

CHEMICAL COLOURING FINISHES

The colouring of untreated aluminum surfaces can be accomplished by simple dipping in certain chemical solutions. This appears to be a more economical method for the mass production of coloured aluminum articles than that of dyeing artificially thickened oxide layers. Many colouring methods have been proposed but few have attained any commercial importance since it is difficult to reproduce the same colour, and the colour produced is frequently non-uniform. In addition, the adherence of the film is usually poor. Much work remains to be carried out in this field, but with careful experimenting and control satisfactory and inexpensive coloured coating may be produced.

The preliminary cleaning of the surface is carried out with trichlorethylene or some similar organic solvent. The surface may be scoured alternatively with a paste consisting of Vienna lime and water followed by a thorough water rinse. In other cases, an alkaline or acid etch may serve as the basis for a chemical colouring process, although in order to avoid a spotted finish it is recommended that, after etching, the surface be brushed with a soft steel wire brush or rubbed with powdered pumice stone. After the surface has been prepared, the colouring process should be carried out as quickly as possible.

Permanganate baths are used in the production of a variety of dark colours. The objects to be coloured are immersed in the solution which is maintained close to the boiling temperature. Baths containing 0.8 to 1.6 oz. per gallon (5 to 10 grams per litre) potassium permanganate, approximately 0.5 oz. per gallon (3 grams per litre) of concentrated nitric acid, and 0.8 to 4.0 oz. per gallon (5 to 25 grams per litre) copper nitrate, produce a range of colours from brown to black depending on the copper concentration and the duration of the treatment.

A quick method for colouring aluminum black is immersion in a boiling solution containing 1.6 to 3.2 oz. per gallon (10 to 20 grams per litre) ammonium molybdate and 0.8 to 2.4 oz. per gallon (5 to 15 grams per litre) ammonium chloride.

A uniform velvety grey colour is produced on aluminum using a solution containing 14.5 oz. per gallon (90 grams per litre) ammonium

phosphate $(\text{NH}_4)_2\text{HPO}_4$, and 0.8 oz. per gallon (5 grams per litre) manganous nitrate at the boiling point. This has been used for the large scale colouring of small parts.

A dull grey colour is given an aluminum surface upon immersion in a solution containing 4.0 oz. per gallon (25 grams per litre) potassium sulphide and 0.16 oz. per gallon (1 gram per litre) vanadium sulphate. The solution is heated to 175° to 200°F (80° to 90°C). Subsequent scouring with steel wool causes the surface to take on an iron-like appearance.

Instead of colouring the aluminum directly, chemical deposition may be used to apply a metal coating to the surface which is then coloured in a manner suited to the deposited metal. For instance, a thin layer of copper is deposited on a clean aluminum surface upon immersion for 2 to 5 minutes in a cold 1.6 oz. per gallon (10 grams per litre) solution of copper chloride in 95 per cent ethyl alcohol. After a water rinse, the coppered surface is subjected to one of the various processes adapted to the colouring of a copper surface. For example, a brown colour is readily obtained by immersion in a solution containing 0.8 to 1.6 oz. per gallon (5 to 10 grams per litre) Hepar (potassium sulphide).

Coloured coatings obtained by applying organic dye solutions on M.B.V. or Alrok films (see pages 29, 30) are far more satisfactory than those obtained by precipitation of coloured inorganic compounds on the surface of aluminum sheet. A variation of the M.B.V. treatment using an M.B.V. solution containing:

sodium carbonate	11.2 oz.	70 grams
sodium chromate	2.4 oz.	15 grams
water to make	1 gallon	1 litre

gives a more satisfactory result when the coating is to be coloured with organic dyes. An excellent even black colour can be produced on aluminum coated with the M.B.V. treatment by immersing the coated article for 10 minutes in a solution consisting of potassium permanganate 4.0 oz. per gallon (25 grams per litre) and sodium carbonate 0.16 oz. per gallon (1 gram per litre) at 203° to 212°F (95° to 100°C). The article is then washed and placed in a (3.2 oz. per gallon; 20 grams per litre) solution of cobalt acetate for another 10 minutes.



Figure 5: Hand-polished aircraft finish.

This coating will contain traces of brown so it is given a second immersion in the permanganate and acetate solutions which produces a deep black colour. Washing and sealing in a 1.5 oz. per gallon (10 grams per litre) sodium silicate solution for 5 minutes at 212°F (100°C) follows and the article is then finished with wax.

CHEMICAL COATING FINISHES

When an aluminum surface is exposed to the atmosphere it is rapidly covered with a thin film of oxide which protects the underlying metal against further attack. While the thickness of this natural oxide film is about 0.0004 mil (0.01 μ) there are several methods by means of which the oxide layer may be increased in thickness. The metal is thus given a substantial amount of increased protection against corrosion and abrasion, and, with occasional washing, the surface so obtained is capable of retaining its original appearance under all but severe industrial conditions. Furthermore, such a surface will absorb certain dyes and pigments as well as furnish an excellent base for painting and similar finishing operations.

Characteristics of Chemical Coating Finishes

Chemical coating finishing methods take the form of dip treatments in various acid and alkali solutions. The coatings so produced have a thickness of approximately 0.04 to 0.12 mils (1 to 3 μ), and are softer and less resistant to corrosion and abrasion than anodized coatings. They increase the emissivity and can thus be used to increase the heat-radiating power of an aluminum surface. Chemical coatings also reduce the reflectivity of visible light. Most of the coatings can be coloured by absorption of inorganic and organic pigment, although the colours produced are neither as brilliant nor as fast to light as those obtained with anodized coatings. On the other hand, the ease and economy with which they are applied have resulted in their extensive use when the service conditions are not too rigorous.

The chemical film cannot be detached by fabricating processes such as bonding, rolling, and pressing. The film is not sufficiently elastic to adapt itself to these various deformation processes and will crack during formation, although it will still adhere perfectly to the base metal almost completely covering it. Sheet and strip aluminum

should be coated after forming, particularly in the case of severe forming such as deep drawing or impact extrusion.

The time of treatment is relatively short and no electricity is necessary. The equipment used is simple in construction and there are no serious operational problems in racking. Care should be taken with fabricated articles to see that all surfaces come into contact with the solution and that air pockets are eliminated. The work may be handled on jigs, racks, wire hooks, baskets or in revolving perforated drums. Spray machines may be designed to handle large quantities of similarly shaped articles. In automatic processes, provision must be made by means of baffle plates and drainage sections to ensure that no mixing of the various solutions takes place. Tanks constructed of wood, enamelled metal or welded mild steel are used for the solutions.

Pretreatment of the Surface

As with most other finishing processes, the original state of the metal surface determines to a large degree the appearance of the final surface. Chemical coatings cannot hide blemishes such as riser defects in castings and rolling marks in sheet. In fact, they will accentuate such markings, and may bring out "banding", a streaked appearance, which previously may not have been apparent. Scratches and surface roughness will show up in the final finish and therefore must first be removed by mechanical or chemical etching methods. In addition, it is necessary to remove excessive oil, grease, or other surface contamination although the alkaline nature of the hot M.B.V. bath will take care of small amounts of foreign matter, and the preliminary cleaning and degreasing may be omitted, but this is not recommended. A hot caustic etch (see page 20) provides a satisfactory uniform surface for chemical oxidation.

The M.B.V. Process

The M.B.V. (modified Bauer Vogel) process produces a coating, varying from greyish to colourless on pure aluminum and dark grey when the metal is highly alloyed. In the case of sheet and other wrought products, the grain structure shows through and is emphasized by the coating, producing a decorative effect. On smooth, rolled, or polished objects, the oxide films are lustrous; a rough surface yields a greyish coat.

The M.B.V. bath is usually a water solution of sodium carbonate, and potassium chromate, but for alloys which contain over 3% magnesium about 1.6 oz. per gallon (10 grams per litre) of sodium hydroxide is added and the bath is operated at a somewhat lower temperature.

Details of the various chemical oxidizing processes are given in Table No. 4 on page 30.

The E.W. Process

The E.W. (Erftwerk) process is a development of the M.B.V. process in which sodium silicate is included in the bath in order to obtain clear transparent films not only on pure commercial aluminum but also on alloys containing high percentages of silicon which normally give dark grey dull coatings.

The Alrok Process

Alrok coatings differ in colour and appearance with the specific process employed, however the normal coating, without a sealing treatment, has a grey or greenish-grey colour. After sealing in dichromate the colour has a yellow-green tint. A further variation produced by altering the ratio of alkali to dichromate produces a white finish with a very slight grey tint.

Alrok coatings are applied by immersion of the article in a suitable alkaline solution for a predetermined period. The composition of the solution is determined by the alloy which is to be treated and by the character of the coating that is desired. The proper ratio of alkali to dichromate is important in the operation of the process and differs with cast and wrought products. The solution should be worked for about 60 minutes at 185° to 189°F (85° to 87°C) with aluminum scrap before the actual coating process is started.

The first step in carrying out the process is a cleaning operation. A mild alkaline cleaner is preferable, but it should be noted that for this process the cleaner should not be inhibited with sodium silicate because the silicate forms a resistant film on the metal which interferes with the coating operation. Cleaning is followed by rinsing in cold water. The Alrok treatment is then applied, followed by a further water rinse and finally the coating is sealed.

Chemical Oxidizing Processes

PROCESS	OXIDATION BATH				SEALING				COLOUR OF FILM	SUITABLE FOR		
	Composition		TIME	Temperature		Composition		TIME			Temperature	
	oz./gal.	g/l		of	°C	oz./gal.	g/l				of	°C
M.B.V.	Na ₂ CO ₃ 8 K ₂ CrO ₄ 2.4	Na ₂ CO ₃ 50 K ₂ CrO ₄ 2.4	5 - 10 min.	194	90	*Sodium Silicate 4.8 - 9.6	Sodium Silicate 30 - 60	15 min.	194	90	All alloys except copper-rich	Greyish
E.W.	Na ₂ CO ₃ 7.5 Na ₂ CrO ₄ 2.2 0.010 - 0.016 Sodium Silicate (40 Bé)	Na ₂ CO ₃ 47 Na ₂ CrO ₄ 14 0.06 - 0.1 Sodium Silicate (40 Bé)	10 min.	194 - 212	90 - 100	3.2 Sodium Silicate	20 Sodium Silicate	15 min.	203	95	Same as M.B.V.	Clear to grey
ALROK	Na ₂ CO ₃ 3.2 K ₂ Cr ₂ O ₇ 0.16	Na ₂ CO ₃ 20 K ₂ Cr ₂ O ₇ 1	10 - 20 min.	185 - 203	85 - 95	K ₂ Cr ₂ O ₇ 8	K ₂ Cr ₂ O ₇ 50	10 min.	185	85	All alloys	Grey to Yellowish-green

* This is a syrupy liquid sold commercially as 40° Baumé sodium silicate, commonly called water glass.

Chromodizing

The chromodizing process produces a very thin oxide coating which, however, provides a good base for subsequent painting. The work, after a normal degreasing, is cleaned in a hot alkaline cleaner followed by a water rinse. The article is then immersed for 5 minutes in a bath containing 8 oz. per gallon (50 grams per litre) chromic acid at about 130°F (55°C) and the treatment completed by a water rinse.

Phosphatizing

This process, which is similar to chromodizing, produces a thin film of aluminum phosphate which is firmly adherent to the metal. Phosphatizing forms an excellent base on which to apply an organic coating, and is often used as a prepaint treatment.

A solution recommended in the U.S. Army Specifications No. 98-20007, Amendment No. 4 is widely used. It has the following composition:

Butyl Alcohol	4 gallons	18.2 litres
Isopropyl Alcohol	3 gallons	13.7 litres
Phosphoric Acid (85%)	1 gallon	4.55 litres
Water	2 gallons	9.1 litres

The work is left in contact with the solution for one or two minutes, then scrubbed lightly with a bristle brush and rinsed thoroughly with water.

Alodine Process

This is a patented process for chemically treating aluminum surfaces that is becoming increasingly popular. The coating produced is thin, tight, hard and skin-like and is an integral part of and continuous with the basis metal. The colour ranges from an iridescent blue-green to a greenish-yellow. The coating provides an excellent bond for paint.

The articles are cleaned and rinsed, then alodized either by immersion, power spray, flow coating or brushed on. A stainless steel tank is required for the Alodine solution. The coating time is 2 minutes or less when the parts are immersed and 30 seconds or less when the parts are sprayed. The solution temperature is 120°F (49°C) maximum. If the alodine surface is to be painted the work is rinsed, then

immersed in a "Deoxylyte" solution and heat dried. If the surface is to be left unpainted the work is dried after alodizing without further rinsing.

Bonderite 170

Another process, which produces a paint-holding phosphate coating on aluminum, is Bonderizing, a patented process. This is similar to the Bonderizing of iron, steel, zinc and cadmium. Bonderite 170 may be applied either by spraying or immersion in the solution or it can be readily adapted to conveyor production methods. Mild steel equipment is used. The process consists of cleaning, rinsing in hot water, Bonderizing using a water solution of Bonderite 170 made up according to direction, rinsing in hot water, then a rinse in Parcolene which removes any residual alkali from the Bonderizing solution. The solutions are maintained at 180 to 190°F (82 to 88°C), and the time of treatment in the Bonderizing solution is one to five minutes depending upon the type of metal being treated.

IV.

Electrochemical Finishes

The number of uses to which aluminum and its alloys have been put has increased considerably because of certain special electrolytic surface treatments. Of these, there are two main classes, the first being the production of an artificially strengthened oxide film on an aluminum surface by anodic treatment in certain electrolytes, including electrolytic brightening (see page 55), and the second being electroplating on aluminum which is described in Chapter V.

ANODIZING

In certain electrolytes when aluminum is made the anode and current applied, a dense oxide coating is built up on its surface which possesses many desirable characteristics. Anodizing, as the procedure is called, leads to a much superior degree of protection than is obtained by chemical oxidation, however it is somewhat more expensive. An anodic coating may be defined as a film of aluminum oxide that is formed by electrochemical reaction of the metal surface with an aqueous electrolyte. Hence an anodic coating is also a conversion coating formed from the metal itself and integrally bonded to the surface.

The properties of the anodic film depend upon the electrolyte and the anodizing conditions such as electrolyte composition and concentration, temperature of operation, time of treatment, current density, voltage, and alloy used. Thickness is limited by the fact that while the film is growing from the inside out, chemical solution by the electrolyte also takes place simultaneously. Ultimately an equilibrium point is reached because as the film thickness increases so does the surface exposed to the solution as the pores become long channels and consequently the rate of solution is increased. This means that the rate of film growth will slowly decrease and finally a maximum value of film thickness will be reached. At this point the rate of electrochemical formation and chemical dissolution are equal, and no further increase in film thickness can be secured by continued treatment under the same conditions. If the treatment is unduly prolonged the outer layer of oxide may become loose and powdery and of little value as a protective film.

Corundum, or emery, a crystalline modification of aluminum oxide, is extremely hard, and thus it is to be expected that anodic coatings which are aluminum oxide will be hard and resistant to abrasion. Anodic coatings have a hardness comparable to that of Topaz—No. 8 on the Moh scale of hardness. The base metal is considerably softer than the oxide film, but the latter may be rather easily punctured or cracked under high pressures. Even so, the adherence of the oxide layer to the base metal is such that the film does not chip or flake off, and, indeed, the corrosion protection at the point of damage is not greatly affected.

The light reflectivity of the anodically coated metal is only about 10 per cent less than that of the original surface. In the case of reflectors for electric heaters a marked improvement in the reflection has been obtained by heating the reflectors at 390°F (200°C) and impregnating the surface with wax.

An outstanding use of the absorptive qualities of anodic coatings is to produce coloured coatings impregnated with organic and inorganic substances as described under the section Dyed Anodic Coatings. The nature of the film makes it ideal for retaining a wide variety of substances, such as lubricants and wax emulsions, within the pores.

All processes of anodic oxidation, by increasing the thickness of the natural oxide film on aluminum, naturally increase the resistance to corrosion by atmospheric conditions and the attack of a large number of chemicals. While the corrosion resistance of the oxide coating is greatest towards approximately neutral attacking media, good service is afforded in slightly acid solutions, providing the pH does not fall below 4 or 5. Contact with organic materials which form stable complexes with aluminum and the use of strongly alkaline or uninhibited cleaners should be avoided.

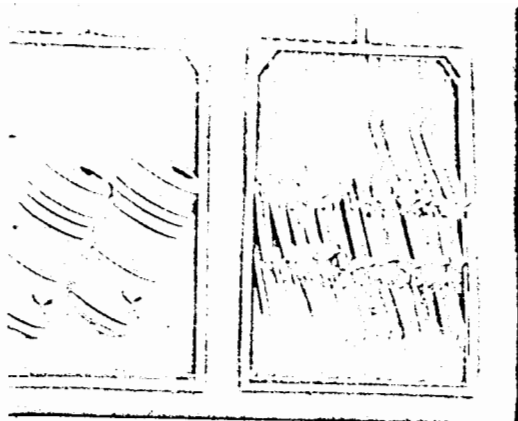
Anodic films produced on aluminum are characterized by their good insulating properties. This property finds practical importance in anodized aluminum electric wires and in foil for vacuum tube condensers.

PRETREATMENT OF SURFACE TO BE ANODIZED—Irregularities of the metal surface not removed by the usual finishing methods are generally quite apparent after anodizing, even if they were hardly visible before.

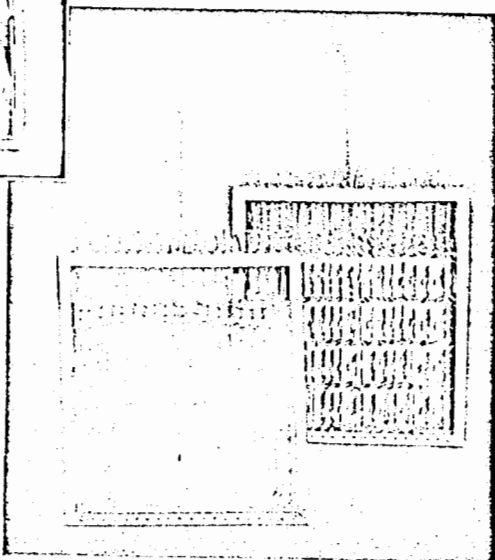
Porosity and irregular coarse grain structure in castings and wrought products militate against the formation of a uniform oxide coating. Sand castings require considerable pretreatment before anodic oxidation; the position at which gates and risers have been attached are often visible after anodizing in spite of careful polishing treatments. On the other hand, the fine close-grained structure on the surfaces of permanent mould castings, because of the relatively rapid cooling, are particularly favourable to a good anodized appearance. Pressure die castings, which often contain high percentages of silicon anodize well, but the surface is somewhat dark, though it is especially suitable for black dyeing. Even aluminum sheet, highly polished by rolling, may present "banding" (see page 28) or a honeycombed appearance after anodizing. Extrusions sometimes offer the same difficulty, the partial solution of which is a suitable heat treatment followed by quenching. It should be noted that the heat treatment of an aluminum alloy may have an important effect on the colour of the anodized film. The effect may be to lighten or darken the anodic coating depending on the change in the manner in which the constituents of the alloy are distributed.

The use of special anodizing sheet (as Alumilite Quality Sheet) is recommended in order to obtain the most satisfactory results. This type of sheet produces an exceptionally bright colourless coating completely uniform in appearance and of special value for dyed coatings.

RACKING—In anodizing great care must be taken to secure the work rigidly in the racks, jigs or other holding devices, used to immerse the object in the anodizing bath and to carry current to it. Unless the work is held rigid the movement caused by the stirring of the solution will shift the contact allowing a thin coating of oxide a chance to form, and because the oxide coating is an insulating layer the electrical contact will be broken and the anodizing process will cease. Mechanically rigid, screwed or spring-loaded mechanisms are used for most work, while baskets may be used successfully for treating small objects such as nails, etc. The rack design depends largely on the shape and size of the articles and the number of pieces to be treated. Many ingenious racking techniques are now in use which cut to a minimum the time required to rack and unrack individual items.



Above: Aluminum water tanks and frame sections before anodizing.



Racks and Baskets used in an anodizing plant and a variety of common methods of suspending materials for efficient anodizing.



Above: Aluminum backplates for radio equipment before and after being anodized and dyed black.

Above: Baskets with perforated sides may be used for anodizing small articles such as rivets. By means of spacers a number of different articles may be treated at same time without mixing.

Above: Aluminum gasoline tanks, boxes and quantities of small articles can be treated effectively by means of these clamping arrangements.

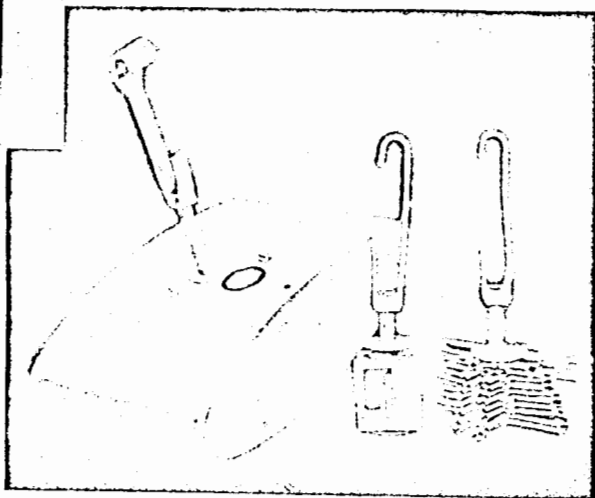


Figure 6: Racking for anodizing.

The racks must be made of aluminum alloy since other metals would dissolve and contaminate the bath as well as draw an undue share of the anodizing current. Those alloys which draw the least current and which may be sprung are the ones usually chosen. Alcan 17ST or 24ST, drawing a current of approximately 6 to 8 amperes per square ft. (0.65 to 0.86 amperes per square decimetre), are suitable. Alcan 65S is sometimes used. Spring or tension type clips give the best electrical contact. Racks that come in contact with the electrolyte are usually stripped after each using. Aluminum wire often serves to connect the workpiece to the rack and in this case new wire is used every time so that no stripping is necessary. The racks can also be insulated from the electrolyte by wrapping with tape.

Although the high resistance of the oxide film as compared with that of the electrolyte creates good throwing power in anodizing, it is necessary to make special provision for the anodizing of the inside of narrow hollow castings, tubes, and similarly shaped objects. Auxiliary cathodes, placed inside the cavities of tubes, and insulated from the tube wall, serve to ensure the formation of a sufficient anodic film on all surfaces. Precautions must be taken to avoid entrapping the small amount of evolved gases which might shield part of the surface and prevent its oxidation.

CLEANING PRIOR TO ANODIZING—The aluminum surface may be cleaned by degreasing (see page 15), followed usually by an alkaline cleaning or dip (see page 17). Electrolytic cleaning as described on page 19 may also be used.

After cleaning and rinsing, if the work is not going into the anodizing tank right away, it is held under the water of the rinse tank to prevent surface contamination.

The Sulphuric Acid Process. (Alumilite Process)

The sulphuric acid or Alumilite process is the one most commonly used, especially in North America. The oxide coatings obtained are considerably more transparent and less grey than those produced in chromic acid solutions; consequently, they are of great value for decorative and ornamental work.

OPERATION OF THE SULPHURIC ACID BATH—Sulphuric acid concentrations varying from 15 to 25 per cent (23 to 42 oz. per gallon; 165 to 295

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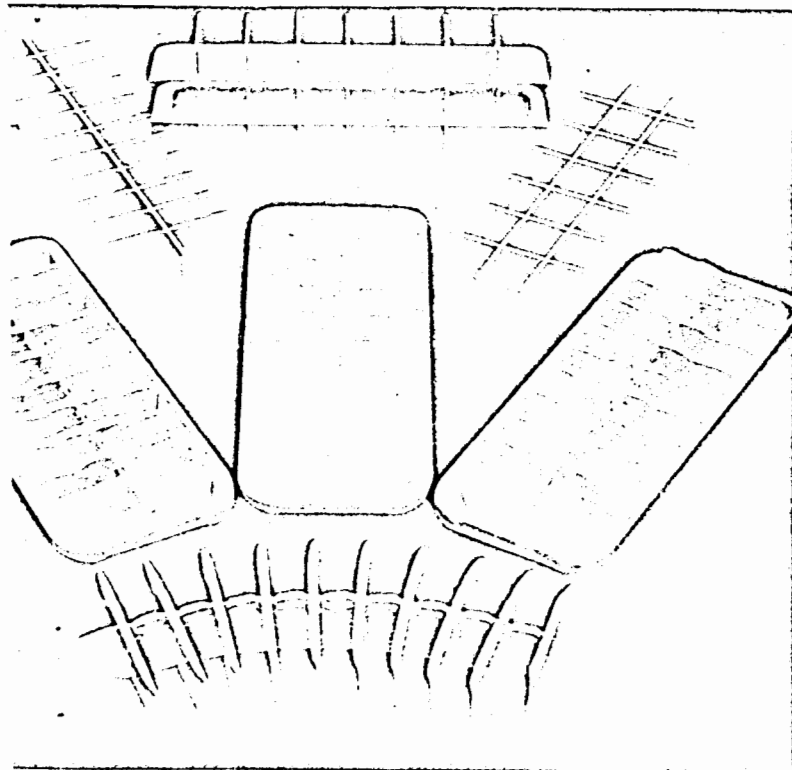


Figure 7: Alumilite finishes.

grams per litre) are used. The process is usually operated at room temperature and seldom at temperatures greater than 77°F (25°C). The electrolyte may be contained in a lead-lined, monel, wood or steel tank, and because of the low operating temperature of the bath, careful arrangements are required for the dissipation of heat generated in the bath. This may be accomplished by the use of a water-jacketed design, the use of lead-cooling coils on the bottom or sides of the tank, or a combination of both of these methods. Gentle air agitation aids in keeping the temperature uniform and is provided by releasing air under pressure through a perforated lead pipe on the bottom of the tank. Too much agitation is undesirable, since this may interfere with the electrical contacts. The temperature of the electrolyte should be controlled to within 1.8° to 3.6°F (1° to 2°C) to ensure uniform films; automatic regulation of the cooling water system is considered desirable if not essential.

The voltage required varies from 15 to 24 volts with the more dilute sulphuric acid solution and from 10 to 12 volts with the more concentrated solution. The standard time of treatment is 30 minutes, although this may be increased or decreased for particular conditions. In general high acid concentrations and high operating temperatures produce softer, thinner, and more porous coatings than the lower acid concentrations. A satisfactory coating is obtained with a sulphuric acid solution maintained within 1 per cent and operating at 70°F (21°C) for 30 minutes, using the lower sulphuric acid concentration at 12 to 18 amperes per square foot (1.3 to 1.9 amperes per square decimetre).

Following the anodic treatment, the work is carefully rinsed in cold water to remove any traces of sulphuric acid and is then subjected to any of the sealing treatments described further on.

CHARACTERISTICS OF THE SULPHURIC ACID FILM—The thickness of the oxide film produced on Alcan 2S in a 15 per cent sulphuric acid bath at 70°F (21°C) is 0.4 to 0.6 mils (10 to 15 μ) after a 30 minute period, and 0.6 to 0.8 mils (15 to 25 μ) after a one-hour period. In comparison, the chromic acid oxide film is 0.1 mil (2.5 μ) thick after a one hour period. The appearance of the natural finish with the sulphuric acid process

The bath is made up of a solution kept in a steel or lead-lined tank containing:

boric acid	12 oz.	75 grams
borax	0.25 oz.	1.6 grams
water to make	1 gallon	1 litre

Cooling coils are not usually required, since the bath is operated close to the boiling point, 200°F (93°C). Direct current of 200 to 250 volts is applied for 15 minutes at a current density of 10 to 40 amps/sq. ft. (1.1 to 4.3 amps/sq. dm).

The films are usually thin and iridescent. The thickness is proportional to the formation voltage. At 220 volts it is about 0.01 mil (0.25 μ). Sealing treatments after anodizing are not usually required. Films produced by the boric acid process are not suitable for sealing and dyeing as the film is too impervious to absorb sealants or dyes.

Sealing the Oxide Coating

The sealing process is of very considerable importance. Sealing makes the highly porous and absorptive oxide coating impermeable and non-absorptive, so that the finished surface will retain its uniform appearance in service. One effect of sealing in hot water or aqueous salt solution is to hydrate the pore and external surface of the amorphous alumina coating thus effectively sealing the pores and providing a surface film with greatly increased resistance to corrosion or staining.

Sealing processes for oxide films fall into three main categories:

- 1.—Water sealing.
- 2.—Sealing with aqueous salt solutions.
- 3.—Sealing by means of oils and waxes.

WATER SEALING—Water sealing finds wide application when no change in the appearance of the oxide coating is desired. It is carried out by immersing the surface in hot or gently boiling water for 30 to 60 minutes. Soft water is preferred since hard water may cause staining because of the presence of dissolved salts. If the pH is brought down to about 5.5 by the addition of sulphuric acid ordinary tap water may be used without causing staining.

SEALING WITH AQUEOUS SALT SOLUTIONS—Sealing may be carried out in aqueous solutions of potassium dichromate, sodium silicate or nickel acetate.

Sealing in an aqueous solution of potassium dichromate leaves the surface with a green to yellow colour, but since it is usually applied where severe corrosive conditions are to be opposed, and in these circumstances painting usually follows, the colour is not objectionable. In general greatly increased protection results from dichromate sealing; the excellent results obtained by the use of zinc chromate as a primer for paint are probably accounted for by the presence of the chromate salts. The process is carried out by immersing the article, while it is still wet from the rinsing operation after anodizing, in an 8 oz. per gallon (50 grams per litre) solution of potassium dichromate, kept just short of boiling. The sealing time varies, but is commonly of 30 minutes duration. After a thorough rinsing in water, the articles are dried.

The solution used for sodium silicate sealing contains 3.2 to 8 oz. per gallon (20 to 50 grams per litre) of commercial sodium silicate (40° Bé), and is operated at 212°F (100°C). This type of sealing is especially suitable for porous castings.

For sealing dyed coatings a nickel acetate solution is usually used since it has particular value in setting the organic dye. The concentration of the nickel acetate is 0.8 oz. per gallon (5 grams per litre), and sealing is carried out for 3 to 5 minutes at 208° to 212°F (99° to 100°C).

OIL AND WAX SEALING—Certain oils such as lanolin and linseed oil when absorbed in the oxide film yield surfaces which possess good corrosion and wear resistance. In addition, the insulating characteristics of the surface are considerably improved. The oils and waxes are applied to thoroughly dry surfaces. They may be applied in the pure liquid state or as solutions in volatile solvents such as gasoline. Brush and spray application may be substituted when large components are to be treated.

Following any one of the sealing operations described above, a gentle polishing treatment with a soft rag may be applied to bring out the lustrous character of the surface and to remove any slight chalky film which may have formed during the sealing process. Polishing with liquid wax after water sealing enhances and preserves the initial lustre.

Anodic Coating Processes For Aluminum

FILM TYPE	ELECTROLYTE	CONDITIONS								PROPERTIES		
		oz./gal.	grams/litre	Volts	amp./ft. ²	amp./dm ²	of	°C	Time	Type	Tank	
Porous	Sulphuric Acid	23	165	15	12	1.3	70	21	30 mins.	Batch or continuous	Lead lined	White to grey in colour. Thickness on Alcan. 2S 0.4 mil (10 μ)
		4.8	30	50	3	0.3	104	40	60 mins.	Batch only	Steel plate	Light grey to dark grey. Thickness on Alcan. 2S 0.1 mil (2.5 μ)
		4.8 - 16.1	30 - 100	65	10 - 30	1.1 - 3.2	77 - 95	25 - 35	60 mins.		Lead lined Rubber lined or Stone-ware	Cream coloured. Thickness up to about 1 mil (25 μ)
Non Porous	Boric Acid and Borates	12 0.25	75 1.6	50 - 500	10 - 40	1.1 - 4.3	200	93	15 mins.	Batch or continuous	Steel or Lead lined	Usually thin and iridescent. Thickness is proportional to the formation voltage. 0.01 mil (0.25 μ) at 220 volts

Comparison of the Anodizing Processes

All the electrolytes described have some solvent action on the oxide coating being formed so that the final film is the resultant of anodic oxidation and chemical dissolution. It is assumed that solvent action leads to film porosity which allows contact of the electrolyte with the underlying metal surfaces and this carries the current and permits the film to continue growing. As the film itself is non-conducting, unless it is porous, upon formation it will interrupt the electrical current as soon as the breakdown voltage exceeds the operating voltage. Non-porous films are formed by electrolytes which have little solvent action on the oxide. Boric acid anodizing is of this type.

The processes differ principally in the composition of the electrolyte and as a result, in the type of coating produced and the ease and cost of operation. There is a wide difference in the motor generator requirements. Since voltage control is very important in the chromic acid process, a motor-driven rheostat with automatic cut-off for each cycle is usually used. Such an elaborate generator and accessories are not required for the sulphuric acid process.

The processing tank for sulphuric acid must be lead lined, and since the operating temperature is lower, cooling of the electrolyte is a greater problem. The chromic acid process offers the advantage that in the anodizing of assemblies, traces of chromic acid which may be retained in the joints or recesses even after careful washing, have no harmful effect, while traces of sulphuric acid are very undesirable. For maximum protection with anodizing, parts are usually treated individually before assembly so that all surfaces are equally coated. Alloys containing more than 5 per cent copper are not suitable for chromic acid anodizing, while there are no such limitations on the sulphuric acid process.

DYED ANODIC COATINGS

Inorganic Pigments

Coloured coatings can be produced on anodized aluminum by the precipitation of certain pigments within the pores of newly formed oxide coatings. A few inorganic pigments are especially suitable for

exterior use since they weather well and are reasonably fast to sunlight. A variety of useful decorative effects may be obtained and evenly coloured surfaces result. Thicker anodic films are recommended since these give better results with inorganic pigments. The range of colours is limited and the colours are less brilliant than those produced by organic dyes. It is also difficult to match colours with different batches.

The aluminum surface is first anodized, usually using the sulphuric acid process. The temperature of the sulphuric acid solution must be controlled within very narrow limits or the shade of colours after dyeing will vary noticeably. After anodizing, the surface is rinsed with cold water only and treated successively with various solutions, depending on the desired colour.

A bright orange yellow colour may be produced by immersing an article in a solution of potassium dichromate (32.4 oz. per gallon, 202.5 grams per litre) at 125°F (51.8°C) for 2 to 3 minutes, rinsing thoroughly in water to remove the outer layer of absorbed dichromate, dipping into a solution of lead acetate (32.4 oz. per gallon, 202.5 grams per litre) at 125°F (51.8°C) for 5 to 10 minutes, and finally treating for a further 5 to 10 minutes in the previous potassium dichromate bath. The presence of insoluble lead chromate firmly secured within the pores of the oxide film gives the bright colour to the finished surface.

A jet black cobalt sulphide colour is obtained, using first a cobalt acetate solution of 32.4 oz. per gallon (202.5 grams per litre) concentration at 120° to 125°F (49° to 51.8°C) with a dip time of 10 to 15 minutes, then an ammonium sulphide solution of 16.2 oz. per gallon (101.3 grams per litre) concentration at room temperature with a dip time of 5 to 10 minutes (the fumes must be exhausted to protect the workers). This coating may turn brown if the pigments are not properly applied. The cause appears to be a change in the concentration of the ammonium sulphide bath, and therefore the solution composition of this must be constantly checked.

The precipitation of lead permanganate yields a mahogany red colour. The anodized aluminum is dipped first into a lead acetate solution containing 32.4 oz. per gallon (202.5 grams per litre) for 5 to 10 minutes at 125°F (51.8°C), then into a potassium permanganate solution containing 32.4 oz. per gallon (202.5 grams per litre) for 5 to

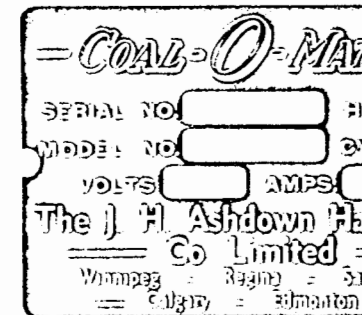
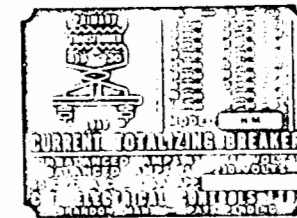
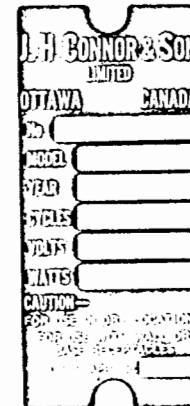
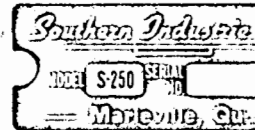
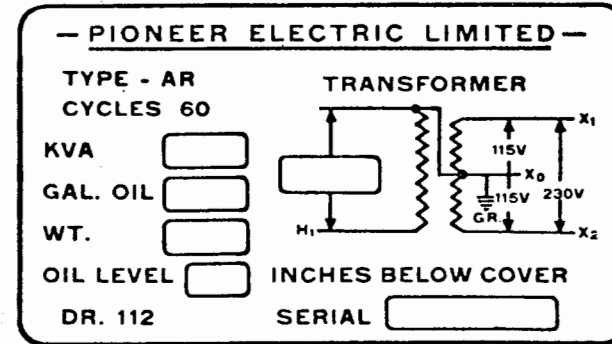
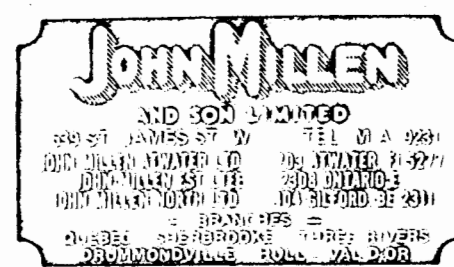


Figure 10: Alumilited and dyed name plates.

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10 minutes at 125°F (51.8°C), followed by a 1 minute immersion in the lead acetate solution.

Shades of blue are obtained using solutions of potassium ferrocyanide and ferric sulphate according to the following procedure: the anodized aluminum is first immersed in boiling ferric sulphate solution (8 to 16 oz. per gallon, 50 to 100 grams per litre) for 5 to 10 minutes. After rinsing in warm water it is immersed for 5 minutes in potassium ferrocyanide solution (9.7 to 12.9 oz. per gallon, 60 to 80 grams per litre) at room temperature, and finally rinsed in warm water again.

The deposition of photo-sensitive inorganic compounds within the anodic film forms the basis of the production of photographic records of unusual permanence compared with ordinary plates and films. Their fire-resisting qualities are of great value. Silver halides are precipitated in thick anodic films formed on high purity (99.5 per cent minimum) hard-rolled aluminum using solutions of silver acetate and ammonium halide. The deposition is, of course, carried out without exposure to light and after exposure the image is developed and fixed following ordinary photographic technique. Advantage may be taken of the fact that following the photographic process the uncoloured anodic film remains absorbent and contrasting colour effects may be imparted by subsequent dyeing.

The sealing of anodized surfaces which have been coloured with inorganic pigments is accomplished by one of the methods commonly employed in sealing oxide coatings. Sealing by treatment with boiling nickel or cobalt acetate solutions (0.8 to 3.2 oz. per gallon, 5 to 20 grams per litre) or sealing by treatment with boiling water alone is recommended. When a metal acetate solution is used a 5 minute treatment is generally sufficient whereas water sealing may take up to 30 minutes. If a hot or boiling solution is employed in precipitating the pigment, then, a prolonged treatment in this bath is often sufficient to seal the dyed surface. Linseed oil varnish, applied to the carefully dried surface, furnishes effective sealing when inorganic pigments are used.

Organic Dyestuffs

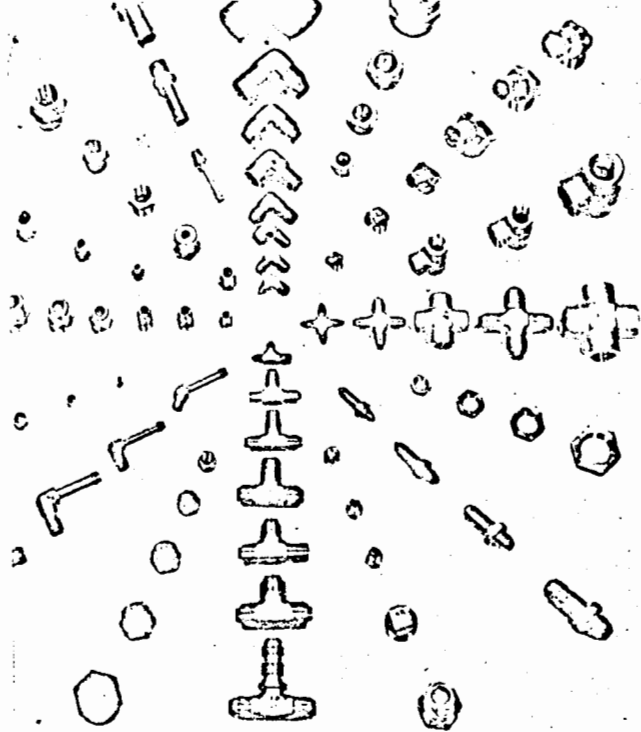
Organic dyestuffs when used to dye anodic films produce coloured coatings having a very attractive metallic lustre. The colours on

transparent anodic films show a clarity and depth that is striking and unusual. The light fastness of dyed anodic films is not great enough under outdoor conditions or exposure to strong sunlight to allow satisfactory service under such conditions. In the past few years considerable work has been done in selecting dyes that give the most satisfactory light fastness for interior use.

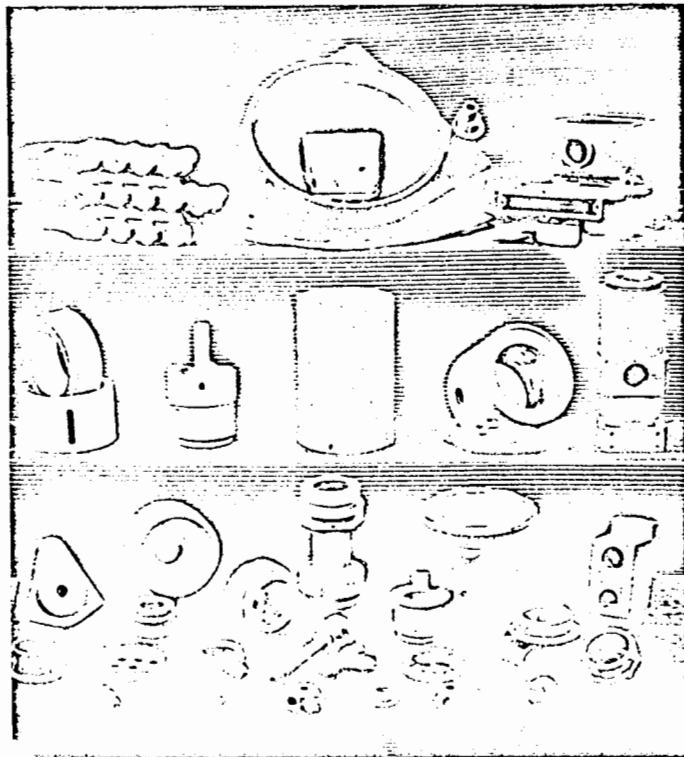
The best films for dyeing are those that are thick, transparent and colourless as these give bright sparkling clear colours, and with suitable dyes give good light fastness. The films produced using the sulphuric acid process, and especially on Alumilite-Quality sheet, are the most suitable since they fulfill all the above requirements. Dyeing chromic acid anodic films produces a matte surface, though sometimes this may be the effect desired, especially for matching painted or enamelled finishes. However, since the film thickness is not normally as great as that produced with sulphuric acid or oxalic acid, the dyestuff penetration is slight thus decreasing the depth of colour and its light fastness. The oxalic acid films, while normally of a thickness comparable to that formed in the sulphuric acid process, are yellowish in colour thus affecting the end colour after dyeing, so that while reds and yellows are satisfactory, good blues cannot be obtained.

The composition of the alloy plays an important part in determining the colour of the original anodic film and this in turn limits the choice of colours which may be successfully applied. For instance, high silicon alloys yield a light to dark grey coloured anodic film and deep brown or black colours alone are satisfactory. Furthermore, variations in the conditions of the anodizing procedure may influence the colour of the dyed surface. For example, a variation in the procedure of anodizing with chromic acid giving 30 minutes instead of 5 at the 50-volt step produces a much superior finish using nigrosine black; or alternatively, the same result can be obtained by anodizing at a higher temperature.

The selection of the proper dye is important; the dye should be fast to washing, and since all dyed films are generally sealed, the dyestuff should be unaffected by the sealing agent. Water soluble dyes are more commonly used than oil soluble dyes, the latter finding little application except in special cases. The nature and depth of colour obtained are influenced by variations in dyeing conditions such as dye concentration, temperature and immersion time.



At left: The colourless oxide coating produced on aluminum fittings, sometimes dyed for identification purposes, and sealed by a standard method, is considerably harder and more abrasion resistant than the coating produced in a chromic acid electrolyte.



Right: The chromic acid process is widely used where corrosion protection is the primary requirement in coating or where subsequent painting is to be

Figure 11: Chromic acid anodizing finishes.

In general, the concentration of the dyestuff lies between 0.1 and 1 per cent the lower value applying when lighter shades are desired, while for the deeper colours and black higher concentrations are necessary.

Procedure for Dyed Alumilite Coatings

The following procedures are described for dyeing surfaces anodized by the sulphuric acid process since this is the most usual, however the same technique may be applied, as well, to either chromic acid or oxalic acid anodized aluminum.

In anodizing prior to dyeing, the specified acid concentration, temperature and current density must be maintained. Adequate agitation is necessary to ensure uniform bath temperature around all parts of the work. Otherwise the porosity and film thickness of the anodic coating will vary and the coating will dye to a non-uniform shade. In dyeing, the concentration, pH value, temperature and time must be carefully controlled. It is important to have all the dye dissolved in the solution and to remove any scum which forms on the surface of the bath if spotted surfaces are to be eliminated. To obtain the proper depth of colour with black dyes, a thicker coating is necessary than with the other colours.

The anodizing is carried out in a 15% sulphuric acid solution at a current density of 15-18 amp/sq. ft. (1.6 to 2.0 amp/sq.dm). If a higher concentration of acid is used, it may be found necessary to adjust this procedure. A 10 minute dyeing period at a temperature of 140° to 160°F (60° to 71°C) is suggested for all cases. Variations in shade are produced by decreasing or increasing the time of dyeing and the concentration of the dye. Distilled or de-ionized water should be used in making up the dye solution and also to replace water lost by evaporation. After dyeing, a cold water rinse is used to remove excess of the dye which has not been absorbed, followed by a sealing treatment in a nickel acetate (0.8 oz. per gallon, 5 grams per litre) solution for 3 to 5 minutes at 208° to 212°F (99° to 100°C) at a pH of 5.5 to 5.8. The nickel acetate seal is often followed by a 30 minute water seal. However, a water seal alone is frequently given with satisfactory results. The surface may then be waxed if a highly polished nonabsorbent surface is desired. This is often done with black coatings to enhance their glossy sheen.

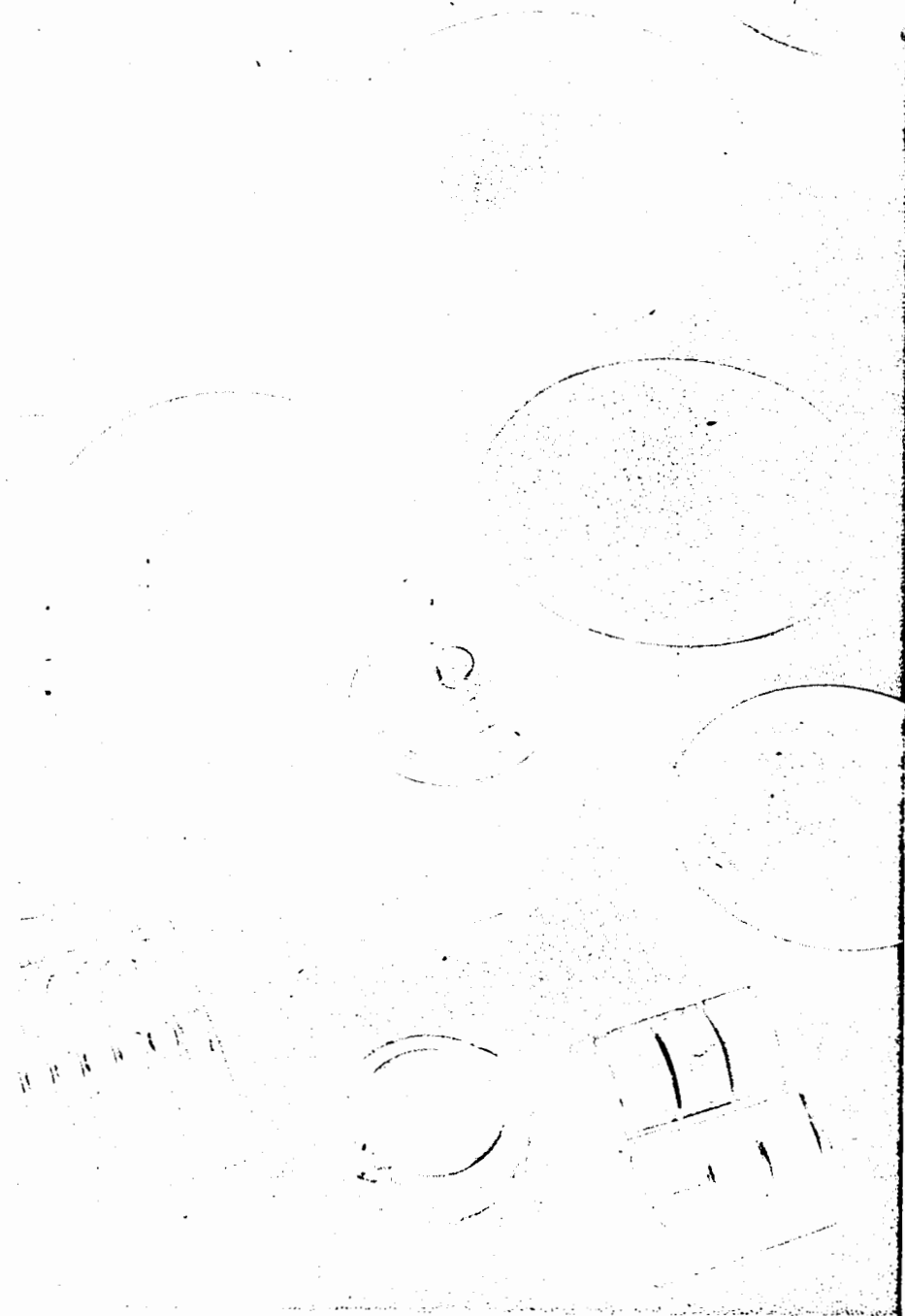


Figure 12: Anodized and dyed aluminum.

Various methods are available by means of which multicoloured patterns may be applied. A simple method is to cover part of the anodic film with a resist not absorbed into the coating, and immerse the work in the dye solution, thus dyeing all the uncovered parts. This is followed by sealing. Afterwards the resist is removed by a suitable solvent and a coloured pattern is revealed. A variation of this procedure enables the parts still uncoloured to be dyed a colour different from that applied previously. Unusual and attractive two-tone mottled effects can be obtained by spotting or lightly spraying the surface with one colour, before immersing in the background colour.

Almost limitless possibilities are opened up by the use of coloured anodic films on aluminum and its alloys. Decorative as well as utilitarian purposes may be served; art objects, interior architectural fittings and exceedingly durable maps and plans are but a few examples of the uses in which these serviceable and attractive aluminum surfaces have found application.

ELECTROLYTIC BRIGHTENING

It has been mentioned earlier that during the anodic treatment of aluminum surfaces, oxide formation on the metal base is accompanied by chemical solution in the electrolyte of the outer portions of the oxide coating. The relative rates of these two opposing processes may be controlled by a suitable choice of electrolyte, bath and electrical conditions. In electrolytic brightening, or electrolytic polishing as it is often called, the preferential solution of the surface is the predominant feature of the treatment. Electrolytes such as hydrofluoboric acid, a mixture of sulphuric and phosphoric acids, or perchloric acid and acetic anhydride are generally used in conjunction with direct current. An alkaline solution containing sodium phosphate and carbonate has also been used with satisfactory results.

Electrolytic brightening processes effect a substantial amount of smoothing of the surface, and are often referred to as a polishing process. In fact, efforts have been made to substitute for mechanical polishing a modified form of electrolytic brightening, especially in cases where intricate shapes are to be given a highly polished surface.

Modern development in lighting has demanded some type of reflector which can compare favourably with silvering and still be rugged