and die castings were not usually enamelled because of their inherent subsurface porosity.

Aluminium coated steel and aluminium coated galvanized steel have also been enamelled[52,53] and provided good combinations of strength, appearance and corrosion resistance.

5. PRETREATMENT

The choice of pretreatment for vitreous enamelling was mainly governed by the composition of the alloy being processed but, as with other forms of metal finishing, cleanness of the surface to be coated was essential. When discussing a procedure for the evaluation of organic contamination on sheet metal, Currie[54] suggested that the presence of only 0.43 mg/dm^2 (4 mg/ft^2) of carbon would

interfere with the adhesion of a vitreous enamel coating, although at this level of contamination a conventional water-break test would give a satisfactory result.

Alloys 1100, 3003 and clad sheet materials generally only required a thorough cleaning in an organic solvent such as trichloroethylene and/or a mildly alkaline solution. After alkaline cleaning the aluminium required a desmutting operation in an acid solution (e.g., 20% nitric acid) followed by a final rinse in demineralized or distilled water. Water staining in conjunction with dried-on residues from rinse tanks could cause localized failure of enamel adhesion. Badly contaminated surfaces could require shot blasting, and pre-firing of the metal at between 400 and 500°C produced a uniform oxide layer[55] which assisted enamel adhesion.

Magnesium-silicide and magnesium-zinc-aluminium alloys required a chemical oxidation treatment before enamelling. In the du Pont[56] pretreatment procedure, parts were first cleaned by immersing them in a 0.6% solution of sulphuric acid containing a small amount of wetting agent and then, after rinsing in water, were immersed in an alkaline chromate solution approximating to the following composition:

chromic acid	0.2%
potassium dichromate	15.0%
sodium hydroxide	8.0%

Cast alloys were treated for 7 minutes at 40°C, and wrought alloys for 4 minutes at 50°C. After water rinsing and drying the treated parts were prefired at 400-500°C.

In the Alcoa R100 process,[57] which also used an alkaline chromate conditioning treatment, the prefiring operation was considered to be optional although it was originally recommended.

Castings which came to the enamelling shop straight from the foundry were often cleaner than wrought products but showed a tendency to dewetting during the firing operation. This was corrected, according to Whitaker,[58] by pickling in caustic soda followed by a nitric acid (50%) dip. Nitric-hydrofluoric acid solutions were also found suitable, particularly for the treatment of silicon-containing alloys. Castings containing large amounts of copper or manganese were not found suitable for enamelling."

Bailey[19] described the effect of various pretreatments on the appearance and adhesion of two lead-free enamels on different wrought and cast alloys. He concluded that although there was convincing evidence that the presence of the natural oxide film on aluminium aided the adhesion of enamel, artificial films such as those formed by chemical oxidation in M.B.V., Alrok or Alocrom solutions, and by phosphate processes such as Bonderizing, gave poorly adherent enamel films. The worst results were obtained by applying the enamel to anodized aluminium. The best adhesion results were obtained on shot blasted or prefired surfaces. while Pylumizing gave only slightly lower adhesion values.

The work by Bailey did show that aluminium gave, on the whole, better results than most of its alloys. These results were only partially confirmed by Yamada,[60.61] who found that while chemical oxide coatings proved satisfactory as a basis for lead-free phosphate frits, anodized aluminium gave a far better bond and stood up better to thermal shock. Yamada[62] made a further study of enamel/metal interfaces, using the electron microscope, and concluded that the anodic pretreatment produced a compact uniform film, and that the intermediate layer formed enhanced the enamel adhesion. The oxide films formed by chemical treatment contained cracks through which the enamel could penetrate to the basis metal, causing discoloration and spalling of the enamel.

Gugeler and Ballard[63] also studied aluminium/vitreous enamel interfaces as part of an investigation into the mechanism of adhesion of vitreous enamels to aluminium. An electron microscope examination of various cross sections of the aluminium/enamel interface showed variations in microstructure. Those specimens which had good spall resistance showed a smooth uninterrupted transition from aluminium to enamel, while poor spall resistance was associated with a layer of variable continuity which would be susceptible to corrosion. This work, as already indicated, was confirmed by Baker,[?] who showed how the presence of magnesium affected this intermediate layer, and by Howlett[13] who stated that magnesium in alloys for vitreous enamelling should either be absent or in the form of intermetallic particles such as Mg_2Si. The presence of MgO in the intermediate layer has been confirmed by German workers.[64]

Various modified pretreatments which improved the adhesion of vitreous enamel to aluminium alloys have been suggested. Pretreatments for lead-bearing enamels required stricter control than those used with lead-free ones. Three recommended solutions are given in Table 15-5.

The use of a pickling operation in a 6% sulphuric acid solution prior to chemical conditioning was suggested by Sigler.[65]

TABLE 15-5

Alkaline chromate solutions for keying leaded frits

	I		*II*		*III*
	lb/gal	*g/l*	*lb/gal*	*g/l*	*per cent* **(wt)**
sodium hydroxide	1.94	194	1.19	119	4
potassium chromate	0.39	37	–	–	20
chromic acid	–	–	1.00	100	–
chromic sulphate	0.02	2	0.02	2	–

Treatment in strongly alkaline solutions of sodium molybdate or tungstate containing borax and a chelating agent was claimed to improve the adhesion of enamel to aluminium.[66] The use of an alkaline solution of antimony oxide in conjunction with a prefiring operation has also been proposed.[67]

6. ENAMEL PREPARATION

Vitreous enamels for use on aluminium are generally supplied **in** the form of frits, and methods of manufacture have been described elsewhere.[14,15] The enamel slip was prepared by grinding the frit together with appropriate mill additions (Table 15-6) into a water suspension in a porcelain-lined ball or pebble mill.

TABLE 15-6

Typical ball mill formula for an aluminium enamel"

Frit	100.0 parts
Boric acid	3.0
Potassium hydroxide	2.5
Sodium silicate	2.0
Potassium silicate	4.0
Titanium dioxide	10.0
Colour oxide	5.0
Deionized water	38.0

In such a formulation boric acid was present to promote setting and improve ageing, potassium hydroxide to increase the enamel-metal reaction, sodium and potassium silicate to promote gloss and help firing, and titanium dioxide as an opacifier.[68]

Milling techniques were developed for vitreous enamels for aluminium[6"] and the grinding was much finer than for sheet steel enamels, so that from a 50 ml sample less than 0.1 g was retained on a 325 mesh sieve.[70] The relative density was maintained between 1.8 and 2.1. Clay additions were not normally made to enamels for use on aluminium but small additions were used to produce a matt finish, although anatase grades of titanium dioxide were more frequently used for this purpose.

In a good general description of vitreous enamelling practice, Hoens and Kreuter[72] pointed out the importance of avoiding impurities in the milling agents. The slip had to be stored cold, and agglomerating or ageing reactions had to be

eliminated. The slip should be applied relatively wet and a dry weight of about 150 g/m^2 was required to give a final fired coating thickness of about 70 μm.

The coating thickness of aluminium enamels was usually maintained between 75 and 125 μm (3-5 mil), and they were applied in a single application. Yellows and pastel shades were often applied as two-coat systems.[73] Water-soluble thixotropic resins have been described[74] for use in conjunction with a frit to produce a vitreous enamel which looked, felt and was applied like a paint. The organic portion was burnt off during the firing operation leaving a thin coating of vitreous enamel.

7. APPLICATION METHODS

Automatic or hand spraying were the most usual methods of applying vitreous enamels to aluminium. Enamels were also applied by flow coating,[75] slushing, or by dipping the work in the wet slip. Less frequently they were applied dry, using a metal spray pistol of the powder type.[76,77]

Electrostatic spraying of vitreous enamels was carried out at a number of installations in the U.S.A. and in Europe. The development of electrostatic spraying and its application to production was described by a number of workers.[78,79] Hughes[80] described the effects of time, temperature and voltage on the thickness of the enamel coating deposited on metal from simple suspensions of solids by electrophoretic techniques, and Plankenhorn[81] referred to the encapsulation of ceramic particles in an organic gel before dispersion in a slurry used for electrophoretic deposition of a vitreous enamel coating. German workers suggested electrophoretic deposition of enamel.[82]

The use of preheated metal near to the melting point of the enamel has been suggested,[83] but generally enamels were applied at room temperature and fired while still wet. This was important to avoid hairline cracks and blister formation.[72]

A flow chart outlining the sequence of operations possible in the vitreous enamelling of aluminium is shown in Fig. 15-3.

8. FIRING

This operation was best carried out in a muffle furnace at temperatures varying with the enamel composition between 500 and 550°C. Firing of enamels on aluminium had to be rather more strictly controlled than on other substrates and the furnace temperature had to be regulated within ± 10°C. This was particularly important when the firing temperature was near the melting point of the alloy, or the article could be distorted, or the mechanical properties could be impaired.

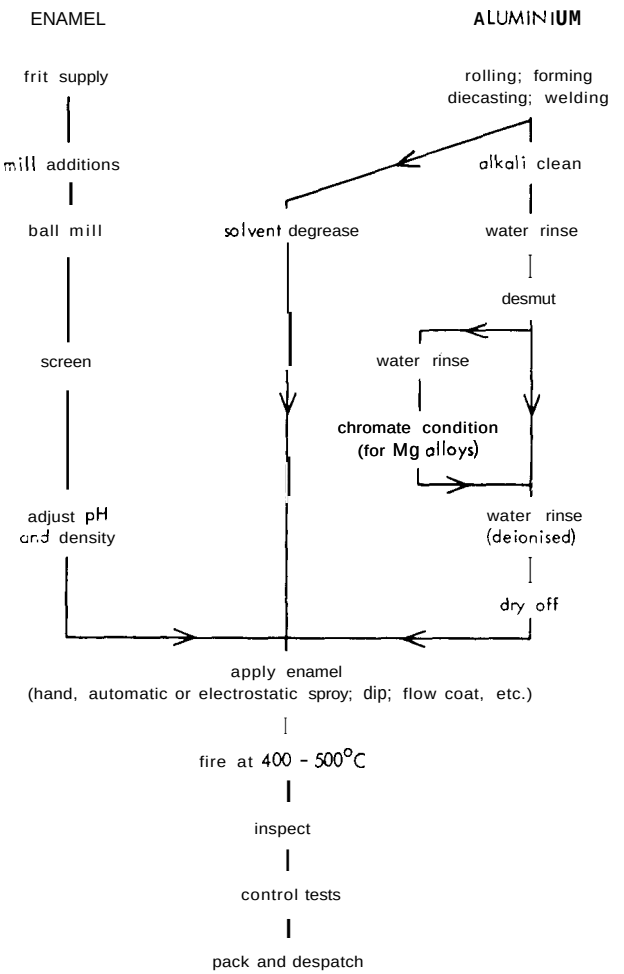

Fig. 15-3. Flow line diagram for the vitreous enamelling of aluminium

Adequate air circulation had to be provided in the muffle to avoid over-heating in parts of the muffle. Filtered air had to be used for this purpose if possible.

Sullivan and King[84] showed that the presence of water vapour in the furnace atmosphere improved the appearance and chemical durability of enamel coatings on aluminium, and Baker" found that it did not affect tendency to spalling. An excessive amount of sulphur in the atmosphere could be the cause of large bubble formation in the enamel coating, and Engler[85] suggested that sulphur might be produced from the enamel itself (from sulphates or sulphides) as well as from the fuel used.

Firing was normally carried out for 7-15 min. at 550-560°C for non-leaded enamels and 520-580°C for leaded enamels. The time was not particularly critical, but it was essential to ensure that the work reached the desired temperature and that the time was long enough to ensure complete fusion of the enamel. Schulze *et al.*[64] showed that 20-30 min. firing was required with leaded enamels to ensure complete wetting of the metal surface. In other work,"' up to 60 min. firing was given, with only slight loss in the intensity ofcolour, where a coloured enamel had been applied over a colourless ground-coat. In a continuous furnace, the work was rapidly pre-heated to 450°C and reached 560°C almost immediately on reaching the firing zone. The cooling time to room temperature was about 5 minutes.[51]

Electric convection and radiation, and gas radiant tube furnaces could be used, the first being the most generally suitable.

The firing temperature affects the choice of enamel for specific aluminium alloys. As an instance of this, the higher temperatures used for firing lead-free enamels rendered these unsuitable for the heavy-metal-containing heat-treatable alloys. It was important that those alloys which did not undergo solution-heat treatment were also annealed at the firing temperature and were, therefore, in the soft condition after firing. On the other hand, some of the lead-silicate enamels were found to withstand quenching in water from the firing temperature[86] and this could permit a combination of firing with heat-treatment, thus enabling the full development of the mechanical properties on some of the wrought or cast alloys.

9. DEFECTS

If an enamel coat was cracked or blistered it could be possible to apply a very thin new coat over the old one. Cracked enamel could be due to a number of causes, such as poor cleaning, incorrect mill composition, application of too thick a coating (over 4.3-7.5 g/dm^2 (40-70 g/sq ft) solid enamel constituents), or too rapid drying. Cracks and blisters could also occur if the enamel was not 'wet' when it entered the furnace, due to gas evolution in the initial stages of firing. Pits and craters in the enamel could result when the metal was highly porous or its gas content was too high. or when the frit itself reacted with the metal to form gaseous reaction products. The same defect might also be caused by spraying enamel at too high a pressure. 'Strain-lining', another form of cracking,[45] was caused by double firing treatments, which were required when two or more colours were being used.

The microsection shown in Fig. 15-4 illustrates extensive bubble development in a vitreous enamel layer. The bubbles are numerous but not very large and could be innocuous except where they break the surface to appear as pits. Trouble could be occasioned however if they coalesced during firing to form larger bubbles. Fig. 15-5 illustrates spalling of enamel from 1100 aluminium, where the fracture is initiated at a bubble on the surface of the aluminium and tends to follow a line of bubbles through the coating.

As in spray painting, it was very important that dust was not allowed to settle on a freshly-applied wet enamel coating.

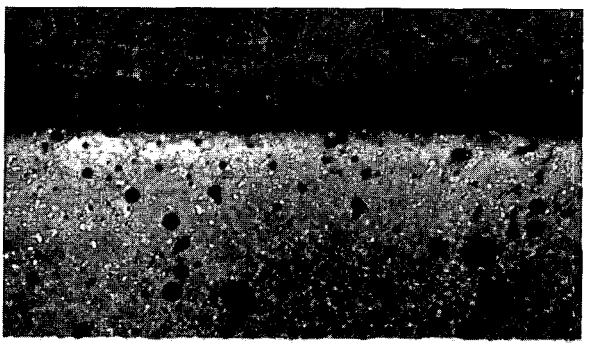

Fig. 15-4. Cross section of vitreous enamel coating showing extensive bubble development. Magnification x 500

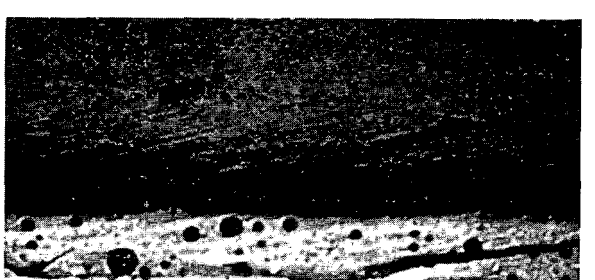

Fig. 15-5. Cross section of vitreous enamel on 1100 aluminium showing spalling associated with bubble formation. Magnification x 250

10. ENAMELLING IN ARCHITECTURE

The architectural use of vitreous enamelled aluminium in Great Britain[87,88] did not develop to the same extent as it did in the U.S.A.[89,90] where one manufacturer" reported that up to 1968 over 5 million square feet (465,000 m^2) of finished panels had been erected in exposed conditions. Building applications included profiles, wall and roof panels,[87,88] shop fittings[65] and roof fascia." The use of enamelled road signs[92,93] and decorative screens[94] has also been described. Most applications in Great Britain were on commercial purity aluminium (1 100) and Al-1¼% Mn alloy (3003), and a one coat application was generally considered adequate. Other applications include flats and office buildings.[95] On the continent, vitreous enamelling was used particularly in Germany, and Bunk[96] described buildings produced in the late 1950s. Grosskopf[97] in 1978 estimated that 800-1000 vitreous enamelled aluminium facades had been produced in Europe, and this included thermal facings for sandwich panels as well as purely decorative applications.

Alloys used in the U.S.A. for vitreous enamelled architectural parts as well as for column covers, ships' bulkheads and highway control and sign posts,[98] included 1100,3003,6061,6062,6063, and 43 and 356 casting alloys. Of these, 1100 and 3003 were usually enamelled directly while the others were frequently prepared by applying a phosphate/chromate conversion coating. 0.1 mm (4 mil) enamel coatings were applied by spraying or dipping and were fired at 500-550°C. Such coatings could be sawn, panelled, drilled or cut and subjected to moderate forming operations without damage.

Considerations relating to alloy, design and fabrication when using vitreous enamelled aluminium were given in PEI document P-402(69).[44] In particular the importance of using 'porcelain enamel grade' clad sheet alloys, and the care necessary in the selection of products for vitreous enamelling, were stressed. In the latter case it was important to avoid sharp edged patterns or designs, and an absolute minimum radius of 1.5 mm ($^1/_{16}$ inch), preferably a minimum of 3 mm ($^1/_8$ inch), was recommended when using extruded sections. In welding fabrications, magnesium containing filler wires should not be used.

11. TESTS ON ENAMELLED ALUMINIUM

There are currently no British Standards Institution tests for the assessment of the quality of vitreous enamels applied specifically to aluminium. However, the test procedures given in the various parts of B.S. 1344[99] are suitable for the quality control of enamels on aluminium. The greater use of enamelled aluminium in the U.S.A. has resulted in the issue of a recommendation in that country for testing procedures for vitreous enamels on aluminium.[100,101] The porcelain Enamel Institute

in the U.S.A. also produced a specification for external architectural use of vitreous enamel."" This required tests for acid resistance, and spall resistance, and indicated a minimum coating thickness requirement of 50 microns (2 mil).

Bailey and Whitaker[86] have described fourteen tests which are suitable for the evaluation of enamels on aluminium and some of their best results are shown in Table 15-7.

Thermal Shock (B.S. 1344, Part 1: 1994 and Part 16: 1998 (ISO 2747))

When the method of evaluating thermal shock was revised it was divided into two parts, the first (Part 1 of B.S. 1344) dealing with thermal shock on articles other than cooking utensils, and the second (Part 16) dealing with thermal shock on cooking utensils.

In the first test, a specimen about 320 cm^2 (50 in^2) in area is heated to 185-195°C within 10 min. by radiant heat and placed within 5 sec. in a standard stream of water at 15-20°C. This cycle is repeated six times, failure being shown by flaking or crazing of the coating.

In the cooking utensil test a series of single thermal shock tests, with a temperature increase of 20°C each time, is carried out. The specimen is heated from the outside and then chilled inside with water at 20°C. The initial temperature used is 200°C and this is raised in 20° intervals until failure occurs. Testing is carried out on at least three utensils which are representative of the batch, and the average failure temperature of the utensils is reported.

Resistance to Heat (B.S 1344, Part 7: 1984 (ISO 4530))

Here the specimen is heated so that the temperature of the enamelled surface rises at a uniform rate of 30-40°C per min. to 50°C above the specified usage temperature of the component. The specimen is maintained at this temperature for an agreed period and is then allowed to cool to atmospheric temperature. If no failure, in the form of cracking, flaking or blistering, occurs, the heating and cooling cycle is repeated until damage takes place, or the agreed number of heating and cooling cycles has been carried out.

Abrasion test

The specimen is abraded with lumps of eight abrasives, viz.:

1.	Talc	5.	Apatite
2.	Selenite	6.	Felspar
3.	Calcite	7.	Quartz
4.	Fluorspar	8.	Topaz.

TABLE 15-7

Results of performance tests on enamels applied to commercially pure aluminium[19]

Enamel finish	*Pre-treatment*	*Abrasion (hardness) test*	*Acid test*	*Alkali test*	*Deterroration of gloss*			*Humidity test*	*Lead solubility test*	*Spalling* test*	*Weathering*
					Cold water test	*Boiling water test*	*Steam test*				
Lead-base undercoat and top coat U.S.A. **1949**	Special pickle	**4**	Passed except red sample	Red and blue dulled. Rest passed	Passed	Passed	–	Passed. Slight dulling	–	Passed	After **12** months marine atmosphere, slight **loss** of **gloss,** flaking and some cracks
Lead-free two coats, Gt. Britain **1949**	Pickled	6	Red and blue bleached. Rest passed	Failed	Passed	Passed	–	No change	–	Passed	
Lead-base blue, two coats, U.S.A.	Pre-fired	3	Passed	Passed. Some loss of gloss	Passed	Passed	–	Passed	Ground **54%.** Cover coat 52% PbO	Passed	Surface dulled after **4** months in an industrial atmosphere - no spalling
Lead-free three coats U.S.A. **1950**	Special Cu interlayer	6	Passed	Failed	Passed	Failed	–	Passed		Passed	
Lead-base two coats U.S.A. **1946**	Not stated	**4**	Failed, except yellow. white, and deep blue		Passed	Passed	Slight **loss** of gloss	Slight loss of gloss	Ground 56%. Blue cover **13%** PbO	Passed	After 2 years industrial environment, yellow, green and blue unaffected. Red and white failed
Lead-base two-coats, Gt. Britain **1948**	None	***5***	Failed	Failed	Same loss of glass	Some **loss** of **gloss**	Some loss of **gloss**	Failed	**56-90%** PbO	-	Gloss deteriorated and colour faded in green and yellow. 17 months industrial atmosphere
Lead-free, Gt. Britain **1948**	Not stated	*6*	Failed	Failed	Passed	Passed	Passed	Passed	–	–	Gloss and colour of white and green deteriorated after 6 months industrial atmosphere with spalling

* Immersion in 5% ammonium chloride to accelerate spalling; the amount of spalling in twenty-four hours or ninety-six hours gives some indication of the probable adhesion in service.

The softest of these which causes the appearance of scratches seen by the naked eye determines the hardness number. Among the enamels tested, a lead-free coating obtained a rating of 6, while others were already scratched by minerals 4 and 5. There is some evidence that colour, i.e., the pigment employed, affects the abrasion resistance.

An oscillating table, with a charge of steel balls and sand, is described in the obsolescent B.S. 1344, Part 4: 1968 for measurement of the abrasion resistance of vitreous enamel finishes. The weight loss of the specimen was determined in this method.

Qualitative impact test

A 1 in. diameter steel ball attached to a *2* lb. weight is dropped through 15 in. onto the surface, which is supported during test. This test also gives some indication of the degree of adhesion of the coating.

Bend test

Strips enamelled on one side are bent slowly around a 9 mm diameter former through an angle of 180 degrees. The enamel cracks or crazes at the bend and the adhesion is indicated by the tendency to flake. Due to their greater hardness, the leaded enamels have a stronger tendency to crack in this and the preceding test.

Resistance to alkali (B.S. 1344, Part 6: 1971)

The test specimen is immersed in a 5% solution of anhydrous sodium carbonate maintained at 80 ±5°C for 20 min. The surface of the enamel is rubbed with a small quantity of colloidal graphite. A uniform staining of the enamel indicates a lack of resistance to alkali.

Resistance to citric acid at room temperature (B.S. 1344, Part 2: 1975 (ISO 2722))

A few drops of a 10% (wt) citric acid solution are placed on the specimen at 23°C and left for 15 min. The degree of enamel attack is assessed by marking the treated area and the adjacent untreated area with a HB pencil. Various classifications for acid resistance are used in this test.

Resistance to boiling citric acid (B.S. 1344, Part 8: 1984 (ISO 2742))

In this test the specimen is fixed into a cylindrical testing apparatus so that it forms the bottom of the cylinder. 450 ml of a 6% (wt) citric acid solution is placed in the cylinder and the solution simmered at boiling point for 2% hours. Other times up to 24 hours are sometimes used. The loss of mass from the specimen as a result of the test is recorded.

Steam test

Specimens are exposed to steam for 2 to 4 minutes in order to reach *50°C* and held at this temperature for 2 minutes before being allowed to dry and cool. The cycle is repeated 10 times. Lead-based enamels are attacked by this test. Enamelled iron and stoved paints on aluminium are unaffected. Lead-free enamels on aluminium are intermediate.

Humidity test

The specimens are placed horizontally above water in an air-tight container at normally fluctuating room temperature. Lead-less enamels fare better in this test than leaded ones, though inferior to stoved paints or enamelled iron.

Resistance to cold water

Six days' immersion in distilled water causes permanent damage to some of the lead-bearing enamels.

Resistance to boiling water (B.S. 1344, Part 9: 1998 (ISO 2744))

Bailey and Whitaker[86] showed that six hours immersion in boiling water caused, on the whole, less damage than the last test. Vitreous enamels stood up better than stoved paint finishes to this test.

B.S. 1344, Part 9: 1998 gives a test procedure involving 48 hours contact with boiling water, and the loss in mass after this period is measured.

Salt spray

Twice daily salt spray (3% NaCl) showed no attack on lead-free enamels after two months.

Resistance to spalling

The evaluation of resistance to spalling is probably the most important single test used for the evaluation of enamels on aluminium. The standard method of evaluating spall resistance has been to use a 5% (wt) ammonium chloride solution for a period of 96 hours at room temperature, but it is generally considered that the more severe 1% (wt) antimony trichloride test, which was developed specifically for vitreous enamelled aluminium is preferable. B.S. 1344 does not cover a spalling test, but ASTM C703-72 (1993) covers both the ammonium chloride and the antimony trichloride tests, and PEI T51 covers the antimony trichloride test. In the antimony trichloride test the specimen is left in contact with the solution for 20 hours.

The introduction to ASTM C703 indicates that 'it is difficult to over-emphasise the importance of the spall test. Porcelain enamelled aluminium that fails this test will probably spall in service if subjected to moisture or weathering'. A failure in the spall tests is indicated by any spall area extending 3 mm ($^1/_8$ inch) or more in from an edge and more than 25 mm (1 inch) in length, or more than 6 spall spots in an area of 929 cm^2 (1 ft') on an interior surface.[102] Specimens for test are usually cut from production parts and it is important that the metal-enamel interface is exposed before testing. Specimens are often bent round a mandrel to crack the enamel, in order to do this.

Resistance to weathering

In the Bailey and Whitaker work[86] exposure to a mildly industrial atmosphere showed up considerable differences in the behaviour of different enamels, which failed after periods varying from 1 day to 6 weeks. Leaded enamels were inferior and there was a definite correlation between results from this test and water and chemical tests. Again, the colour of the enamel was significant.

Rushmer and Burdick[103] described the testing of steel and aluminium enamelled panels for 7 years at various sites in the U.S.A., and related the results obtained to the acid resistance values of the enamels. Similar work, based on a 3 year exposure test, was reported by Moore and Potter[104] who commented that while some red and yellow enamels had good acid resistance they showed very poor colour stability. Baker reported weathering tests on matte and glossy enamels on steel and aluminium,'"' and excellent correlation was found between accelerated results and those obtained during outdoor exposure.

Home Office solubility test

The powdered frit is shaken for 1 hour with 1000 times its weight of 0.25% hydrochloric acid solution. The solution is allowed to stand for 1 hour, filtered and lead is precipitated as lead sulphide in an aliquot of the filtrate and is converted to lead sulphate and weighed.

The values obtained with several leaded enamels lay between 13 and 90% PbO, the higher values being those of samples of poorer resistance to chemical attack and weathering. The results obtained by this test mean, however, that Health and Safety regulations regarding the protection of operators apply in processing such enamels, while their unsuitability for application to components that come in contact with foodstuffs is clearly indicated.

12. COMPARISON WITH ORGANIC FINISHING AND WITH ANODIZING

Although the use of vitreous enamelled aluminium developed rapidly in the 1960s, it never achieved the widespread use predicted for it, and today it is used only for relatively few specialized applications. In many applications, vitreous enamelling must compete with organic and anodic finishes. The organic type of finish is much less critical in the merhod of its application, is considerably cheaper both in material and processing costs and does not require heat-treatment at high temperatures. Furthermore, the development of organic finishes is rapid and backed by powerful industrial firms willing to spend time and money on research, particularly, of course, because as distinct from enamels, the organic coatings applied to aluminium alloys are the same as those for other metals. It was this development of improved organic coatings, especially for extrusions and continuous coil coating of sheet, that made vitreous enamelling uneconomical.

Anodizing will produce coatings of almost comparable abrasion resistance on sheet material at much lower cost than enamelling, and anodic coatings of the colour and appearance of enamels can be obtained by the Ematal and related processes such as the integral colour anodizing processes described in Chapter 8. Colour anodized finishes are widely used for exterior cladding of buildings, but anodic coatings do not have the resistance to chemical attack by alkalis which vitreous enamels display.

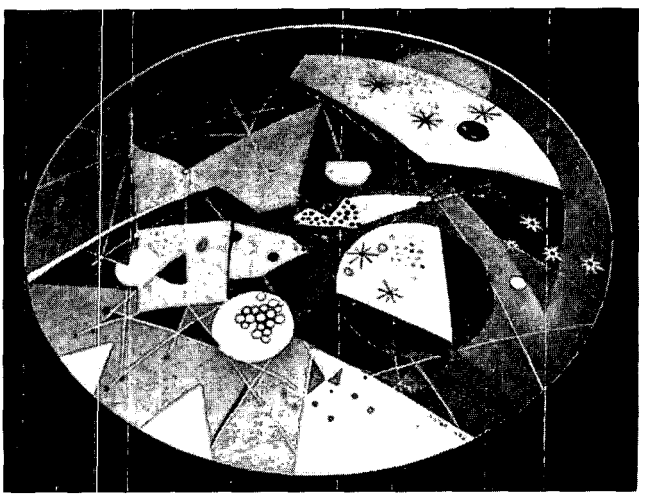

Fig. 15-6. A vitreous enamelled aluminium plaque. The decorative technique, of which this is an example, was developed by Edward Winter in the U.S.A. with the use of du Pont enamels

There seemed to be a field of application for vitreous enamelled aluminium for architectural applications, holloware and domestic fittings, but in many of these areas vitreous enamelling was overtaken by the improved organic coatings that have been developed. Nevertheless Grosskopf in 1978[97] described uses in Germany in architecture, gas flues and oven pipes (aluminium-clad steel), sanitary ware and particularly holloware. In this latter field the ease of cleaning of the enamelled surface was an important factor, and, in architecture, the ability, as distinct from enamelled steel, of the enamelled aluminium to be drilled or sheared without fracture or spalling was significant. Against this, however, the high cost of enamelling, the necessity for special alloys and the uncertainty of performance of some of the lead-free enamels made it less attractive.

Applications where there were positive benefits for vitreous enamel coatings included its use as a substrate for abrasion-resistant non-stick coatings of PTFE on domestic kitchenware.[''' 107] In this case the enamel coating was applied sparingly as a discontinuous film with very little coverage. After firing, the PTFE was applied as an aqueous suspension, as described in Chapter 14, and sintered. The composite coating thus formed had a high wear resistance along with the non-stick properties of PTFE, since the minute projections of vitreous enamel bore any load or offered resistance to scratching or damage. The decorative enamel coat on the outside, and the enamel providing adhesion on the inside, could be fired together, and this system was said to be cheaper than flame spraying or coating with alumina as a basis for PTFE coating.[72]

Rocket exhaust nozzles made in aluminium have been finished internally with vitreous enamel to protect the metal from the high temperature gases that propel the rocket. Vitreous enamel was one of the few surfaces that could be washed free from radio-active contamination, and for this reason it could find application in the field of nuclear energy engineering.

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CHAPTER 16

Effluent from Aluminium Finishing Operations

1. GENERAL

Finishing processes that involve the chemical or electrochemical treatment of aluminium or the application of some form of coating to the aluminium substrate, inevitably produce some type of effluent. Irrespective of whether the effluent is toxic, non-toxic,, liquid or gaseous it usually requires some form of treatment. This treatment may be designed to achieve a number of objectives. One would be to render any toxic: constituents in the effluent harmless. Another would be to remove any contaminants or solids from rinse water, to a level where it meets the local authority wastewater discharge limits. These limits may be related to the public sewer or a local watercourse. Finally any spent process solutions or waste products would need to be treated to render them suitable for dumping. This may be done in situ by the plant effluent treatment system or they may be taken away and treated by an approved operator.

Environmental legislation[1,2,3] in most countries is now very stringent with respect to the treatment and handling of industrial waste. Discharge limits are by no means universal but they have been considerably tightened up in all countries over the past 10 years.

In the case of aluminium surface finishing operations the main practices employed are associated with the preparation of the surface to receive the coating and the application of the coating itself. These practices can be quite diverse depending upon the final coating required. Examples of the latter would be anodic

films, paint coatings, PTFE or electroplated coatings. Anodizing and painting are the most widely used finishes[4] for aluminium and as such they will be covered in the greatest detail in this chapter.

In many surface treatment operations the part or parts to be treated have to be immersed in or pass through a number of treatment stages. This is done by placing the parts on a suitable rack or conveyor by which they are transported through the various process stages. This may involve immersion in the process solution or passing through a spray station. Some process solution always remains on the parts as they are removed from or pass through a spray of the treatment solution. To prevent contamination of subsequent process solutions by this carry over it is usual to give the parts a water rinse between each process stage. This results in the rinse water becoming contaminated with process chemicals and hence the necessity to treat it before it can be reused or discharged.

Chemicals in process solutions are usually consumed in two ways, one is by the reaction that may occur in the process stage itself, the other is by carry over or drag out into the post process rinse. The latter is often the greatest source of usage of chemicals in a finishing process. In the case where chemicals are consumed in a process reaction there is inevitably a build up of the reaction by-product in the process solution. This is mainly aluminium but, depending upon the type of aluminium alloy being processed, alloying elements such as Fe, Si, Mg, Mn, Cu and Zn may also build up in the process solutions. This contamination may mean that the solution efficiency is reduced and that it has to be dumped or partly dumped and replenished with active ingredients to maintain its function. This dumping or partial dumping of process solutions can produce a major proportion of the effluent requiring treatment.

Periodic bulk dumping can put a considerable strain on any effluent treatment system and a better practice is to continuously dump a small volume of a solution to control its contamination. If this is not practical then the dumped solution should be held in a suitable container from which it can be slowly fed under controlled conditions into the effluent treatment plant. This minimises surge conditions in the treatment plant. The alternative is to have the used solutions tankered away, treated and discharged by an approved effluent disposal company.

The technology is now available to treat many process solutions to remove the contaminants and to recover the active ingredient and return it to the process solution. These processes will produce a by-product, which still has to be dealt with, but they do save on chemical costs and considerably reduce the solids content of the rinse water effluent.

Gaseous effluent also has to be dealt with; this may be solvent fumes, gases from a hot process solution, spray from the solution due to the chemical reactions occurring or overspray from spray pretreatments. Systems involving solvents, such as some paints, will require specialised fume extraction technology to render the effluent harmless. Fume scrubbing techniques are available for most gaseous effluent. Dusts can cause explosion hazards and the appropriate precautions need to be taken.

Consideration is given to aluminium finishing operations that can be conveniently divided into specific groups. These are pre-treatment for anodizing, the anodizing process and its post treatments, pre-treatment for painting, the painting processes and pre-treatment for electroplating. Electroplating on aluminium is the same as electroplating on any other metal once a specialised surface conditioning treatment has been carried out on the aluminium. Many books and papers have been written on the subject of effluent treatment in plating plants and the recovery of plating solution chemicals and, as such, this subject will not be covered in this Chapter.

2. ANODIZING PLANT PROCESS EFFLUENT

Anodizing plants consist of a series of well-defined stages, which are pre-treatment, anodizing, colouring and sealing. These stages are described in greater detail elsewhere in this book and only factors relevant to the process effluent and its treatment will be discussed in this Chapter.

Pre-treatment

The pre-treatment stage is usually a degrease followed by chemical etching or brightening after which there is usually a desniut.

Degreases are usually non-etching alkaline' solutions, as the use of trichloroethylene vapour degreasing is now covered by very stringent regulations[6,7,8,9]. Emulsion cleaners have never found any real favour in anodizing plants. Degrease solutions generally have a long life and do not produce any fumes other than water vapour. Acid cleaners are generally preferred by the aerospace industry'".

The etch formulations" used are usually based on NaOH with the addition of sequestering agents and a surfactant. They are operated at around 60°C. Most etching practices remove from 50 to 100 g of aluminium per square metre of surface processed. The aluminium builds up in the etching solution until either it precipitates, or an equilibrium is reached, where the amount of aluminium being dissolved into the etch equals the amount of aluminium removed by drag out. This is the principle of the long life etch. It is really a form of continuous dumping into the rinse water system, controlled by the throughput in the line. Should it be necessary to control the aluminium at a level below the equilibrium it is usually necessary to periodically dump part of the solution or regularly bleed off some of the solution into the effluent treatment system, the quantity dumped being controlled by analysis or in proportion to the production throughput.

The fumes from the etching solution can contain caustic droplets and as such are usually extracted at the tank via lip extraction. An overhead roof extraction fan

is often used to remove any spray from the work pieces while in transit from the etch to the post etch rinse. The fumes may be scrubbed with water, which is then returned to the effluent rinse water treatment system.

Chemical brightening[12] produces a degree of specularity to the part, and it is usually carried out in solutions based on mixtures of concentrated acids at about 100°C. It is not as widely used as matt etching but bright-anodized aluminium trim or hollow ware are still produced. **A** typical brightening solution removes about 50 g of aluminium per square metre of surface processed. The solution is very viscous and drag out loss to the post brightening rinse is high. During the brightening process, fumes containing acid droplets are released and some solutions generate nitrous oxide. These both require extracting **and** scrubbing with an ammoniacal or other alkaline solution. The solutions have a long life and are replenished with acid or water, based on chemical analyses.

Desmut solutions[13] are acidic in nature, are relatively dilute and are operated at room temperature. They have a long life and are usually replenished with acid to replace drag out losses. Generally they do not produce any fume and are usually not extracted.

Anodizing

The electrochemical anodizing process is carried out in an acid electrolyte[14]. The most common electrolyte is sulphuric acid; other electrolytes used are phosphoric acid and chromic acid. During the anodizing process some aluminium is dissolved into the electrolyte and the aluminium concentration will usually require controlling below a maximum level. Although some aluminium is removed by drag out into the post anodizing rinse, it is usually necessary to remove aluminium in some other way to keep its concentration below the permitted maximum. This may be done by periodic dumping of part of the electrolyte, or regular bleed off into the effluent treatment system, based on chemical analysis of the electrolyte or empirically on a production throughput basis.

During the anodizing process acid spray is produced by gas evolution and air agitation of the electrolyte. Spray suppressants are used in these electrolytes but, if this is not effective in maintaining good working conditions, then fume extraction is required. The fume is usually scrubbed with water before discharging to the atmosphere. The water from the scrubber can be treated in the anodizing effluent treatment plant.

Colouring

The colouring of anodized aluminium can be carried out in a number of ways[15]; the main processes being integral colour anodizing, electrolytic pigmentation in a metal salt solution or pigmentation with organic or inorganic dyes.

The integral anodizing process requires a special electrolyte containing sulphonic acids, oxalic acid or mixtures with organic acids. The process is little used these days because of its high energy requirements, but where used appropriate treatment of any of the acids discharged to the rinse water would need consideration.

The most common architectural colour anodizing practices use electrolytic colouring. Solutions of Sn, Co, Ni or Cu salts are used in these processes, the most common being the Sn or Co based electrolytes. The main consumption of chemicals in these electrolytes is by drag out into the post process rinse. The Sn electrolyte is more acidic than the Co electrolyte but both can be neutralised, and the metals removed, in the effluent treatment system.

The dye solutions used are normally operated around 60°C and again solution is lost by drag out to the post dye rinses. The main effect of this is a discolouration of the water. To prevent the discolouration of all the effluent rinse water a static rinse may be used after the dye solution, from which the dye is usually removed by a suitable carbon filter on a closed loop system.

There is no significant fume produced by these processes.

Sealing[16]

The hydrothermal sealing process uses deionised water at 96 to 99°C; and the solution may also contain small quantities of nickel acetate or ammonium acetate. In addition, an anti-smut additive containing glucose or dextrose compounds, acrylic acid or phosphonic acid may be added in very small quantities. The sealing solution becomes contaminated with aluminium and sulphate ions. The aluminium tends to precipitate as the hydroxide when the level is much above 3 or 4 ppm; this does not inhibit the sealing process but results in an unacceptable white stain on the finished product. Contamination with sulphate ion, above about 400 ppm, tends to reduce the sealing efficiency of the solution. A common practice is to dump the seal bath on a regular basis, and this may be as frequent as once per week and will depend on the volume of solution and the quantity of work processed. The main problem with this is the high volume of hot water (can be as high as 30,000 litres) that has to be dumped. The nickel content of the solution is very low but it would be removed in the effluent treatment system.

The main fume problem with hydrothermal sealing is water vapour, and this can cause a problem with condensation. Extractor fans in the roof above the seal tank help to reduce the problem, as do sliding or hinged lids. Plastic insulating balls (croffles) floating on the surface are frequently used. Fume extraction is not recommended as it results in a considerable increase in the losses of water by evaporation.

An alternative sealing process is cold impregnation, and this is carried out in a nickel fluoride based solution at about 30°C. The recommended practice involves a post seal static hot water rinse. The solution has a relatively long life if the chemical composition is controlled, and it is filtered as required to remove any precipitates of metal hydroxides, which could stain the finished product. When the need arises to dump the post seal rinse or the seal bath itself, the nickel could be treated in the

conventional effluent treatment system but the fluoride may present a problem. There is no significant fume from this process.

3. ANODIZING PLANT PROCESS EFFLUENT TREATMENT OPTIONS

The efficient and economic design of any effluent treatment system relies on an accurate and detailed knowledge of the following:–

What is the effluent?

What are the local authority discharge limits to **a)** the sewer or b) the local river or water course?

What are the treatment options?

Does the local authority accept solid waste and in what form; if not where is the nearest approved dumping site?

What will be the transport and dumping charges for solid waste?

Can the solid waste be produced in a more useful and perhaps saleable form?

What constraints does the finish required put upon the selection of processes used for pre-treatment or anodizing?

Once this has been established it is then possible to look at the various options for treating the effluent and compare their economics. The cheapest plant to install may not always be the cheapest plant to run.

The effluent will essentially consist of rinse water containing aluminium, sodium and sulphate ions. In addition, it may also contain some cobalt, nickel or tin ions as well as small quantities of fluoride, sequestering agents, nitrate, phosphate, ammonium ions, acetate ions, carbonates, boric acid, tartaric acid, magnesium, iron, silicon, copper, manganese and zinc. The type and amount of any contaminant will depend upon the processes used, the drag out from these processes and the composition of the aluminium alloys being processed.

The rinse waters will be acid, alkaline or neutral depending upon the process from which the drag out originates. Neutralisation of these rinse waters will result in the precipitation of most metals, the predominant one being aluminium. These precipitated hydroxides can be separated from the rinse waters and further consolidated.

There are three main options that can be used to treat the anodizing process effluent, which are:–

1. Rinse water neutralisation and periodic partial dumping of the contaminated process solutions. The neutralised rinse water may be discharged to the sewer and the spent process solutions tankered away by an approved treatment company. The amount of process solution that has to be dumped will depend upon the maximum level of contamination it can tolerate and the rate of build up of that contaminant.

   This is the simplest option but it is not likely to comply with the present

environmenial legislation. Depending upon the rinse water volume allowable and the limit for suspended solids in the neutralised rinse water, the use of a long life etch with this option may or may not be possible.

2. An alternative is the use of a long life etch solution (continuous dumping by drag out) and continuous bleed off of other process solutions into the rinse water effluent to control the level of contaminants in the respective solution. This, in combination with neutralisation of rinse waters followed by precipitation and consolidation of solids, is a very common procedure. The treated rinse water is usually discharged to the sewer or a water course and the solids, which are in the form of a filter cake containing mainly aluminium hydroxide, are (dumped on an approved site. In some cases a use for these solids may be found such as the production of low-grade aluminium sulphate.

3. Conventional rinse water neutralisation in combination with the recovery of many of the process solutions is now an option that may be considered. Recovery or regeneration processes have been developed for sodium hydroxide based etching solutions and sulphuric acid or phosphoric acid anodizing solutions. The solutions are treated to remove the aluminium contaminant and the respective sodium hydroxide or acid is returned to the process baih. Similarly Ni or Co can be recovered in the case of electrolytic colouring electrolytes. This is achieved by removing the ions from a post process rinse and returning them to the colouring electrolyte.

This last option allows the aluminium levels in the etching and anodizing solutions to be controlled at a constant and relatively low level. This reduces the amount of aluminium dragged out into the rinse waters and hence the level of solids in the treated rinse waters. This can result in a considerable reduction in the size of the neutralisation, precipitation and filtration plant required to treat the rinse water. This will not, however, offset the added cost of the recovery systems, which entail considerable capital investment.

Figure 16-1 is a schematic diagram of a rinse water neutralisation system for a basic anodizing plant. There are often several rinse water stages between one process stage and the next. Where this is the case then it is normal to use counterflow rinsing[17] to conserve water.

Where an organic dye solution is being used it is normal to pass the post dye rinse through a carbon filter to remove dye pigment from the effluent stream.

It is good practice to separate the acid rinse water stream from the alkaline rinse water stream until the mixing tank in the effluent treatment plant. If the acid and alkaline rinse water streams are collected in separate holding tanks prior to mixing, these tanks serve as buffer tanks and prevent unnecessary surges of acid or alkaline rinse water into the effluent treatment mixing stage. This minimises seesawing of toe pH in the mixing tank and the excessive use of fresh acid or alkali to adjust these fluctuations in pH.

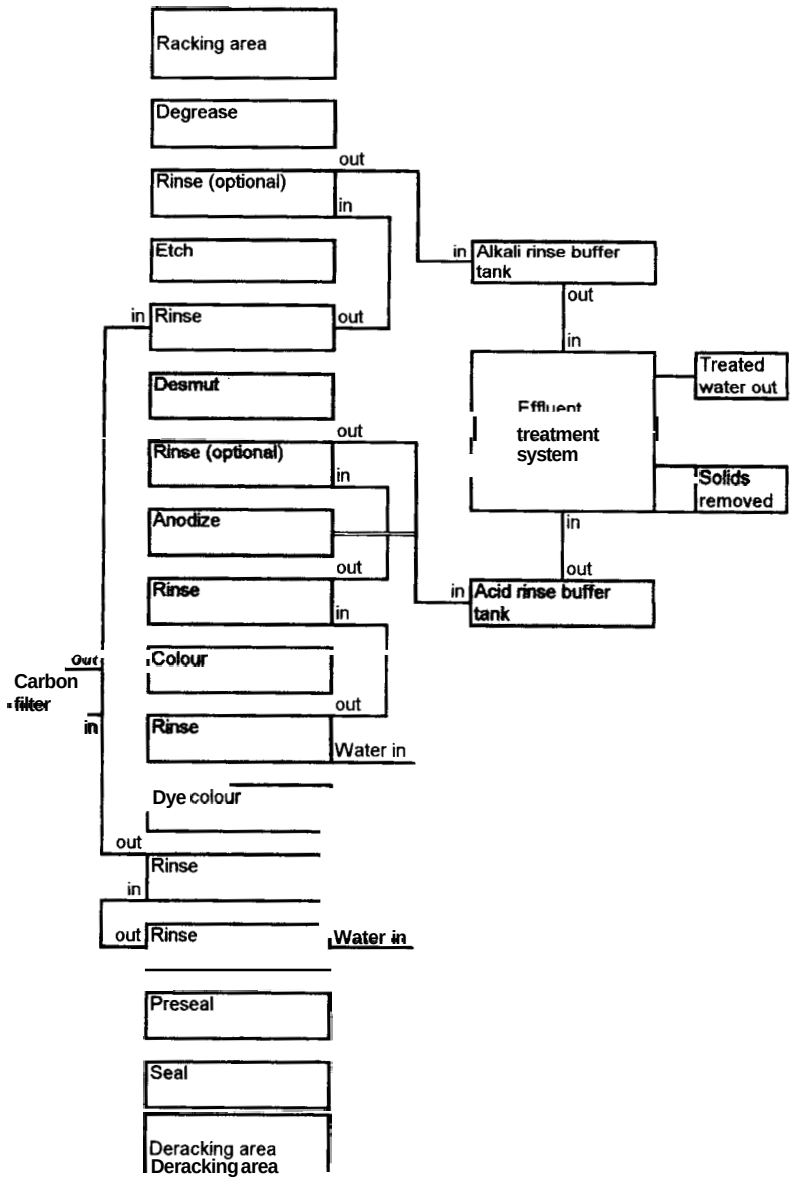


Fig. 16-1. Anodizing plant effluent treatment system

The options selected for operation of process solutions will influence how the etch and anodizing stages, are operated as well as the effluent plant design. In general the more recovery systems that are employed the smaller is the size of the effluent treatment plant. Each process stage can be considered separately.

Etching

Fig. 16-2 illustrates the options available for operating the etching solution and controlling its aluminium level.

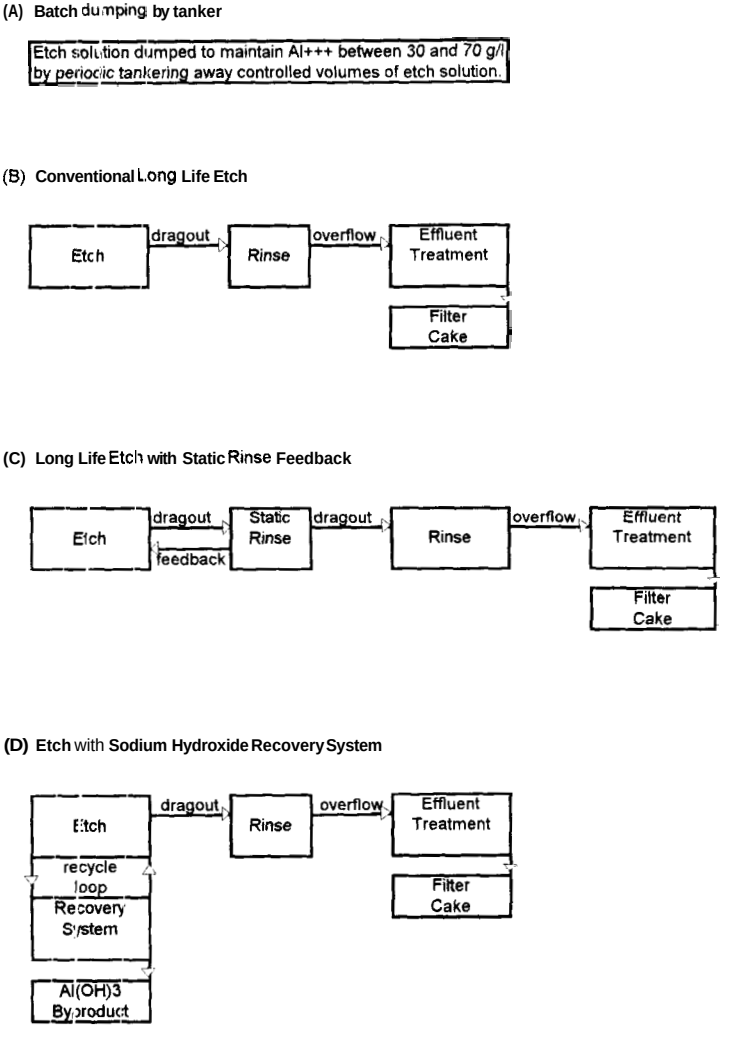


Fig. 16-2. Schematics of available etch operating systems

The most common etch system is the 'never dump' or 'long life' etch, the aluminium content of which is stabilised by drag out. The ratio of aluminium to free sodium hydroxide must be controlled to keep the aluminium in solution.

Using a static rinse after a long life etch to top up evaporative losses from the etching solution can increase the aluminium content of the solution to a level that is higher than can be obtained by the normal 'Long life' system. The higher aluminium content, and the additives required to hold the aluminium in solution, produce a good matt finish with less metal removal. This will result in a reduction of the level of solids in the effluent.

The principle of the regeneration process is based on the Bayer process. It[18,19] involves the recirculation of the etch solution between the etching tank and a crystalliser tank where a large percentage of the dissolved aluminium is precipitated, by seeding, as the alumina tri-hydrate. The precipitate can easily be dewatered to achieve a moisture content of less than 10%.

A schematic of the sodium hydroxide recovery system is illustrated in figure 16-3. The net effects of using such a regeneration system are:

- A reduction in sodium hydroxide consumption per square metre processed.
- Less acid required to neutralise the alkali rinse water.
- A reduction in the rinse water sludge filter cake volume and hence in waste disposal costs.
- **A** potentially saleable by-product.

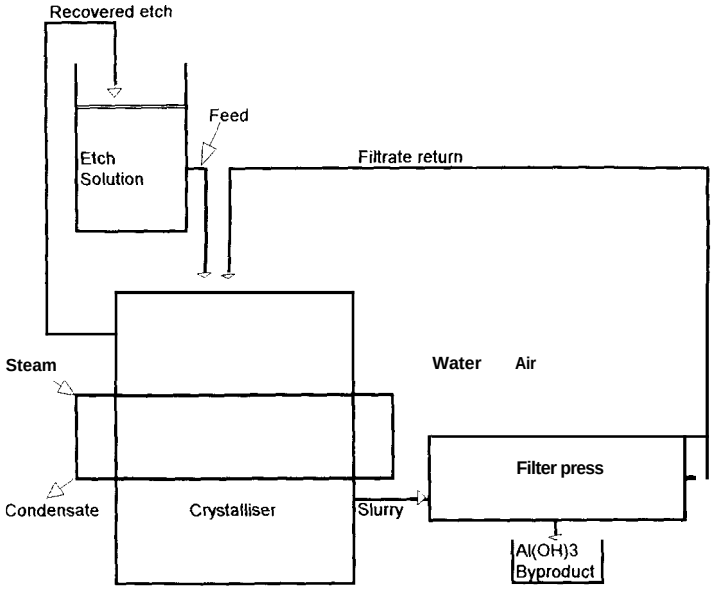


Fig. 16-3. Schematic of caustic etch recovery system

Typical solution compositions reported for the sodium hydroxide regeneration process are:

Process stream	*NaOH g/l*	*A1 +++*
Etch solution	50	30
Regenerated etch	60	20

A typical analysis of the recovery process by-product is:

Element	*% in dried solid*
Na_2O	0.3
Al_2O_3	51.8
PO,	<0.1
F	0.001
Si	0.15
Fe	0.06
Mg	0.13
SO_3	0.2
Loss on drying at 110°C	9
Loss on ignition	34

This by-product may he saleable depending upon the local market for a low quality aluminium hydroxide. **A** possible use is in the manufacture of aluminium sulphate for use in the paper industry.

Anodizing

Fig. 16-4 illustrates the options available for controlling a sulphuric acid anodizing electrolyte. The continuous dumping of the anodizing electrolyte to control its aluminium content is a very common practice, the dumped acid being used to control the pH of the rinse water effluent. In cases where sodium hydroxide recovery is installed, the continuous dumping of the anodizing acid may result in an excess of acid in the effluent treatment systein. This then necessitates the use of new sodium hydroxide to neutralise the excess, thus defeating the objective of sodium hydroxide recovery. In such cases the use of a sulphuric acid recovery system usually makes economic sense.

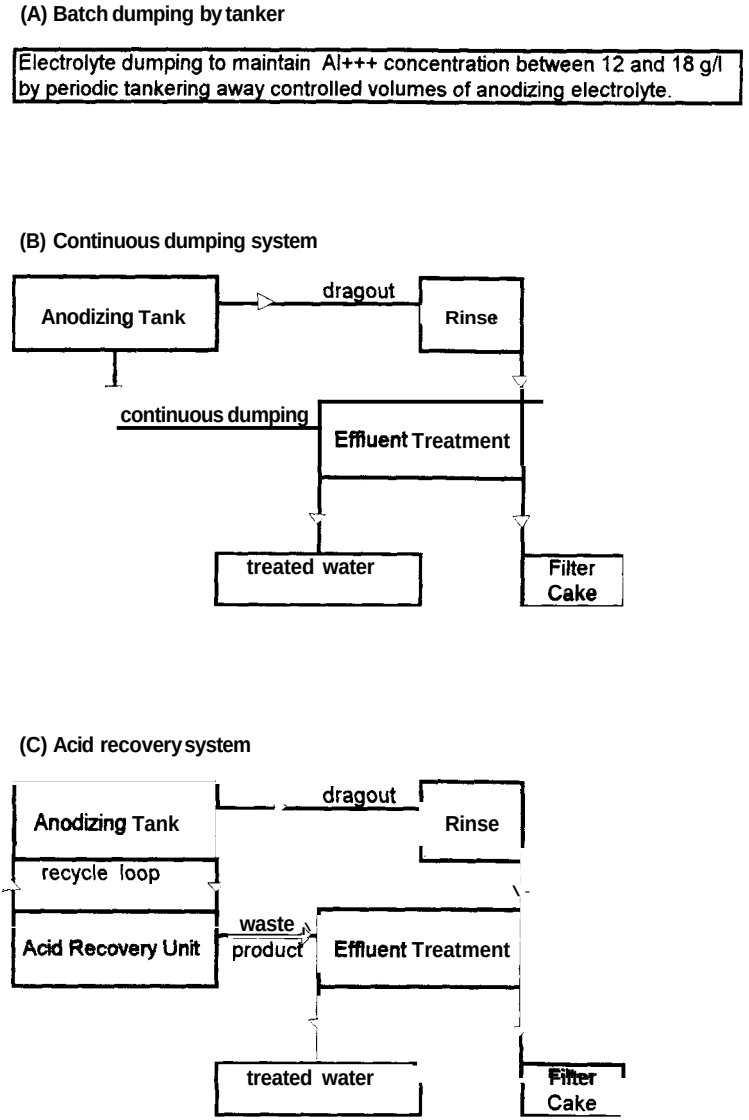
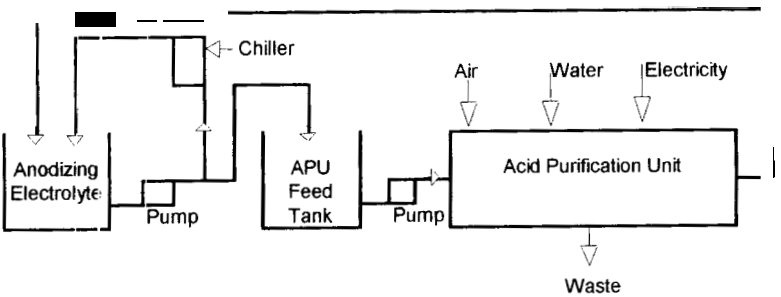


Fig. 16-4. Schematics of available anodizing operating systems

The systems available for sulphuric acid recovery are usually based on reciprocating flow ion exchange[20] or dialysis[21,22]. These systems remove aluminium from the anodizing electrolyte and return the sulphuric to the anodizing tank.

The principle of the techniques is illustrated in Fig. 16-5.

(A) Reciprocating Flow Ion Exchange



(B) Membrane Dialysis

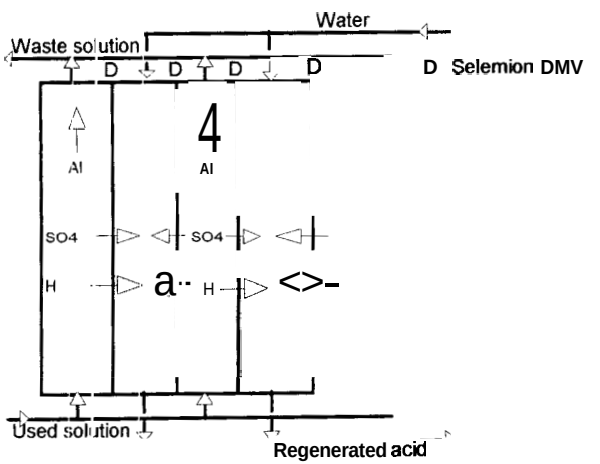


Fig. 16-5. Principle of sulphuric acid electrolyte recovery systems

Typical process data for the two techniques has been reported as:–

Process stream	*Reciprocating flow ion exchange*		*Dialysis*	
	H_2SO_4 *g/l*	Al^{+++} *g/l*	H_2SO_4 *g/l*	Al^{+++} *g/l*
Electrolyte feed	I84	12	I SO	18
Recovered product	175	S	127	1
Waste product	13	11	36	16

The waste product is treated in the effluent neutralisation plant.

The treatment of waste from chromic acid anodizing is a little more complex and will be covered in the section on chromate conversion solution waste.

Colouring

Systems are also available for the recovery of cobalt or nickel from the post electrolytic colouring rinse, the recovered salts being returned to the process solution. The economics of these systems are very dependent upon the cost of the cobalt or nickel salts used in the electrolyte. In some cases the local rinse water discharge limits may be *so* stringent that the use of a metal recovery unit **is** necessary to ensure compliance. Techniques used for the recovery of electrolytic colouring solutions from the post colouring rinse are usually based on reciprocating flow ion exchange?' or reverse osmosis[24 25 26].

Schematics of the principle of these two processes are shown in Fig. 16-6.

A well-controlled recovery system will reduce the consumption of cobalt or nickel sulphate by about 75%. The recovery of tin salts by these processes has been less successful due to the dual valency states of this metal.

Sealing

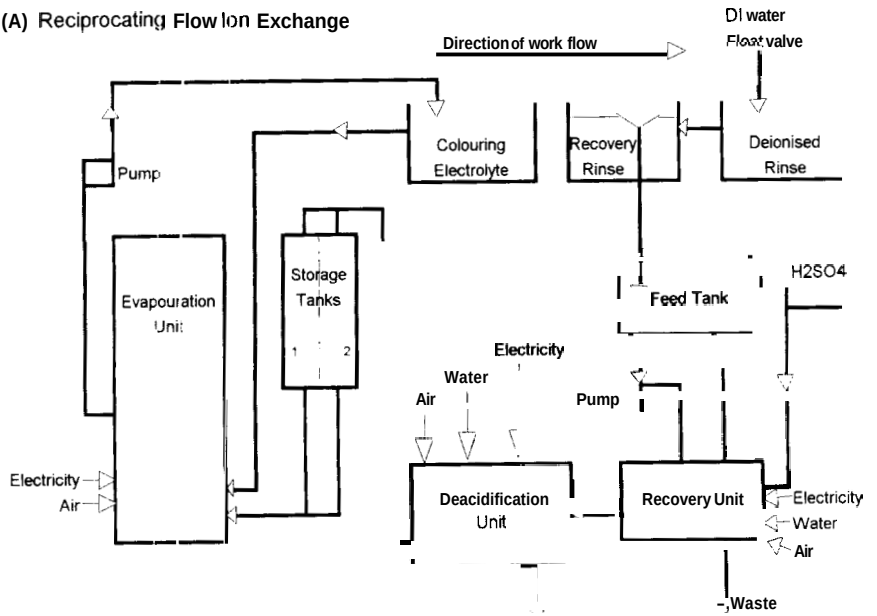
The final stage of the anodizing process is to seal the anodic film. This may be done using boiling deionised water or by cold impregnation with nickel from a solution of the metal salt at 20 to 25°C.

The dumping of hot seal solutions due to contamination with sulphate (~500ppm) or aluminium (~10ppm) does not normally present any difficulties providing the solution is cooled before disposal into the rinse water treatment system. Where dumping of large volumes of water is restricted, contamination of the seal may be controlled by continuous bleed off of controlled volumes of seal water.

In the case of cold impregnation the solutions are relatively stable and usually do not require dumping. However, if and when the need to dump such a solution arises, treatment of the nickel and fluoride ions present will have to be carried out to meet local discharge limits. Neutralisation with lime could be a possible method of treatment.

Rinse water neutralisation

Whether continuous dumping or recovery systems are used there will always be drag out from the process solutions into the post process rinses. Most contaminants in the rinse waters are precipitated when they are neutralised,[27] but others such as Na^+ and SO_4^- remain in solution. Sulphates can be reduced to about 2000ppm by neutralisation with lime, but reducing it below this level would require ion exchange or the use of expensive barium salts. Even with ion exchange'* the regeneration by-product still has to be dealt with in some way.



(B) Reverse **Osmosis**

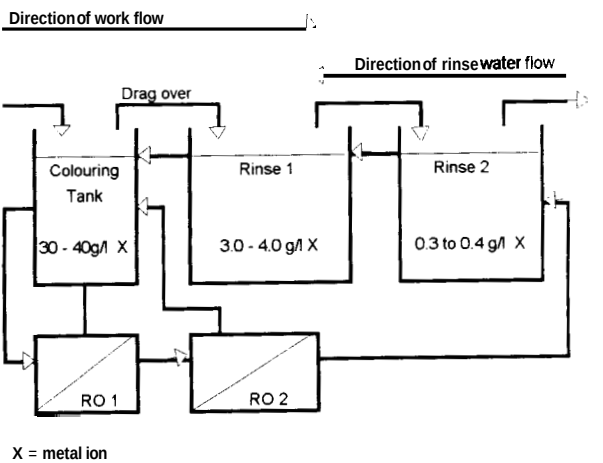


Fig. 16-6. Schematic of systems used lor recovery of colouring electrolytes

Precipitation

The neutralisation of the rinse water followed by precipitation and consolidation of metal hydroxides[29] is an important part of the process. The use of flocculants to improve precipitation and settling rates is a science in itself and beyond the scope of this Chapter.

After neutralisation the rinse water is treated with a flocculating agent to aid precipitation and the settling is usually carried out in a purpose designed settling tank. The treated water flows from the top of this settling tank to a final tank for pH check and adjustment, if necessary, before discharge to the sewer or watercourse. If required the water can be given a final filter by passing through a sand bed filter. The sludge is taken from the bottom of the settling tank for further consolidation. The principle of a typical effluent treatment system is illustrated in Fig.16-7.

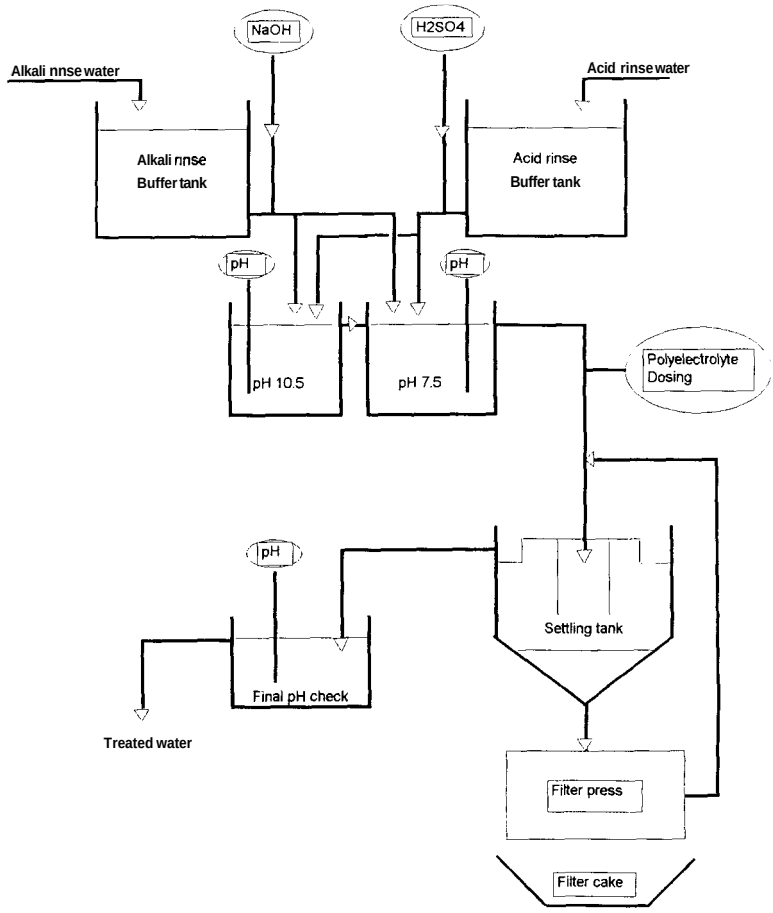


Fig. 16-7. Typical layout for anodizing effluent treatment plant

Sludge consolidation

Several techniques ate available for the consolidation of the sludge from the settling tank. The most common and probably the most efficient is the plate filter press". Plate filter presses will generally give the driest filter cake (20 to 30% solids). They are operated on a batch process principle having the following sequence:– filler, air dry, blowback and cake cut down.

The settling tank capacity or the sludge storage tank must therefore be of sufficient volume to hold the cyclic build up of sludge awaiting filtration.

The alternatives to the plate filter press are centrifugal separation, Archimedean screw pressure extraction of the liquid, or a rotary vacuum filter. These three are, in theory, all continuous processes. However, they all have moving parts and the precipitates in the sludge are very abrasive. The experience with these pieces of equipment has been that the maintenance down-time has been higher than was envisaged. The solid's content of the consolidated sludge is much lower than that from the plate filter press. Solid contents between 12 and 20% are quite normal.

The percentage of solids in the final cake can be important where cost of dumping is weight or volume related. A typical architectural anodizing plant will produce about 1600kg of 20% solids filter cake per 1000m² processed.

4. PAINT LINE IPRE-TREATMENTPROCESS EFFLUENT

Many of the principles described for treating waste from an anodizing line apply to the treatment of waste from a paint line, the main differences being the chromate pre-treatment stage for painting and the treatment of solvents from wet paint systems or powder from the dry paint systems. Fumes from the stoving treatment will also require attention.

The degrease, etch and desmut stages are similar to those used for anodizing. The main problem is the treatment of the waste from the chromate conversion coating.

Chromate conversion coatings

The solution required to form a chromate conversion coating on aluminium contains a mixture of chemicals, usually hexavalent and trivalent chromium, phosphate, aluminium arid fluoride ions. The concentration of these ions will vary from one proprietary product to another and some may contain nitrite ions or other accelerators.

Chemicals likely to cause a problem in the effluent are hexavalent [30] and trivalent chromium, phosphate and fluoride ions. Several optionc are claimed to be suitable for their treatment but some may have limitations. These limitations can be capital cost, running cost, unproven technology or availability of suppliers or treatment facilities in a particular area.

Examples of treatments in use or claimed to be available are:–

(I) Reduction of Cr ions to trivalent form followed by precipitation and filtration.
(2) Removal of Cr^{3+} and Al^{3+} ions from the process solution and Cr, CN and F ions from the post process rinse by ion exchange cartridges that are regenerated by a chemical company.
(3) Recycling the chromate/phosphate rinse.
(4) Chrome/phosphate bath regeneration.
(5) Recycling chromium/aluminium waste.

Treatment number one is conventional and perhaps most reliable and will be discussed in more detail. Treatment number two is used in Japan but relies on a chemical company being willing to regenerate the ion exchange resin cartridge. The chromic acid recovered is a saleable product. This facility is not available worldwide and therefore its use depends on the local situation.

Option number three can be achieved in two ways. One technique entails the use of electrolytic regeneration" of the rinse water. Hexavalent chromium is returned to the process solution. Trivalent chromium and aluminium ions are converted to their respective hydroxides and then separated from the treated rinse water in a clarifier. The treated rinse water is returned to the process rinse.

The other technique involves operating the chromate solution on a never-dump basis. The post process static rinse is returned to the chromate solution and the level controlled by evaporation (likely to be expensive). This idea is little more than a laboratory process and has not been used commercially. Any long-term effect of contaminants in the process solution may not be fully known.

Eco-Tec manufactures a system" (based on ion exchange) that can be used to regenerate the chrome/phosphate solution (option four) and presumably the post chromate solution rinse. Examples of its commercial use have not been reported, perhaps because of the capital cost, although this may be insignificant with respect to the potential cost penalties of exceeding environmental discharge limits.

The chemical formulation of solutions used to produce conversion coatings is very complex. Often the analytical techniques to control the formulation by addition of the separate chemicals or unbalanced chemical mixtures are not available or are beyond the capabilities of many finishing plant control laboratories. Consequently., monitoring the effects on solution composition of options three and four is not easy.

These options have to rely on the solution being of a never-dump type if treatment of spent process solution is to be avoided. The electrolytic regeneration and the Eco-Tec ion exchange system should remove impurities from the chromate solution. The static rinse feedback with evaporation will concentrate impurities.

In the case of options one and two, the chemical composition is controlled by analysis of one or two components of the solution and then it is replenished by addition of a balanced make up mixture. This analysis technique has been developed by experience by the supply house and is often carried out by them for their customer.

Treatment five is a method proposed by AMAX Metals Recovery Inc., and describes a technique for producing chromium oxide or sodium chromate solution from an Al-Cr or high phosphorous Al-Cr sludge. This type of treatment would be used after settling and filtration of the Al-Cr sludge in a conventional treatment system. As such, it is unlikely to be used by a finishing plant, but would be installed by a chemical recovery plant handling such wastes.

	3	4 5	6	7

Stage 1	Reduction Cr^{6+} to Cr^{3+}
Stage 2	Neutralisation
Stage 3	Precipitate settling. Clarified water overflowed to a sewer
Stage 4	Sludge consolidation. Solids to an approved dump site

Stage 1. Reduction

The reduction of hexavalent chromium to the trivalent form is carried out in an acid solution in the pH range 2.5 to 3.5. The effluent will be predominantly acid but any further acidification required is usually carried out with 30% v/v sulphuric acid; dosing is pH controlled by means of a suitable dosing pump. Reducing agents such as sodium bisulphite or ferrous sulphate are generally used.

Stoichiometrically, 3 grams of sodium bisulphite or 9 grams of ferrous sulphate are required to reduce one gram of Cr^{6+} to Cr^{3+}. The literature reports variable values for the quantities required and they would need to be confirmed by measurement on a laboratory basis.

The reaction time for this reduction to take place is dependent on pH but is relatively short. A residence time of 20 to 30 minutes in the reaction tank should be more than adequate.

The state of the reduction in an oxidation/reduction chemical reaction can be monitored by measuring the Redox potential.

Stage 2. Neutralisation

The method of neutralisation will depend upon the limits of discharge for ions other than chromium. Rinse water or spent process solution from a chromate conversion pre-treatment system will usually contain Cr^{6+}, Cr^{3+}, F^- Al^{3+} and PO_4^{3-} ions. When the effluent reaches the neutralisation stage all of the chromium ions, having been reduced in Stage 1, will be in the trivalent form. If the effluent is neutralised with sodium hydroxide solution the chromium and aluminium ions will be precipitated, and most of the fluoride and phosphate ions will remain in solution. The separated solids will therefore mainly contain the hydroxides of trivalent chromium and aluminium.

Where it is necessary to remove the fluoride and phosphate ions, calcium hydroxide (lime) is used. Calcium phosphate and calcium fluoride are both practically insoluble in water and will be precipitated. The trivalent chromium and aluminium will also be precipitated. This will increase the volume of precipitated solids to be separated from the rinse waters.

If solids containing trivalent chromium are considered to be toxic waste, or there is a cost penalty or constraint for dumping, a double precipitation procedure is worth considering. In this system the precipitation takes place in two separate reaction tanks. In the first reaction the effluent is neutralised with sodium hydroxide to precipitate the trivalent chromium and aluminium, but the fluoride and phosphate will remain in solution. The effluent then flows into the first settling tank where the chromium and aluminium hydroxide precipitates are settled. The overflow from this settling tank will flow into the second reaction tank where it is mixed with lime to precipitate the fluoride and phosphate ions. This effluent then flows into the second settling tank where the calcium fluoride and calcium phosphate precipitates are settled. The overflow from this tank may

be discharged to the waste stream. Alternatively, it may be passed through a sand bed filter and an ion exchange resin for final purification if required before discharge.

The net result is that two sludges are produced, one that might be considered a hazardous sludge, and the other non-hazardous sludge. The volume of sludge produced by neutralisation with calcium hydroxide will generally be greater than the volume produced by neutralisation with sodium hydroxide. This may be of significance if the treatment of spent chromate solution is being considered, because, if the two-stage process were used, the volume of hazardous sludge would be much less than if a single stage process was used. This is only true if there is a need to remove phosphates and fluorides and the cost of dumping hazardous sludge carries a premium.

Stage 3. Settling of precipitates

The precipitates formed in the neutralisation process (stage 2) can be gelatinous and can take a long time to settle. Seeding of these precipitates by means of a flocculent or polyelectrolyte is common practice. The main flocculent is usually a cationic polymer at a level of 5 to 20ppm plus perhaps a small amount of an anionic polymer at a level of about 0.5ppm. The concentration of flocculents is best determined experimentally using the actual water and effluent from the plant concerned. This ensures that the effect of any local contaminants or impurities in the local water supply, which may affect the flocculation efficiency, are taken into account.

Addition of the flocculent is always a subject for discussion. Experience has shown that it is usually more efficient if it is added under shear conditions, by pumping it into the feed pipe running from the neutralisation tank to the settling tank.

Settling tanks are usually of a specific design, the base of which is an inverted cone shape. The settled sludge is removed from the bottom of this cone. This sludge can be collected and periodically dumped on an approved site or alternatively. it may be further consolidated. The settling tank has to be designed to have sufficient retention time for the precipitates to settle. A very slow moving paddle. located about two thirds of the distance from the top to the bottom of the tank, is used to help move the precipitate to the take off point at the tank bottom. The settling time will depend upon the type of precipitate and the flocculent used but a residence time of at least 180 minutes should be planned. This usually means the settling tank is the largest in the effluent treatment plant. **A** rinse flow of $1m^3$ per hour would require a $3m^3$ settling tank. Settling tank design is critical and the liquid upward flow rate should be taken into consideration. A reported figure for settling aluminium sludges suggests that the upward flow rate should be no greater than 7.50 mm per hour. This explains why settling tanks usually have a diameter to height ratio between 2.5:1 and 3:1.

Stage 4. Sludge consolidation

The same comments and techniques made in the anodizing section will apply.

Effluent plant design

The layout and sizing of the plant will depend on the volumes of wastewater and spent process solution to be treated as well as the discharge limits that have to be met.

The simplest installation is illustrated schematically in Fig.16-8. This **is** not designed to consolidate the sludge by filtration. Settled sludge would be periodically pumped from the sump of the two-section settling tank (Tank ***3)*** and dumped on an approved site or treated by a specialist company.

The principle illustrated in Fig.16-9 is typical of plant installed on a modern chemical conversion treatment line. It is a single stage neutralisation using sodium hydroxide or lime or even a mixture of the two. Should there be a need to separate the solids as previously described then another neutralisation stage, settling tank and filter press would be required after the first settling tank, plus any extra dosing tanks for the extra reaction chemicals.

Water overflowing from the settling tank then flows to a final pH check tank, from where it may be pumped to the sewer or other waste water outlet. If the local authority requirements are very restrictive, the water can be passed through a sand bed filter and an ion exchange unit before being discharged. The backwash from the sand filter and the regeneration waste from the ion exchange resin are returned to the spent solution sump.

The sludge from the settling tank is pumped to a sludge holding tank. This sludge is then periodically pumped to the filter press for further consolidation. Alternatively, the sludge may be periodically pumped from the settling tank direct to the filter press. The cake from the filter press is collected in a suitable skip for transport to an approved dumping site. Liquid from the filter press is returned to the rinse water sump.

Additions of acid or alkali are pH controlled and added by means of a pH sensor which activates solenoids and pumps. The state of the reduction process of the Cr^{6+} to Cr^{3+} is monitored by measuring the Redox potential and reducing agents added accordingly. This measurement is not necessary if an excess of the reducing agent is always added but it should serve to reduce chemical costs. These effluent treatment schemes are designed to treat the waste rinse water continuously. The alternative is to treat it on a batch basis. In this case, rinse waters are collected in a waste collection sump from where they are pumped to a batch treatment tank. In this tank they are systematically acidified, reduced, precipitated and settled. The settled sludge is taken off into a sludge holding tank from where it is pumped to a filter press for consolidation. This system is illustrated in Fig.16-10.

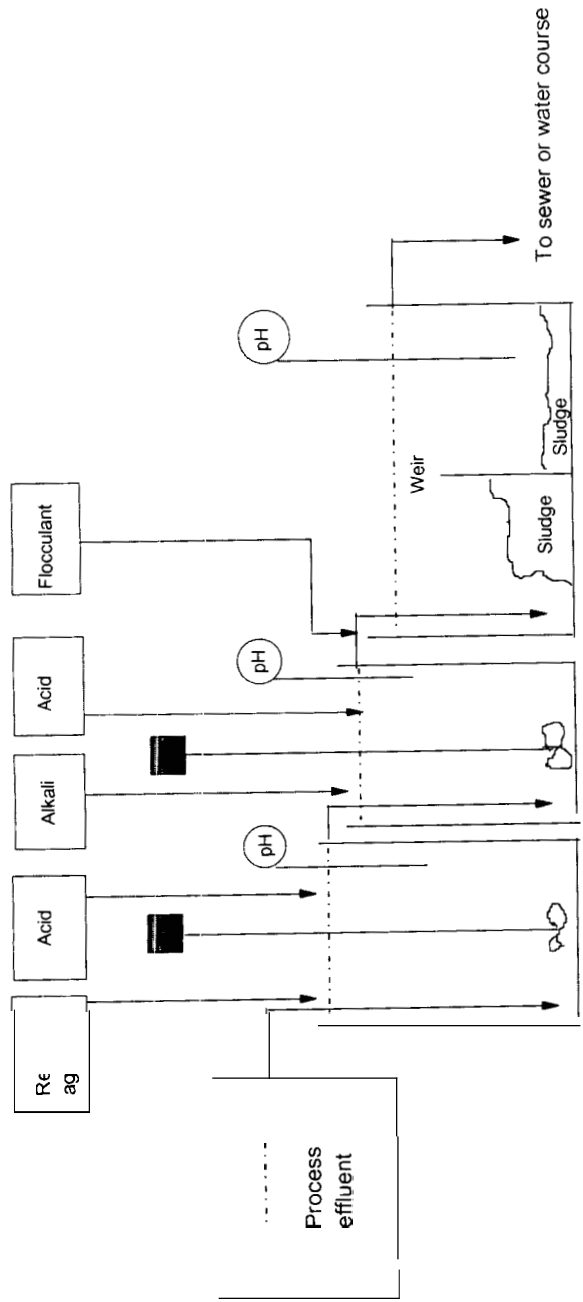


Fig. 16-8. Basic system for chromium effluent treatment

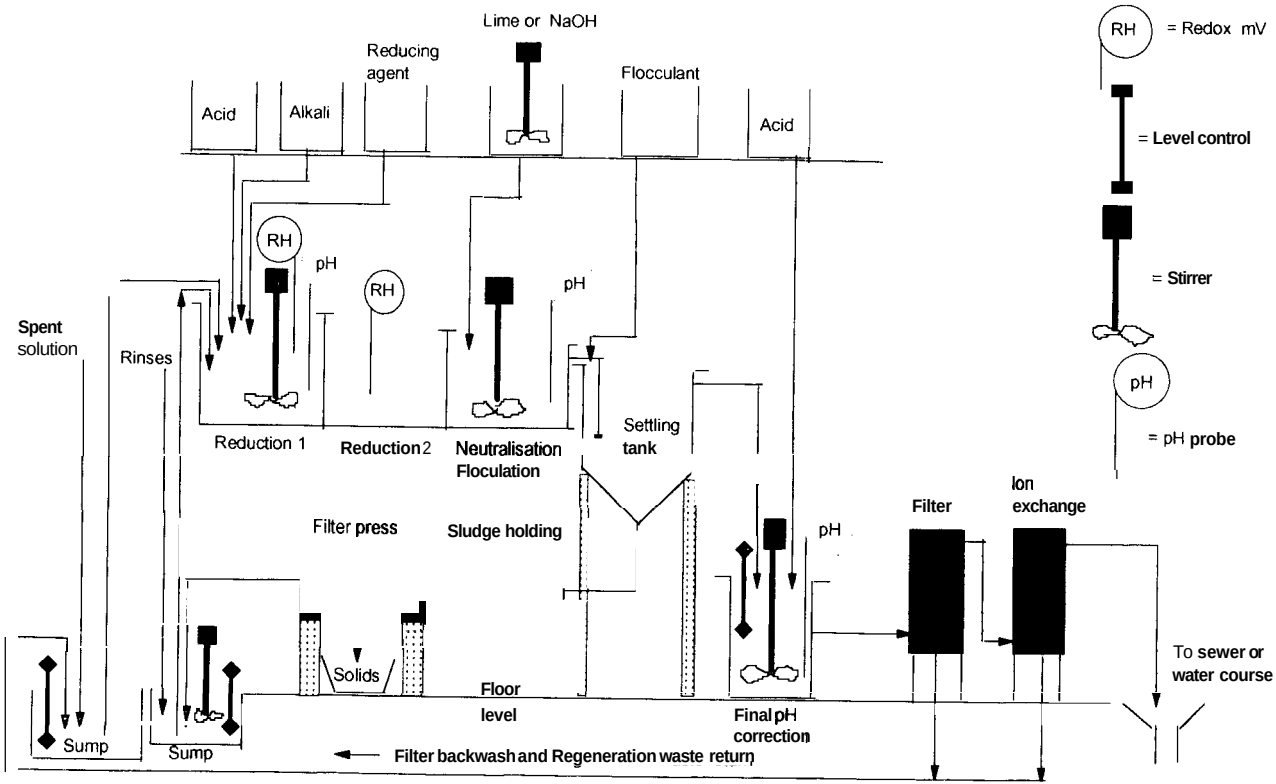


Fig. 16-9. Schematic for chromium effluent treatment

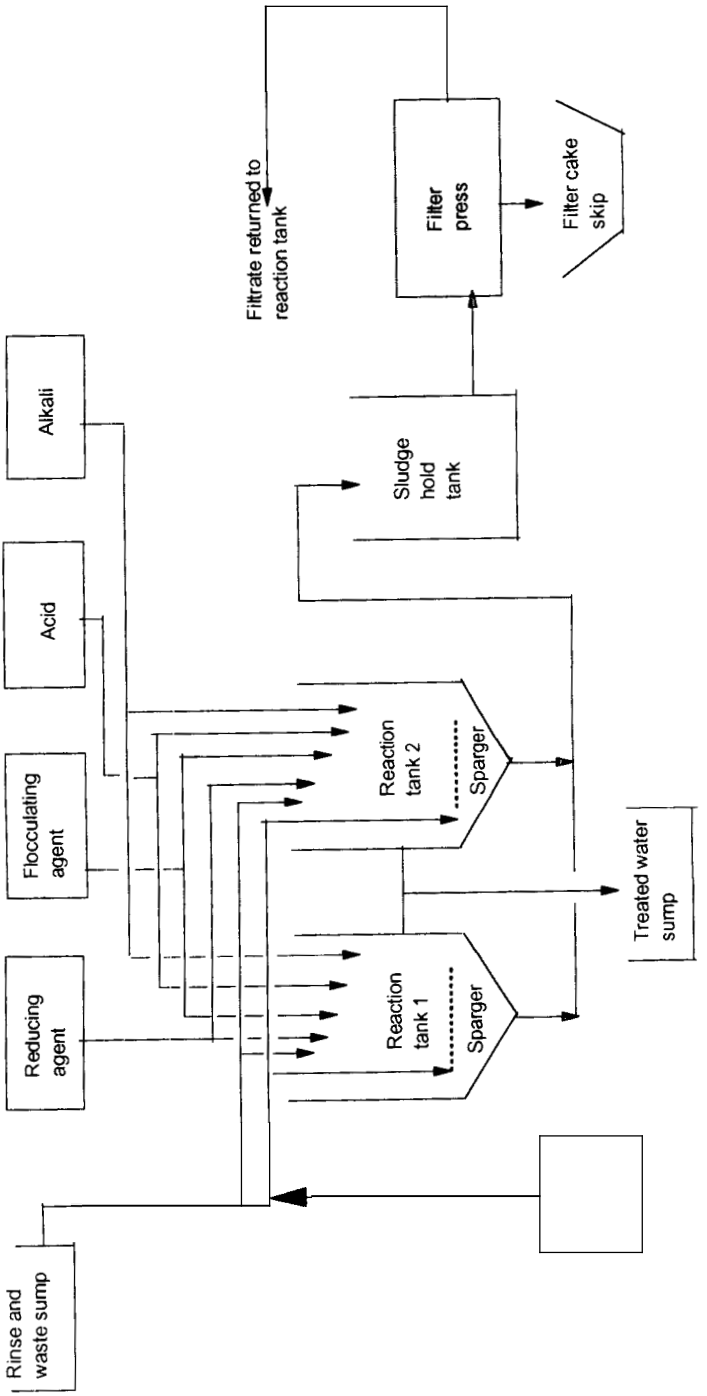


Fig. 16-10. Batch treatment for chromium effluent

A paper on this system[33] claims that the acidification stage takes about 5 minutes and the chromium reduction stage requires a retention time of 10 minutes after the mV reading for a predetermined Redox potential has been reached. The neutralisation stage is carried out with sodium hydroxide to a pH of 8.7 and stabilised between 7.5 and 8.5, and it is then held for 10 minutes before seeding with flocculent (about 5ppm). After 2 minutes mixing the agitation is shut off and the precipitate is allowed to settle for 90 minutes. At this stage the quality of the treated water is tested. If, after solids settling, the treated effluent is acceptable for discharge, decantation takes place. The decantation of the clarified water is followed by pumping the settled sludge to the sludge holding tank from where it is pumped to a filter press for filtering on a batch basis. The whole sequence is then repeated. Two reaction tanks are installed in parallel, and this makes the process sem-continuous and reduces the size of treatment tanks required.

An analysis of the filtered sludge was reported as:–

Element	%
Aluminium	8
Total chromium	4.5
Hexavalent chromium	< 0.1
Orthophosphate	17
Fluoride	0.5
Water content	70

The claims for the efficiency of this method were illustrated by the figures in Table 16-1.

TABLE 16-1

Results of analysis on samples treated by batch process

Constituent	*Concentration Untreated water*	*Concentration Treated water*	*Concentration* Typical maximum allowance*	*Concentration* Most severe maximum limits*
pH	3.0 - 6.0	7.5 - 8.5	6.0 - 9.0	6.5 - 8.0
Hexavalent Cr	50 - 70 ppm	< 0.05 ppm	0.1 ppm	0.05 ppm
Total Cr	75 - 110 ppm	< 1 ppm	2 ppm	1 ppm
Aluminium	30 - 60 ppm	< 2 ppm	50 ppm	10 ppm
Orthophosphate	400 - 600 ppm	< 50 ppm	100 ppm	50 ppm
Fluoride	30 - 70 ppm	< 50 ppm	50 ppm	10 ppm
Suspended solids	< 25 **ppm**	200 ppm	30 ppm	

* These figures can only be guides and they will vary considerably from state to state, and country to country.

The paint system

A solvent paint system will require suitable spray booths and solvent extraction. Purpose built exhaust systems are available to effectively burn off any solvents before discharge to the atmosphere. In the case of non-solvent systems such as powder paints, the over-spray is recycled by means of cyclones on the spray booth exhausts. The fines are captured in special filters the cleaning of which requires specialised care. Because some fines are lost as they are carried into the filters and some heavier particles may be recycled constantly, there will be a point when the particle size distribution in the recovered powder becomes unbalanced. This must be monitored by process control, and additions of new powder made to address the imbalance.

5. OTHER PROCESSES

The brightening of aluminium is mainly carried out using chemical brightening solutions based on phosphoric acid. Phosphates in an effluent can be precipitated by using lime. Ion exchange systems are also available for the recovery of phosphoric acid from the post process rinse. The effluent from phosphoric acid anodizing may also be treated in this way.

Pretreatments for aluminium prior to electro-plating may consist of the application of **a** zincate coating from a solution containing sodium-hydroxide and zinc, or a bronze strike from a proprietary plating bath. The drag out from the zincate solution may be treated in a similar manner to that from a caustic etch solution. The bronze strike is electroplated from a stannate based plating solution and the drag out may well contain some cyanides which should be treated by the standard recornmended practices used in the plating industry. The treatment of effluent from electro-plating solutions is a subject in its own right and is adequately covered in the plating literature.

The zero effluent plant[34,35] must be the aim of the future. Although there may always be some waste by-product the ultimate is already being discussed''.

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APPENDIX A

Composition and Properties of Major European and U.S. Aluminium Alloys

(Source: Aluminium Federation Ltd., Birmingham, U.K.)

Notes on grades of aluminium for anodizing

Appearance and colour, maximum anodic coating thickness, reflectivity, abrasion resistance, corrosion resistance and electrical breakdown voltage depend on the purity, composition and metallurgical history of the aluminium. For this reason, wherever possible, the end use of the anodized material should be specified when ordering the aluminium.

Special grades of aluminium and special alloys to give specific properties are available as 'anodizing quality' materials. For example, B.S. Supplementary Specification 4300/4 specifies alloys for bright trim/reflector materials.

For many applications the B.S. General Engineering series of aluminium alloys (B.S. 1470-1475, B.S. 1490 and B.S. 4300/1-16) are suitable, but alloys containing a high proportion of copper, zinc, and silicon are likely *to* present more problems with anodizing, and advice should be sought from the manufacturer or the anodizer.

Guidance on the selection of materials for anodizing should be obtained from the manufacturers and anodizers, and this applies especially in the case of integral colour anodizing processes.

British Standards

These standards have now been replaced by the equivalent CEN Standards.

TABLE A-1

British Standards
General and Supplementary Engineering Standards

Specifications for wrought aluminium and aluminium alloys for general engineering **purposes:**

BS 1470: 1987	Plate, sheet and strip
BS 1471: 1972	Drawn tube.
BS 1472: 1972	Forging stock and forgings.
BS 1473: 1972	Rivet, bolt and screw stock.
BS 1474: 1987	Bars, extruded round tube and sections.
BS 1475: 1972	Wire.

Specification for cast aluminium and aluminium alloys for general engineering purposes:

BS 1490: 1988	Ingots and castings.

The supplementary engineering specifications, for materials with rather more specialised use, include:

BS 4300/1: 1967	52.5 1 Longitudinally welded tube.
BS 4300/4: 1973	6463 Solid extruded bars and sections suitable for bright trim/reflector applications.
BS 4300/5: 1973	201 1 Free cutting bar and wire.
BS 4300/10: 1969	5454 Drawn tube.
BS 4300/11: 1969	54.54 Forging stock and forgings.
BS 4300/12: 1969	5454 Bars, extruded round tube and sections.
BS 4300/13: 1969	5.5.54 Welding wire.
BS 4300/14: 1973	7020 Plate, sheet and strip.
BS 4300/15: 1973	7020 Bar, extruded round tube and sections.
BS 4300/16: 1984	8011 Sheet and strip.

Aerospace Specifications

Aerospace materials are covered by the 'L' series of British Standards and by the DTD specifications issued by the Procurement Executive, Ministry of Defence. These specifications, which are not systematically grouped or numbered are concerned with specific materials and often with particular applications.

European Alloy Standards

British and other European National Standards have been almost completely replaced by equivalent CEN standards which are shown below. The alloy designations for wrought alloys are essentially the same as those used previously but have the prefix EN AW (e.g. EN AW 6063).

TABLE A-2

Packages of European Standards replacing existing British Standards concerning aluminium and aluminium alloys for general engineering applications

BS 1470: 1987	**Wrought aluminium and aluminium alloys for general engineering purposes: plate, sheet and strip**
* EN515	Aluminium and aluminium alloys – Wrought products – Temper designations
* EN 573 – 3	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 3: Chemical composition
* EN 573 – 4	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 4: Forms of products
* EN 485 – 1	Aluminium and aluminium alloys – Sheet, strip and plate – Part 1: Technical conditions for inspection and delivery
* EN 485 – 2	Aluminium and aluminium alloys – Sheet, strip and plate – Part 2: Mechanical properties
* EN 485 – 3	Aluminium and aluminium alloys – Sheet, strip and plate – Part 3: Tolerances on shape and dimensions for hot rolled products
* EN 485 – 4	Aluminium and aluminium alloys – Sheet, strip and plate – Part 4: Tolerances on shape and dimensions for cold rolled products
BS 1471: 1972	**Specification for wrought aluminium and aluminium alloys – Drawn Tube**
* EN515	Aluminium and aluminium alloys – Wrought products – Temper designations
* EN 573 – 3	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 3: Chemical composition
* EN 573 – 4	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 4: Forms of products

* EN 754 – 1	Aluminium and aluminium alloys – Cold drawn rodhar and tube – Part 1: Technical conditions for inspection and delivery
* EN 754 – 2	Aluminium and aluminium alloys – Cold drawn rod/bar and tube – Part 2: Mechanical properties
* EN 754 – 7	Aluminium and aluminium alloys – Cold drawn rodhar and tube – Part 7: Seamless tubes, tolerances on dimensions and form
* EN 754 – 8	Aluminium and aluminium alloys – Cold drawn rodhar and tube – Part 8: Porthole tubes, tolerances on dimensions and form

BS 1472 : 1972 **Specification for wrought aluminium and aluminium alloys – Forging stock and forgings**

* EN 515	Aluminium and aluminium alloys – Wrought products – Temper designations
* EN 573 – 3	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 3: Chemical composition
* EN 573 – 4	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 4 – Forms of products
* EN 586 – 1	Aluminium and aluminium alloys – Forgings – Part 1: Technical conditions for inspection and delivery
* EN 586 – 2	Aluminium and aluminium alloys – Forgings – Part 2: Mechanical properties and additional property requirements
* EN 603 – 1	Aluminium and aluminium alloys – Wrought forging stock – Part 1 : Technical conditions for inspection and delivery
* EN 603 – 2	Aluminium and aluminium alloys – Wrought forging stock – Part 2: Mechanical properties. Part 4: Forms of products
* EN 604 – 1	Aluminium and aluminium alloys – Cast forging stock – Part 1 : Technical conditions for inspection and delivery
* EN 604 – 2	Aluminium and aluminium alloys – Cast forging stock – Part 2: Tolerances on dimensions and form

BS 1474: 1987 **Specification for wrought aluminium and aluminium alloys for general engineering purposes: bars, extruded round tubes and sections**

* EN 515	Aluminium and aluminium alloys – Wrought products – Temper designations
* EN 573 – 3	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 3: Chemical composition

* EN 573 – 4	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 4: Forms of products
* EN 755 – 1	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 1: Technical conditions for inspection and delivery
* EN 755 – 2	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 2: Mechanical properties
* EN 755 – 3	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 3: Round bars, tolerarices on dimensions and form
* EN 755 – 4	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 4: Square bars, tolerances on dimensions and form
* EN 755 – 5	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 5: Rectangular bars, tolerances on dimensions and form
* EN 755 – 6	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 6: Hexagonal bars, tolerances on dimensions and form
* EN 755 – 7	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 7: Seamless tubes, tolerances on dimensions and form
* EN 755 – 8	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 8: Porthole tubes, tolerances on dimensions and form
† pr EN 755 – 9	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 9: Profile, tolerances on dimensions and form
† pr EN 12020 – 1	Aluminium and aluminium alloys – Extruded precision profiles in alloys EN AW 6060/EN AW 6063 – Part 1: Technical conditions for inspection and delivery
† pr EN 12020 – 2	Aluminium and aluminium alloys – Extruded precision profile sin alloys EN AW 6060/ EN AW 6063 – Part 2: Tolerances on dimensions and form

BS 1475: 1972 **Specification for wrought aluminium and aluminium alloys – Wire**

* EN 515	Aluminium and aluminium alloys – Wrought products – Temper designations
* EN 573 – 3	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 3: Chemical composition
* EN 573 – 4	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 4 – Forms of products

* EN 1301 – 1	Aluminium and aluminium alloys – Drawn wire – Part 1: Technical conditions for inspection and delivery
* EN 1301 – 2	Aluminium and aluminium alloys – Drawn wire – Part 2: Mechanical properties
* EN 1301 – 3	Aluminium and aluminium alloys – Drawn wire – Part 3: Tolerances on dimensions
BS 1490: 1988	**Specification for aluminium and aluminium alloy ingots and castings for general engineering purposes**
* EN 1559 – 1	Founding – Technical conditions of delivery – Part 1: General
† pr EN 1559 – 4	Founding – Technical conditions of delivery – Part 4: Additional requirements for aluminium castings (currently under preparation in CEN/TC 190)
* EN 1676	Aluminium and aluminium alloys – Alloyed ingots for remelting – Specifications
† pr EN 1706	Aluminium and aluminium alloys – Castings – Chemical composition and mechanical properties
BS 4300-1: 1967	**Specification (supplementary series) for wrought aluminium and aluminium alloys – Part 1: Aluminium alloy longitudinally welded tube**
* EN 515	Aluminium and aluminium alloys – Wrought products – Temper designations
* EN 573 – 3	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 3: Chemical composition
* EN 573 – 4	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 4: Forms of products
† pr EN 1592 – 1	Aluminium and aluminium alloys – HF seamwelded tubes – Part 1: Technical conditions for inspection and delivery
† pr EN 1592 – 2	Aluminium and aluminium alloys – HF seamwelded tubes – Part 2: Mechanical properties
† pr EN 1592 – 3	Aluminium and aluminium alloys – HF seamwelded tubes – Part 3: Tolerances on dimensions and form for circular tubes
† pr EN 1592 – 4	Aluminium and aluminium alloys – HF seamwelded tubes – Part 4: Tolerances on dimensions and form for square, rectangular and shaped tubes
BS 4300-4: 1973	**Specification (supplementary series) for wrought aluminium and aluminium alloys for general engineering purposes – Part 4: 6463 Solid extruded bars and sections suitable for bright trim/reflector applications**

* EN515	Aluminium and aluminium alloys – Wrought products – Temper designations
* EN 573 – 3	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 3: Chemical composition
* EN 573 – 4	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 4: Forms of products
* EN 755 – 1	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 1: Technical conditions for inspection and delivery
* EN 755 – 2	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 2: Mechanical properties
* EN 755 – 3	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 3: Round bars, tolerances on dimensions and form
* EN 755 – 4	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 4: Square bars, tolerances on dimensions and form
* EN 755 – 5	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 5: Rectangular bars, tolerances on dimensions and form
* EN 755 – 6	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 6: Hexagonal bars, tolerances on dimensions and form
* EN 755 – 7	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 7: Seamless tubes, tolerances on dimensions and form
* EN 755 – 8	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 8: Porthole tubes, tolerances on dimensions and form
† pr EN 755 – 9	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 9: Profile, tolerances on dimensions and form

BS 4300-15: 1973 **Specification (supplementary series) for wrought aluminium and aluminium alloys – Part 15: 7020 Bar, extruded round tube and sections**

* EN515	Aluminium and aluminium alloys – Wrought products – Temper designations
* EN 573 – 3	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 3: Chemical composition

* EN 573 – 4	Aluminium and aluminium alloys – Chemical composition and form of wrought products – Part 4: Forms of products
* EN 755 – 1	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 1: Technical conditions for inspection and delivery
* EN 755 – 2	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 2: Mechanical properties
* EN 755 – 3	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 3: Round bars, tolerances on dimensions and form
* EN 755 – 4	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 4: Square bars, tolerances on dimensions and form
* EN 755 – 5	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 5: Rectangular bars, tolerances on dimensions and form
* EN 755 – 6	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 6: Hexagonal bars, tolerances on dimensions and form
* EN 755 – 7	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 7: Seamless tubes, tolerances on dimensions and form
* EN 755 – 8	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 8: Porthole tubes, tolerances on dimensions and form
† pr EN 755 – 9	Aluminium and aluminium alloys – Extruded rod/bar, tube and profiles – Part 9 Profile, tolerances on dimensions and form

Existing British Standards which are currently not being replaced by European Standards

BS 1473: 1972	Specification for wrought aluminium and aluminium alloys – Rivet, bolt and screw stock
BS 4300-10: 1969	Specification (supplementary series) for wrought aluminium and aluminium alloys – Part 1: 5454 Forging stock and forgings
BS 4300-11: 1969	Specification (supplementary series) for wrought aluminium and aluminium alloys – Part 1: 5454 Forging stock and forgings
BS 4300-13: 1969	Specification (supplementary series) for wrought aluminium and aluminium alloys – Part 13: 5554 Welding wire

TABLE A-3

Alloys and Forms

Forms Normally Available, General Engineering and Aerospace

Alloy Designation	Plate	Sheet and Strip	Drawn Strip	Drawn Tube	Longitudinally Welded Tube	Forging Stock and Tube	Bolt and Screw Stock	Rivet Stock	Bar, etc.	Solid Conductor	Wire
1080A	X	X									X
1050A	X	X		X		X		X	X		X
1200	X	X		X					X	X	X
1350			X						X	X	X
2011									X		X
2014A	X	X		X		X	X	X	X		X
2024	X	X									
2031						X					
2117								X			
2618A	X					X			X		
3103	X	X									X
3105		X									
4043A											X
4047A											X
5005		X									X
5056A							X	X			X
5083	X	X		X		X			X		
5154A	X	X		X		X		X	X		X
5251	X	X		X	X	X			X		X
5454	X	X		X		X			X		
5554											X
5556A											X
6060									X		
6061				X					X		X
6063				X		X			X		X
6063A									X		
6082	X	X		X		X	X	X	X		
6101A									X		
6463									X		
7010	X					X					
7014						X					
7020	X	X							X		
7075	X	X				X			X		
8011		X									

TABLE A-4 European Aluminium Alloy Sheet, Plate,

Alloy designation		Chemical Composition %				
Numerical	Chemical symbols	Si	Fe	Cu	Mn	Mg
EN AW-1080A	EN AW-AI 99,8(A)	0,15	0,15	0,03	0,02	0,02
EN AW-1050A	EN AW-AI 99.5	0.25	0.40	0,05	0,05	0,05
EN AW-1200	EN AW-AI 99.0	1,00 SI	Fe	0,05	0,05	–
EN AW-2011	EN AW-AI Cu6BiPb	0,40	0,7	5,0-6,0		–
EN AW-2014A	EN AW-AI Cu4SiMg(A)	0,50-0,9	0,50	3,9-5,0	0,40-1,2	0,20-0,8
EN AW-2024	EN AW-AI Cu4Mg1	0,50	0,50	3,8-4,9	0,30-0,9	1,2-1,8
EN AW-2031	EN AW-AI Cu2,5NiMg	0,50-1,3	0,6-1,2	1,8-2,8	0,50	1,6-1,2
EN AW-3003	ENAW-AI Mn1Cu	0,6	0,7	0,05-0,20	1,0-1,5	–
EN AW-3103	EN AW-AI Mn1	0.50	0,7	0,10	0,9-1,5	0,30
EN AW-3105	EN AW-AI Mn0,5Mg0,5	0.6	0,7	0.30	0,30-0,8	0,20-0,8
EN AW-4043A	EN AW-AI Si5(A)	4,5-6,0	0,6	0,30	0,15	0.20
EN AW-5005	EN AW-AI Mg1(B)	0,30	0,7	0,20	0,20	0,50-1,1
EN AW-5251	EN AW-AI Mg2	0,40	0,50	0,15	0,10-0,50	1,7-2,4
EN AW-5154A	EN AW-AI Mg3,5(A)	0,50	0,50	0,10	0,50	3,1-3,9
EN AW-5454	EN AW-AI Mg3Mn	0,25	0,40	0,10	0,50-1,0	2,4-3,0
EN AW-5556A	EN AW-AI Mg5Mn	0,25	0,40	0,10	0,6-1,0	5,0-5,5
EN AW-5083	EN AW-AI Mg4,5Mn0,7	0.40	0,40	0,10	0.40-1,0	4,O-4,9
EN AW-6101A	EN AW-EAI MgSi(A)	0.30-0,7	0,40	0,05	–	0,40-0,9
EN AW-6060	EN AW-AI MgSi	0.30-0,6	0,10-0,30	0,10	0,10	0,35-0,6
EN AW-6061	EN AW-AI Mg1SiCu	0,40-0,8	0.7	0,15-0,40	0,15	0,8-1,2
EN AW-6063	EN AW-AI Mg0,7Si	0,20-0,6	0,35	0,10	0,10	0,45-0,9
EN AW-6063A	EN AW-AI Mg0,7Si(A)	0,30-0,6	0,15-0,35	0,10	0,15	0,6-0,9
EN AW-6463	EN AW-AI Mg0,7Si(B)	0,20-0,6	0,15	0.20	0,05	0,45-0,9
EN AW-6082	EN AW-AI Si1MgMn	0,7-1,3	0,50	0,10	0.40-1,0	0,6-1.2
EN AW-7010	EN AW-AI Zn6MgCu	0,12	0,15	1,5-2,0	0.10	2,1-2,6
EN AW-7020	EN AW-AI Zn4,5Mg1	0,35	0,40	0.20	0,05-0,50	1,0-1,4
EN AW-7075	EN AW-AI Zn5,5MgCu	0,40	0,50	1,2-2,0	0,30	2,1-2,9
EN AW-8011A	EN AW-AI FeSi(A)	0,40-0,8	0,50-1,0	0,10	0,10	0.10

Strip and Section Compositions from EN 573-3: 1994

Chemical Composition %									
Cr	Ni	Zn	Ga	V	Remarks	Ti	Others Each	Others Total	Aluminium min.
	–	0,06	0,03	–		0,02	0.02	–	99.80
	–	0,07	–	–	–	0,05	0,03	–	99,50
–	–	0,10	–	–	–	0,05	0,05	0,15	99,00
	–	0,30	–	–		–	0,05	0,15	**Remainder**
0,10	0,10	0,25	–	–	0,20 Zr+Ti	0,15	0,05	0,15	**Remainder**
0,10	–	*0.25*	–	–		0,15	0,05	0,15	**Remainder**
–	0,6-1,4	0,20	–	–		0.20	*0.05*	0,15	**Remainder**
	–	*0,10*	–	–		–	*0.05*	0,15	**Remainder**
0,10	–	0,20	–	–	0,10 Zr+Ti		0,05	0.15	**Remainder**
0,20	–	0,40	–	–	–	0,10	*0.05*	0,15	**Remainder**
	–	*0.10*	–	–		0,15	0,05	0,15	**Remainder**
0,10	–	0,25	–	–	–		0,05	0,15	**Remainder**
0,15	–	0,15	–	–	–	0,15	0,05	0,15	**Remainder**
0,25	–	0,20	–	–	0,10-0,50 Mn + Cr	**0.20**	0,05	0,15	**Remainder**
0,05-0,20	–	0,25	–	–		0.20	0,05	0,15	**Remainder**
0,05-0,20	–	0.20	–	–	–	0,05-0,20	0,05	**0.15**	**Remainder**
0,05-0,25	–	0,25	–	–		0,15	0,05	0,15	**Remainder**
	–	–	–	–	–	–	0.03	0.10	**Remainder**
0,05	–	0.15	–	–	–	0,10	0,05	0,15	**Remainder**
0,04-0,35	–	0,25	–	–	–	0,15	0,05	0,15	**Remainder**
0,10	–	0,10	–	–		0,10	0,05	0,15	**Remainder**
0,05	–	0,15	–	–		0,10	*0,05*	0,15	**Remainder**
	–	*0.05*	–	–		–	0,05	0.15	**Remainder**
0,25	–	0,20	–	–		0,10	*0.05*	0,15	**Remainder**
0,05	0,05	5,7-6,7	–	–	0,10-0,16 Zr	0,06	*0.05*	0.15	**Remainder**
0,10-0,35	–	4,0-5,0	–	–	–	–	0,05	0,15	**Remainder**
0,18-0,28	–	5,1-6,1	–	–		0,20	*0.05*	0,15	**Remainder**
0,10	–	0,10	–	–		0,05	0,05	0,15	**Remainder**

TABLE A-5 Comparison of National Specifications

BS and International Grade Number	BS Pre-1980 Designation	Australia Pre-1986 System	France Old Designation System	Germany Werkstoff Number	Germany DIN Designation
1050A	1B	A 1050	A5	3.0255	A199.5
1080A	1A	B 1080	A8	3.0285	A199.8
1199	1	A1 199	A9		
1200	1C	B1200	A4	3.0205	A199
1350	1E		A5/L	3.0257	E-AI
2011	FCI	A2011	A-U5PbBi	3.1655	AlCuBiPb
2014A	H15	82014	A-U4SG	3.1255	AlCuSiMn
2024		A2024	A-U4GI	3.1355	AlCuMg2
2031	H12		A-U2N		
2117			A-U2G	3.1305	AlCu2.5Mg2.5
2618A	H16		A-U2GN		
3103	N3			3.0515	AlMnI
3105	N31			3.0505	AlMn0.5Mg0.5
4043	N21	B4043	A-S5		
4047	N2	B4047	A-S12		
5005	N41	A5005	A-(30.6		
5056A	N6	A5056	A-G5M	3.3555	AlMg5
5083	N8	A5083	A-G4.5MC	3.3547	AlMg4.5Mn
5154A	N5	C5154			
5251	N4	C5152	A-G2M	3.3525	AlMg2Mn0.3
5454	N51	A5454	A-G2.5MC	3.3537	AlMg2.7Mn
5554	N52				
5556A	N61				
5754			A-G3M	3.3535	AlMg3
6060			A-GS	3.3206	AlMgSi0.5
6061	H20	A6061	A-GSUC	3.3211	AlMgSi1Cu
6063	H9	B6063			
6082	H30		A-SGM0.7	3.2315	AlMgSil
6101A	91E				
6463	E6				
7010					
7014					
7020	H17		A-Z5G	3.4335	AlZn4.5Mg1
7075		A7075	A-Z5GU	3.4365	AlZnMgCu1.5
8011		D8011	A-FeS		

– Wrought Alloys

Old UNI	Italy New UNI	Japan	Spain UNE Number	Sweden	Switzerland
4507	900112	A1050	L-3051	4007	A 199.5
4509	900114	A1080	L-3081	4004	A199.8
3567	900111	A1200	L-3001	4010	A199
	9001/5				
6362	900215	A2011	L-3192	4355	
3581	9002/3	A2014	L-3130	4338	AlCu4SiMn
3583	900214	A2024	L-3140		AlCu4Mg1.5
			L-3160		
3577	900211	A2117	L-3180		
3578	900216		L-3171		
3568	900313		L-3811	4054	AlMn
	900315	A3105	L-3831		
		A4043			
5764	900511	A5005	L-3350	4106	
			L-3320		
7790	9005/5	A5083	L-3321	4140	AlMg4.5Mn
			L-3392		
			L-3361		
7789	9005/3	A5454	L-3391		AlMg2.7Mn
		A5554			
			L-3390	4125	AlMg3
3569	9006/1		L-3442	4103	AlMgSi0.5
6170	9006/2	A6061	L-3420		
		A6063	L-3441	4104	
3571	9006/4		L-3453	4212	AlMgSi1Mn
7791	900111		L-3741	4425	AlZn4.5Mg1
3735	9007/2	A7075	L-3710		AlZn6MgCu1.5
			L-3611		

Note: The intention of this table is to provide direct foreign equivalents to grades currently appearing in British Standards only. Additionally there are many grades in popular use which are not part of British Standards. Equivalency information on other grades can be obtained from the Librarian of the Aluminium Federation. An exception is made for grade 5754 which is in widespread use, mainly to French or German standards.

TABLE A-6 General and Supplementary

Castings (BS 1490) Chemical Composition

	Chemical Composition % (1) (2)					
Alloy	c u	Mg	Si	Fe	Mn	Ni
LMO	0.03	0.03	0.30	0.40	0.03	0.03
LM2	0.7-2.5	0.30	9.0-11.5	1.0	0.5	0.5
LM4	2.0-4.0	0.20	4.0-6.0	0.8	0.2-0.6	0.3
LM5	0.1	3.0-6.0	0.3	0.6	0.3-0.7	0.1
LM6	0.1	0.10	10.0-13.0	0.6	0.5	0.1
LM9	0.20	0.2-0.6	10.0-13.0	0.6	0.3-0.7	0.1
LM12	9.0-11.0	0.2-0.4	2.5	1.0	0.6	0.5
LM13	0.7-1.5	0.8-1.5	10.0-13.0	1.0	0.5	1.5
LM16	1.0-1.5	0.4-0.6	4.5-5.5	0.6	0.5	0.25
LM20	0.4	0.2	10.0-13.0	1.0	0.5	0.1
LM21	3.0-5.0	0.1-0.3	5.0-7.0	1.0	0.2-0.6	0.3
LM22	2.8-3.8	0.05	4.0-6.0	0.6	0.2-0.6	0.15
LM24	3.0-4.0	0.30	7.5-9.5	1.3	0.5	0.5
LM25	0.20	0.20-0.6	6.5-7.5	0.5	0.3	0.1
LM26	2.0-4.0	0.5-1.5	8.5-10.5	1.2	0.5	1.0
LM27	1.5-2.5	0.35	6.0-8.0	0.8	0.2-0.6	0.3
LM28	1.3-1.8	0.8-1.5	17-20	0.7	0.6	0.8-1.5
LM29	0.8-1.3	0.8-1.3	22-25	0.7	0.6	0.8-1.3
LM30	4.0-5.0	0.4-0.7	16-18	1.1	0.3	0.1
LM31	0.1	0.5-0.75	0.25	0.5	0.1	0.1

Notes: (1) To determine whether a composition found by analysis conforms to the requirements of the specification. the analytical figure should be rounded off to the nearest unit in the last right hand place of figures used in the corresponding limits in the table (according to BS 1957).

Engineering Standards

Chemical Composition % (1) (2)					Others	
Zn	Pb	Sn	Ti	Additional Elements	Each	Total
0.07	0.03	0.03		Al99.50min	-	
2.0	0.3	0.2	0.2	-		0.50
0.5	0.1	0.1	0.2		0.05	0.15
0.1	0.05	0.05	0.2		0.05	0.15
0.1	0.1	0.05	0.2		0.05	0.15
0.1	0.1	0.05	0.2		0.05	0.15
0.8	0.1	0.1	0.2		0.05	0.15
0.5	0.1	0.1	0.2	-	0.05	0.15
0.1	0.1	0.05	0.2		0.05	0.15
0.2	0.1	0.1	0.2	-	0.05	0.20
2.0	0.2	0.1	0.2		0.05	0.15
0.15	0.1	0.05	0.2		0.05	0.15
3.0	0.3	0.2	0.2	-		0.50
0.1	0.1	0.05	0.2		0.05	0.15
1.0	0.2	0.1	0.2		0.05	0.15
1.0	0.2	0.1	0.2		0.05	0.15
0.2	0.1	0.1	0.2	Cr0.6;Co0.5	0.10	0.30
0.2	0.1	0.1	0.2	Cr0.6;Co0.5	0.10	0.30
0.2	0.1	0.1	0.2	-	0.10	0.30
4.8-5.7	0.05	0.05	0.25	Cr0.4-0.6	0.05	**0.15**

(2) In cases where alloys are required in the modified condition, the level of any modifying element present is not limited by the specified maximum value for other elements.

TABLE A-7

American Casting Alloys

Designation	Composition (%, *remainder Al)*
208.0	4 Cu, 3 Si
213.0	7 Cu, 2 Si
222.0	10 Cu, 0.2 Mg
238.0	10 Cu, 4 Si, 0.3 Mg
242.0	4 Cu. 2 Ni, 1.5 Mg
295.0	4.5 Cu, 1 Si
296.0	4.5 Cu, 2.5 Si
308.0	5.5 Si, 4.5 Cu
319.0	3.5 Cu, 6 Si
332.0	3.0 Cu, 9.5 Si, 1.0 Mg
333.0	3.5 Cu, 9 Si, 0.2 Mg
336.0	12 Si, 2.5 Ni, 1 Mg. 1 Cu
355.0	5 Si, 1.3 Cu, 0.5 Mg
C355.0	5 Si, 1.3 Cu, 0.5 Mg
356.0	7 Si, 0.3 Mg
A360.0	9.5 Si. *0.5* Mg
A 380.0	8.5 Si, 3.5 Cu
384.0	11.5 Si, 3.8 Cu
390.0	17 Si. 4.5 Cu
413.0	12 Si
443.0	5 Si
511.0	0.5 Si, 4 Mg
512.0	1.8 Si, 4 Mg
513.0	4 Mg, 1.8 Zn
514.0	4 Mg
518.0	8 Mg
520.0	10 Mg
710.0	*0.5* Cu, 0.7 Mg, 6.5 Zn
711.0	0.5 Cu, 0.35 Mg, 6.5 Zn, 1 Fe
850.0	6.5 Sn, 1 Cu, 1 Ni
851.0	6.5 Sn. 1 Cu, 0.5 Ni, 2.5 Si
852.0	6.5 Sn, 2 Cu, 1.2 Ni, 0.7 Mg

TABLE A-8 Comparison of National Specifications – Casting Alloys

UK	ISO	France	Germany	Italy	USA AA/ASTM	USA SAE	Japan	Australia
LMO	Al 99.5	AS		UNI 3950	150			
LM2	Al-Si10Cu2Fe	A-S9U3-Y4		UNI 5076	384	383	ADC 12	
LM4	Al-Si5Cu3	A-S5U3	G-AlSi6Cu4 (225)	UNI 3052	319	326	AC 2A	AA303
LM5	Al-Mg5Si1	A-G6	G-AlMg5 (244)	UNI 3058	514	320	AC 7A	
LM6	Al-Mg6 Al-Si12 Al-Si12Fe	A-S13	G-AlSi12 (230)	UNI 4514	A413		AC 3A	BB401 CC401 EA401
LM9	Al-Si10Mg	A-S10G	G-AlSi10Mg (233)	UNI 3049	A360	309	AC 4A	
LM12	Al-Cu10Si2Mg	A-U10G		UNI 3041	295	24		
LM13	Al-Si12Cu Al-Si12CuFe	A-S12UN		UNI 3050	336	321	AC 8A	
LM16	Al-Si5Cu1Mg	A-S4UG		UNI 3600	355	322	AC 4D	AA309
LM20	Al-Si12Cu Al-Si12CuFe	A-S12-Y4	G-AlSi12(Cu) (231)	UNI 5079	A413	305		DA401
LM21	Al-Si6Cu4	A-S5U2	G-AlSi6Cu4 (225)	UNI 7369/4	308	326	AC 2A	
LM22	Al-Si5Cu3	A-S5U	G-AlSi6Cu4 (225)	UNI 3052	319	326	AC 2A	
LM24	Al-Si8Cu3Fe	A-S9U3A-Y4	G-AlSi8Cu3 (226)	UNI 5075 UNI 3601	A380	306	AC4B ADC 10	CA313 BA323 AA325
LM25	Al-Si7Mg	A-S7G	G-AlSi7Mg	UNI 3599	A356	323	AC 4C	AA601 AC601 CC601 DA601
LM26	Al-Si9Cu3Mg	A-S7U3G		UNI 3050	332	332		
LM27	Al-Si5Cu3			UNI 7369 - 79/6			AC 2B	
LM28	Al-Si19CuMgNi			UNI 6251				
LM29	Al-Si23CuMgNi			UNI 6251				
LM30	Al-Si17Cu4Mg				390			
LM31	Al-Zn5Mg	A-Z5G		UNI 3602	712	310		
BS2L99	Al-Si7Mg	A-S7G	G-AlSi7Mg	UNI 7257	A356	336	AC 4C	AA601
BSL119		A-U5NKZr						
BSL154					295			
BSL155					295			
BSL169		A-S7GO6	G-AlSi7Mg	UNI 8392	A357			
BSL173	Al-Si7Mg	A-S7G	G-AlSi7Mg	UNI 7257	A356	336	AC 4C	AA601
RSL174	Al-Si7Mg	A-S7G	G-AlSi7Mg	UNI 7257	A356	336	AC 4C	AA601
DTD716R	Al-Si5Mg	A-S4G	G-AlSi5Mg (235)	UNI 3054				
DTD722B	Al-Si5Mg	A-S4G	G-AlSi5Mg (235)	UNI 3054				
DTD727B	Al-Si5Mg	A-S4G	G-AlSi5Mg (2353	UNI 3054				
DTD735B	Al-Si5Mg	A-S4G	G-AlSi5Mg (235)	UNI 3054				
DTD5008B	Al-Zn5Mg	A-Z5G		UNI 3602	712	310		
DTD5018A			G-AlMg9 (349)	UNI 3057	535			

Notes: (1) The foreign specifications above are only an indication of the alloy type.
(2) BSL and DTD specifications are subject to BS4L101 and other inspection requirements

APPENDIX B Finishing Specifications

INTERNATIONAL,

ISO 1463-1982	Measurement of local thickness of metal and oxide coatings by the microscopical examination of cross sections (BS EN ISO 1463).
ISO 1519-1973	Paints and varnishes. Bend test (Cylindrical mandrel) (BS EN ISO 1519).
ISO 1520-1973	Paints and varnishes. Cupping test (BS EN ISO 1520).
ISO 2064-1980	Definitions and conventions concerning the measurement of thickness (BS EN ISO 2064).
ISO 2079-1971	Surface treatment and metallic coatings – General classification of terms.
ISO 2080-1971	Electroplating and related processes – Vocabulary.
ISO 2085-1976	Anodizing of aluminium and its alloys – Check of continuity of thin anodic oxide coatings – Copper sulphate test.
ISO 2106-1982	Anodizing of aluminium and its alloys – Determination of mass per unit area (surface density) of anodic oxide coatings – Gravimetric method.
ISO 2128-1976	Anodizing of aluminium and its alloys – Determination of thickness of anodic oxide coatings – Non-destructive measurement by split-beam microscope.

ISO 2135-1984	Anodizing of aluminium and its alloys – Accelerated test of light fastness of coloured anodic oxide coatings using artificial light.
ISO 2143-1981	Anodizing of aluminium and its alloys – Estimation of loss of absorptive power of anodic oxide coatings after sealing – Dye spot test with prior acid treatment.
ISO 2177-1985	Metallic coatings – Measurement of coating thickness – Coulometric method by anodic dissolution.
ISO 2360-1982	Non-conductive coatings on non-magnetic basis metals – Measurement of coating thickness – Eddy current method (BS EN ISO 2360).
ISO 2361-1982	Electrodeposited nickel coatings on magnetic and non-magnetic substrates – Measurement of coating thickness – Magnetic method (BS EN ISO 2361).
ISO 2376-1972	Anodizing of aluminium and its alloys – Insulation check by measurement of breakdown potential.
ISO 2409-1992	Paints and varnishes. Cross-cut test (BS EN ISO 2409).
ISO 2810-1974	Paints and varnishes. Notes for guidance on the conduct of natural weathering tests (BS 3900-F6).
ISO 2813-1994	Paints and varnishes. Measurement of specular gloss of non-metallic paint films at 20°, 60° and 85° (BS 3900-D5).
ISO 2819-1980	Metallic and related coatings – Review of methods available for testing adhesion of electrodeposited and chemically deposited metallic coatings on metallic substrates (BS EN ISO 2819).
ISO 2931-1983	Anodizing of aluminium and its alloys – Assessment of quality of sealed anodic oxide coatings by measurement of admittance or impedance.
ISO 2932-1981	Anodizing of aluminium and its alloys – Assessment of sealing quality by measurement of the loss of mass after immersion in acid solution.
ISO 3210-1983	Anodizing of aluminium and its alloys – Assessment of quality of sealed anodic oxide coatings by measurement of the loss of mass after immersion in phosphoric-chromic acid solution.

ISO 3211-1977	Anodizing of aluminium and its alloys – Assessment of resistance of anodic oxide coatings to cracking by deformation.
TSO 3231-1993	Paints and varnishes. Determination of resistance to humid atmospheres containing sulfur dioxide (BS EN ISO 3231).
ISO 3497-1990	Metallic and related coatings – Measurement of coating thickness of metallic coatings – X-ray spectrometric methods.
ISO 3543-1981	Metallic and non-metallic coatings – Measurement of thickness – Beta backscatter method (BS EN ISO 3543).
IS0 3668-1998	Paints and varnishes. Visual comparison of the colour of paints (BS 3900-D1).
ISO 3892-1980	Conversion coatings on metallic materials – Determination of coating mass per unit area – Gravimetric methods (BS EN ISO 3892).
ISO 4516-1980	Metallic and related coatings – Vickers and Knoop microhardness tests.
ISO 4518-1980	Metallic and related coatings – Profilometric method for measurement of coating thickness (BS EN ISO 4518).
ISO 4519-1980	Electrodeposited metallic coatings and related finishes – Sampling procedures for inspection by attributes.
ISO 4536-1985	Metallic and non-organic coatings on metallic substrates - Saline droplets corrosion test (SD test) (BS EN ISO 4536).
ISO 4540-1980	Metallic coatings – Rating of electroplated test specimens subjected to corrosion tests – Coatings cathodic to the substrate (BS EN ISO 4540).
ISO 4541-1978	Metallic coatings – Corrodkote corrosion test (CORR test) (BS EN ISO 4541).
TSO 4542-1981	Metallic and other non-organic coatings – General rules for stationary outdoor exposure corrosion tests.

ISO 5190-1984	Anodizing of aluminium and its alloys – Evaluation of uniformity of appearance on architectural anodic finishes – Determination of diffuse reflectance and specular gloss.
ISO 6270-1980	Paints and varnishes. Determination of resistance to humidity (continuous condensation) (BS EN ISO 6270).
ISO 6581-1980	Anodizing of aluminium and its alloys – Determination of the fastness of ultra-violet light of coloured anodic oxide coatings.
ISO 6719-1986	Anodizing of aluminium and its alloys – Measurement and calculation of reflectance characteristics of aluminium surfaces using integrating sphere instruments.
ISO 6988-1985	Metallic and other non-organic coatings - sulfur dioxide test with general condensation of moisture (BS EN ISO 6988).
ISO 7583-1986	Anodizing of aluminium and its alloys – Vocabulary.
ISO 7599-1983	Anodizing of aluminium and its alloys – General specifications for anodic oxide coatings on aluminium.
ISO 7668-1986	Anodizing of aluminium and its alloys – Measurement of specular reflection characteristics at fixed angle of 20°, 45°, 60" and 85°.
ISO 7669-1986	Anodizing of aluminium and its alloys – Total reflectivity with a photoelectric reflectometer. (Now withdrawnj
ISO 7759-1983	Anodizing of aluminium and its alloys – Measurement of reflectivity characteristics of aluminium surfaces using abridged goniophotometer or goniophotometer.
ISO 8076-1984	Aerospace process – Anodic treatment of aluminium alloys – Chromic acid process 40 V DC, undyed coating.
ISO 8077-1984	Aerospace process – Anodic treatment of aluminium alloys – Chromic acid process 20 V DC, undyed coating.
ISO 8078-1984	Aerospace process – Anodic treatment of aluminium alloys – Sulphuric acid process, undyed coating.

ISO 8079-1984	Aerospace process – Anodic treatment of aluminium alloys – Sulphuric acid process, dyed coating.
ISO TR8125-1984	Anodizing of aluminium and its alloys – Determination of colour and colour difference of coloured anodic coatings.
ISO 8251-1987	Anodizing of aluminium and its alloys – Measurement of wear resistance and wear index of anodic oxidation coatings with an abrasive wheel wear test apparatus.
ISO 8252-1987	Anodizing of aluminium and its alloys – Measurement of mean specific abrasion resistance of anodic oxidation coatings with an abrasive jet apparatus.
ISO 8401-1986	Metallic coatings – Review of methods of measurement of ductility (BS EN ISO 8401).
ISO 8403-1991	Metallic coatings – Coatings anodic to the substrate – Rating of test specimens subjected to corrosion tests (BS EN ISO 8403).
ISO 8565-1992	Metals and alloys. Atmospheric corrosion testing – General requirements for field tests (BS EN ISO 8565).
ISO 8993-1989	Anodizing of aluminium and its alloys – Rating system for the evaluation of pitting corrosion – Grid method.
ISO 8994-1989	Anodizing of aluminium and its alloys – Rating system for the evaluation of pitting corrosion – Chart method.
ISO 9220-1988	Metals and alloys. Atmospheric corrosion testing – Scanning electron microscope method (BS EN ISO 9220).
ISO 9227-1990	Corrosion tests in artificial atmospheres – Salt spray tests.
ISO 9717-1990	Phosphate conversion coatings for metals – Method of specifying requirements (BS 3189).
ISO 10074-1992	Hard anodizing on aluminium and aluminium alloys.
ISO 10215-1992	Anodized aluminium and aluminium alloys – Visual determination of image clarity of anodic oxidation coatings – Chart scale Method.
ISO 10216-1992	Anodized aluminium and aluminium alloys – Instrumental determination of image clarity of anodic oxidation coatings – Instrumental method.

ISO 11341-1994	Paints and varnishes. Artificial weathering and exposure of coatings to artificial radiation alone – Exposure to filtered xenon-arc radiation. (BS EN ISO 11341).
ISO TR11728-1993	Anodized aluminium and aluminium alloys – Accelerated test of weather fastness of coloured anodic oxide coatings using cyclic artificial light and pollution gas.

BRITISH

British Standards Institution

B.S. 1344:	Methods of testing vitreous enamel finishes.
Part 1: 1994	– Resistance to thermal shock **of** coatings on articles other than cooking utensils.
Part 2: 1975 (1994)	– Resistance to citric acid at room temperature (ISO 2722).
Part 3: 1998	– Determination of resistance to sulphuric acid at room temperature (BS EN ISO 4535).
Part 4: 1968	– Resistance to abrasion (obsolescent).
Part 5: 1984 (1990)	– Determination of resistance to hot detergent solutions used for washing textiles (ISO 4533).
Part 6: 1971 (1994)	– Resistance to alkali.
Part 7: 1984 (1990)	– Determination of resistance to heat (ISO 4530).
Part 8: 1984 (1990)	– Resistance to boiling citric acid (ISO 2742).
Part 9: 1998	– Resistance to boiling water and water vapour (ISO 2744).
Part 10: 1987 (1993)	– Resistance to condensing hydrochloric acid vapour (ISO 2743).
Part 11: 1998	– High voltage test for articles for service under highly corrosive conditions (ISO 2746).
Part 12: 1996	– Production of specimens for testing coatings on sheet steel (ISO 2723).

Part 13: 1975 (1994)	– Production of specimens for testing coatings on cast iron (ISO 2724).
Part 14: 1984 (1970)	– Apparatus for testing with acid and neutral liquid and their vapours (ISO 2733).
Part 15: 1997	– Apparatus for testing with alkaline liquid (IS0 2734).
Part 16: 1998	– Resistance to thermal shock of coatings on cooking utensils (ISO 2747).
Part 17: 1998	– Resistance to hot sodium hydroxide solution (ISO 2745).
Part 18: 1981 (1990)	– Determination of fluidity behaviour-fusion flow test (ISO 4534).
Part 19: 2000	– Apparatus for determination of resistance to hot detergent solutions used for washing textiles (BS EN IS0 4535).
Part 20: 1987 (1993)	– Low voltage test for detecting and locating defects (ISO 8289).
Part 21: 1943	– Determination of the resistance of vitreous enamelled articles to impact: pistol test (ISO 4532).
B.S. 1615: 1987 (1994)	Method for specifying anodic oxidation coatings on aluminium and its alloys.
BS EN 2101: 1991	Chromic acid anodizing of aluminium and wrought aluminium alloys (Aerospace series).
BS EN 2284: 1991	Sulfuric acid anodizing of aluminium and wrought aluminium alloys (Aerospace series).
BS EN 2334: 1997	Chromic-sulphuric acid pickle of aluminium and aluminium alloys (Aerospace series).
BS EN 2536: 1995	Hard anodizing of aluminium alloys (Aerospace series).
BS EN 3665: 1997	Test methods of paints and varnishes – Filiform corrosion resistance test on aluminium alloys (Aerospace series).
B.S. 3745: 1970 (1996)	Method for the evaluation of results of accelerated corrosion tests on metallic coatings (IS0 1462).
B.S. 3900:	Methods of test for paint.
B.S. 3987: 1991 (1997)	Anodic oxide coatings on wrought aluminium for external architectural applications.

B.S. 4479:	Design of articles that are to be coated.
Part 1: 1990 (1997)	– General recommendations.
Part 2: 1990 (1998)	– Recommendations for electroplated and autocatalytic coatings.
Part 3: 1990 (1997)	– Recommendations for conversion coatings.
Part 4: 1990 (1997)	– Recommendations for paint coatings and varnish coatings.
Part 5: 1990 (1997)	– Recommendations for anodic oxidation coatings.
Part 6: 1990	– Recommendations for hot-dip metal coatings.
Part 7: 1990 (1997)	– Recommendations for thermally sprayed coatings.
Part 8: 1990	– Recommendations for vitreous enamel coatings.
Part 9: 1990 (1997)	– Recommendations for low pressure and vacuum deposited coatings.
B.S. 4842: 1984 (1991)	Liquid organic coatings for application *to* aluminium alloy extrusions, sheet and preformed sections for external architectural purposes, and for the finish on aluminium alloy extrusions, sheet and preformed sections coated with liquid organic coatings.
B.S. 5411:	Methods of test for metallic and related coatings.
Part 1: 1980	– Definitions and conventions concerning the measurement of thickness (BS EN ISO 2064).
Part 2: 1987	– Review of methods for the measurement of thickness (BS EN ISO 3882).
Part 3: 1984	– Eddy current method for the measurement of coating thickness of non-conductive coatings on non-magnetic basis metals (BS EN ISO 2360).
Part 4: 1986	– Coulometric method for the measurement of coating thickness (BS EN ISO 2177).
Part 5: 1984	– Measurement of local thickness of metal and oxide coatings by the microscopical examination of cross-sections (BS EN ISO 1463).
Part 6: 1981 (1997)	– Vickers and Knoop microhardness tests (ISO 4516).
Part 7: 1981	– Profilometric method for measurement of coating thickness (BS EN ISO 4518).

Part 8: 1991 (1997) – Measurement of coating thickness of metallic coatings: X-ray spectrometric methods (ISO 3497).

Part 9: 1984 – Measurement of coating thickness of electrodeposited nickel coatings on magnetic and non-magnetic substrates: magnetic method (BS EN ISO 2361).

Part 10: 1981 – Review of methods available for testing adhesion of electrodeposited and chemically deposited metallic coatings on metallic substrates (BS EN ISO 2819).

Part 11: 1984 – Measurement of coating thickness of non-magnetic metallic and vitreous or porcelain enamel coatings on magnetic basis metals: magnetic method (BS EN ISO 2178).

Part 12: 1981 – Beta backscatter method for measurement of thickness (BS EN ISO 3543).

Part 13: 1982 – Chromate conversion coatings on zinc and cadmium (BS EN ISO 3613).

Part 14: 1982 – Gravimetric method for determination of coating mass per unit area of conversion coatings on metallic materials (BS EN ISO 3892).

Part 15: 1988 – Review of methods of measurement of ductility (BS EN ISO 8401).

Part 16: 1980 – Scanning electron microscope method for measurement of local thickness of coatings by examination of cross-sections (BS EN ISO 9220).

B.S. 5466: Methods for corrosion testing of metallic coatings.

Parts 1-3 – See BS 7479 (1991).

Part 4: 1979 – Thioacetamide test (TAA test) (BS EN ISO 4538).

Part 5: 1979 – Corrodkote test (CORR test) (BS EN ISO 4541).

Part 6: 1982 – Rating of results of corrosion tests on electroplated coatings cathodic to the substrate (BS EN ISO 4546).

Part 7: 1982 (1993) – Guidance on stationary outdoor exposure corrosion tests (ISO 4542).

Part 8: 1986 – Sulphur dioxide test with general condensation of moisture (BS EN ISO 6988).

Part 9: 1986 – Saline droplets corrosion test (SD test) (BS EN ISO 4536).

Part 10: 1988	– Coatings anodic to the substrate. Rating of test specimens subjected to corrosion tests (BS EN ISO 8403).
B.S. 5599: 1993	Specification for hard anodic oxide coatings on aluminium and its alloys for engineering purposes.
B.S. 6041: 1981 (1995)	Method of sampling of electrodeposited metallic coatings and related finishes: procedures for inspection by attributes (ISO 4519).
B.S. 6161:	Methods of test for anodic oxidation coatings on aluminium and its alloys.
Part 1: 1984 (1995)	– Determination of mass per unit area (surface density) of anodic oxidation coatings (gravimetric method) (ISO 2106).
Part 2: 1981 (1994)	– Determination of thickness of anodic oxide coatings: non-destructive measurement by split-beam microscope (ISO 2128).
Part 3: 1984 (1995)	– Assessment of sealing quality by measurement of the loss of mass after immersion in phosphoric-chromic acid solution (ISO 3210).
Part 4: 1981 (1994)	– Assessment of sealing quality by measurement of the loss of mass after immersion in acid solution (ISO 2932).
Part 5: 1982 (1994)	– Estimation of loss of absorptive power of sealed coatings: dye spot test with prior acid treatment (ISO 2143).
Part 6: 1984 (1995)	– Assessment of sealing quality by measurement of admittance or impedance (ISO 2931).
Part 7: 1984 (1995)	– Accelerated determination of light fastness of coloured anodic oxidation coatings using artificial light (ISO 2135).
Part 8: 1981 (1994)	– Determination of the fastness to ultra violet light of coloured anodic oxide coatings (ISO 6581).
Part 9: 1987 (1994)	– Measurement of wear index and wear resistance with an abrasive wheel wear test apparatus (ISO 8251).
Part 10: 1987 (1994)	– Measurement of mean specific abrasion resistance with an abrasive jet test apparatus (ISO 8252).

Part 11: 1985 (1994) – Measurement of total reflectance using a photoelectric reflectometer.

Part 12: 1987 (1994) – Measurement of specular reflectance and specular gloss at angles of 20°, 45°, 60" and 85" (ISO 7668).

Part 13: 1993 – Visual determination of image clarity - Chart Scale Method (ISO 10215).

Part 14: 1987 (1994) – Determination of infra-red reflectance.

Part 15: 1987 (1904) – Determination of electrical breakdown potential.

Part 16: 1990 (1905) – Rating system for the evaluation of pitting corrosion - Chart Method (ISO 8993).

Part 17: 1900 (1995) – Rating system for the evaluation of pitting corrosion - Grid Method (ISO 8994).

Part 18: 1991 (1907) – Determination of surface abrasion resistance.

Part 19: 1993 – Determination of image clarity - Instrumental Method (ISO 10216).

B.S. 6496: 1984 (1991) Specification for powder organic coatings for application and stoving to aluminium alloy extrusions, sheet and preformed sections for external architectural purposes, and for the finish on aluminium alloy **extrusions, sheet and preformed sections** coated with powder organic coatings.

B.S. 7479: 1991 Method for salt spray corrosion tests in artificial atmospheres (ISO 9227) (Replaced BS 5466-Parts 1-3).

Defence

DEF STAN 03-2/3 (1995) – Cleaning and preparation of metal surfaces.

DEF STAN 03-3/21 (1995) – Protection of aluminium alloys by sprayed metal coatings.

DEF STAN 03-7/1 (1973) – Application of paint materials to metallic surfaces.

DEF STAN 03-18.11 (1979) – Chromate conversion coatings (chromate filming treatments) for aluminium and aluminium alloys.

DEF STAN 03-24/2 1988 – Chromic acid anodizing of aluminium and aluminium alloys.

DEF STAN 03-25/2 1988 – Sulphuric acid anodizing of aluminium and aluminium alloys.

DEF STAN 03-26/2 1988 – Nard anodizing of aluminium and aluminium alloys.

(The latter three standards replaced DEF 151 and have now themselves been superseded by BS EN 2101, 2284 and 2536 respectively).

Others

Aluminium Window Association – Specification for stoved organic finishes on aluminium window products (1976).

EUROPEAN

(Many are dual numbered with BS and ISO Standards)

EN 12373: Aluminium and Aluminium Alloys – Anodizing

This comprises the following parts:

Part 1: 2001 – Method for specifying decorative and protective anodic oxidation coatings on aluminium.

Part 2: 1999 – Determination of mass per unit area (surface density) of anodic oxidation coatings – Gravimetric method.

Part 3: 1999 – Determination of thickness of anodic oxidation coatings – Non-destructive measurement by split beam microscope.

Part 4: 1999 – Estimation of loss of absorptive power of anodic oxidation coatings after sealing by dye spot test with prior acid treatment.

Part 5: 1999 – Assessment of quality of sealed anodic oxidation coatings by measurement of admittance.

Part 6: 1999 – Assessment of quality of sealed anodic oxidation coatings by measurement of the loss of mass after immersion in phosphoric acid/chromic acid solution without prior acid treatment.

Part 7: 1999 – Assessment of quality of sealed anodic oxidation coatings by measurement of the loss of mass after immersion in phosphoric acid/chromic acid solution with prior acid treatment.

Part 8: 1999	– Determination of the comparative fastness to ultra-violet light and heat of coloured anodic oxidation coatings.
Part 9: 1999	– Measurement of wear resistance and wear index of anodic oxidation coatings using an abrasive wheel wear test apparatus.
Part 10: 1999	– Measurement of mean specific abrasion resistance of anodic oxidation coatings using an abrasive jet test apparatus.
Part 11: *2000*	– Measurement of specular reflectance and specular gloss of anodic oxidation coatings at angles of 20, 45, 60 or 85 degrees.
Part 12: *2000*	– Measurement of reflectance characteristics of aluminium surfaces using integrating-sphere instruments.
Part 13: 2000	– Measurement of reflectivity characteristics of aluminium surfaces using a goniophotometer or an abridged goniophotometer.
Part 14: 2000	– Visual determination of image clarity of anodic oxidation coatings – Chart scale method.
Part 15: 2000	– Assessment of resistance of anodic oxidation coatings to cracking by deformation.
Part 16: *200* 1	– Check for continuity of thin anodic oxidation coatings – Copper sulfate test.
Part 17: 2001	– Determination of electric breakdown potential.
Part 18: 2001	– Rating system for the evaluation of pitting corrosion – Chart method.
Part 19: 2001	– Rating system for the evaluation of pitting corrosion – Grid method.
Qualanod (Zurich)	– Specifications for the quality sign for anodic oxidation coatings on wrought aluminium for architectural purposes.
Qualicoat (Zurich)	– Specifications for a quality label for paint, lacquer and powder coatings on aluminium for architectural applications.

FRANCE

NF A 91-450 (1981) (AFNOR) – Anodizing of aluminium and its alloys – general specifications for anodic oxide coatings on aluminium.

GERMANY

DIN 17611 (1985) – Aluminium and wrought aluminium alloy anodized semi-finished products with coatings at least 10 μm **thick: technical delivery** conditions.

SWITZERLAND

SN 237250 (1984) – Anodizing of aluminium and its alloys – general directives and technical specifications.

UNITED STATES

Aeronautical Material Specifications (AMS)

SAE AMS 2420B (1977) – Plating aluminum for solderability – zinc immersion process.

SAE AMS 2427B (1995) – Aluminum plating, ion vapour deposition.

SAE AMS 2450E (1982) – Sprayed metal finish – Aluminum.

SAE AMS 2468E (1992) – Hard coating treatment of aluminum alloys

SAE AMS 2469E (1993) – Hard coating treatment – process and performance requirements of aluminum alloys.

SAE AMS 2470H (1984) – Anodic treatment – aluminum alloys, chromic acid process.

SAE AMS 2471D (1984) – Anodic treatment – aluminum alloys, sulfuric acid process, undyed coating.

SAE AMS 2472C (1984) – Anodic treatment – aluminum alloys, sulfuric acid process, dyed coating.

SAE AMS 2473E (1983) – Chemical treatment for aluminum alloys, general purpose coating.

SAE AMS 2474C (1987) – Chemical treatment for aluminum alloys, low electrical resistance coating.

SAE AMS 2483A (1993) – Blackening solution for aluminum, touch-up method.

Military Specifications (U.S.A.)

MIL-T-704 K (1992)	– Treatment and painting of material (various metals including aluminium).
MIL-S-5002D (1) (1994)	– Surface treatments and inorganic coatings for metal surfaces of weapons systems.
MIL-C-5541E (1990)	– Chemical conversion coatings on aluminium alloys (for paint adhesion or corrosion resistance).
MIL-P-6808C (1) (1994)	– Process for application of primer coating, zinc chromate.
MIL-F-7179G (1'393)	– General specifications for finishes and coatings, protection of aerospace weapons systems, structures and parts.
MIL-A-8625F (1993)	– Anodic coatings for aluminium and aluminium alloys.
MIL-I-8474C (1983)	– Anodizing process for inspection of aluminium alloy parts (chromic acid process for crack detection etc.).
MIL-C-23217B (1971l)	– Aluminium coatings, vacuum deposited.

American Society for Testing and Materials (ASTWI)

B136-84 (1998)	– Method for measurement of stain resistance of anodic coatings on aluminum.
B137-95	– Method for measurement of mass of coating on anodically coated aluminum.
B244-97	– Method for measurement of thickness of anodic coatings on aluminum and of other non-conductive coatings on non-magnetic basis metals with eddy-current instruments.
B253-87 (1993)	– Guide for preparation of aluminum alloys for electroplating.
B322-85 (1994)	– Practice for cleaning prior to electroplating.
B368-97	– Method for copper-accelerated acetic acid salt spray (fog) testing (CASS test).
B374-96	– Terminology relating to electroplating.
B380-97	– Methods for corrosion testing of decorative chromium electroplating by the Corrodkote procedure.

B449-93 (1998) – Practice for chromate treatments on aluminum.

B457-67 (1998) – Method for measurement of impedance of anodic coatings on aluminum.

B487-85 (1997) – Method for measurement of metal and oxide coating thicknesses by microscopical examination of a cross-section.

B537-70 (1997) – Recommended practice for rating of electroplated panels subjected to atmospheric exposure.

B567-98 – Method for measurement of coating thickness by the beta backscatter method.

B568-98 – Method for measurement of coating thickness by X-ray spectrometry.

B571-97 – Test methods for adhesion of metallic coatings.

B578-87 (1993) – Test method for microhardness of electroplated coatings.

B580-79 (1995) – Specification for anodic oxide coatings on aluminum.

B588-88 (1994) – Method for measurement of thickness of transparent or opaque coatings by double-beam interference microscope technique.

B602-88 (1994) – Method of attribute sampling of metallic and inorganic coatings.

B659-90 (1997) – Guide for measuring thickness of metallic and inorganic coatings.

B680-80 (1995) – Test method for seal quality of anodic coatings on aluminum by acid dissolution.

B681-88 (1994) – Method for measurement of thickness of anodic coatings on aluminum and of other transparent coatings on opaque surfaces using the light-section microscope.

B697-88 (1994) – Guide for selection of sampling plans for inspection of electrodeposited metallic and inorganic coatings.

U.S. Specs

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