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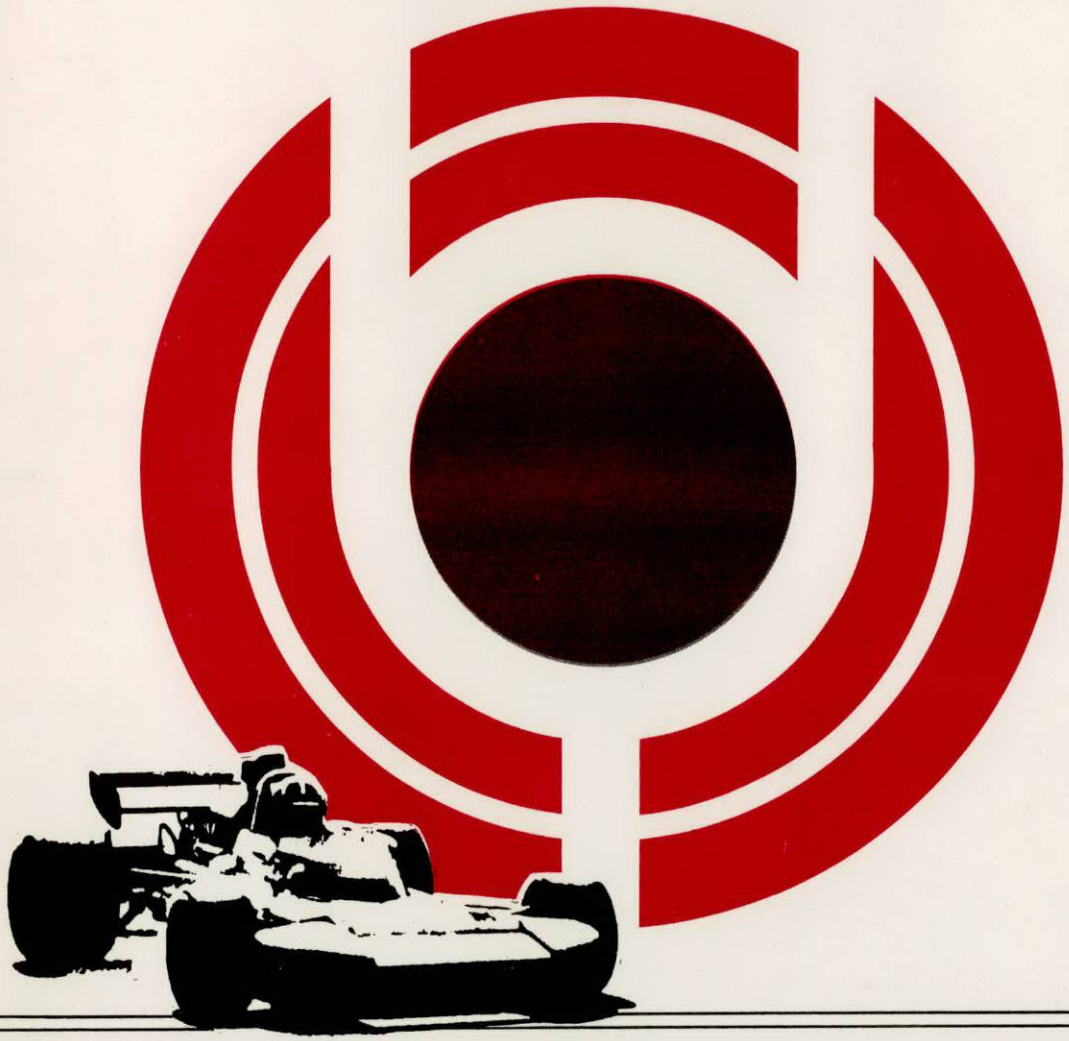
70th Annual Technical Conference



June 27-30, 1983
Hyatt Regency Indianapolis and
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Indianapolis, IN

SESSION J

AMERICAN ELECTROPLATERS' SOCIETY, INC.

70TH ANNUAL TECHNICAL CONFERENCE - INDIANAPOLIS, IN

LIGHT METAL FINISHING I

SESSION J

Page No.

The Relationship of Electrolytic Coloring to Clear Anodizing Techniques.....J-1

Richard W. Mahn, Reynolds Aluminum International Services, Inc., Richmond, VA

The Production and Properties of Cobalt-Based Electrolytic Finishes.....J-2

Peter G. Sheasby, Alcan International Ltd., Banbury Labs., Banbury, Oxon, UK, and W. M. Kellerman, Alcan International Ltd., Kingston Labs., Kingston, Ontario, Canada

Electrolytic Coloring of Anodized Aluminum Using Tin Electrolytes.....J-3

Dr. Hans J. Goehausen, Henkel KGaA, Dusseldorf, W. Germany
Glenn C. Schoener, Amchem Products, Inc., Ambler, PA

Electro-Coloration of Anodized Aluminum Evolution of these Processes.....J-4

Michel LeGrand, Cegedur Pechinery, Montreuil-Juigne, France

J-1

Light Metal Finishing I
Session J

The Relationship of Electrolytic Coloring to Clear Anodizing Techniques

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THE RELATIONSHIP OF ELECTROLYTIC COLORING TO CLEAR ANODIZING TECHNIQUES

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Abstract

The two-step anodizing process, developed by Reynolds International, Inc, requires the production of a high-density aluminum oxide film followed by electrolytic impregnation at the base of the film pores by the metal form of a tin base metallic salt dissolved in a special electrolyte. This paper discusses some of the factors affecting the relationship between the quality of the film produced in the anodizing step and the rate of coloring which occurs in the electrolytic step as a function of voltage and time, as well as the independency of the ability to produce color from the thickness of the anodic film.

The Electrolytic Coloring Step

A simple description of electrolytic coloring is: The deposition of the metallic and/or metallic oxide form of a metal salt at the base of the pores of an aluminum oxide film by the passage of an electric current. This requires the use of a suitable electrolyte solution, in which the metal salt is dissolved, and a power supply, which is normally controllable alternating current. The A.C. power is supplied to the work load and counterelectrodes at the side of the tank act to complete the circuit back to the power supply. As in any electrolytic cell the current flows as the ion species in the electrolyte migrate to the appropriate electrodes.

A representation of the electrolytic coloring step is graphically shown in Figure 1. After a brief period to allow the solution to saturate the film (1), the power is supplied using a balanced voltage and the current flows in response to the electrical conditions of the circuit. Application of the voltage results in the movement of electrons through the barrier layer at the base of the film pore, which is the path of lowest resistance (2). As the electrons begin to flow into the pore the positive metal ions begin to migrate to the source of the electrons at the base (3). As the positive metal ions pick up the electrons they are reduced to metal particles which deposit at the bottom of the pore and pile up on each other (4). Even though the positive and negative components of the voltage are balanced, the electrochemistry of the process favors the reduction of the metal ion to metal and results in an excess of negative current over positive current. Buildup of the metal in the pore causes an accompanying increase in resistance which reduces total current flow (electron flow per unit time), reduces the ratio of negative current over positive current at the initial voltage, and slows down the deposition rate (5). There are two ways to increase the rate again:
1) Increase the total voltage to increase total current flow. This increases positive current, which does not contribute to metal deposition, along with the desired negative current. Or,
2) Increase the negative voltage and reduce the positive voltage through independent control of the half-wave potentials of the alternating current. This results in an increase in the ratio of negative current over positive

current which overcomes the resistance to electron flow into the pore and significantly increases the rate of metal deposition (6). As the layer of metal deepens, the effects of diffraction and absorption of light impart color to the surface of the workpieces (7). Control of the metal buildup to a desired color intensity is achieved by the amount of power supplied and by the amount of time it is supplied (8). In this manner it is possible to obtain color shades from champagne (9) to black (10) passing through a range of bronzes. The power supply rectifier to provide modulation of the half-wave potentials (Figure 2.) was first developed in the late 1960s[1] and has been modified and upgraded to allow for programming of the various shades of color desired.[2,3]

Controlling The Color

A program for a particular color is determined experimentally to establish the factors of time and voltage necessary to achieve that color. These values can then be electronically set into the power supply control system (Figure 3.) and can be expected to repeat time after time. The power supply and control unit only control the time, which is independent of the electrochemistry of the process, and the voltage, which, once programmed, does not control the fate of the current produced. Therefore, for a color program to be effective it is necessary to control the parameters which can affect the flow of current during electrolytic coloring.

The more important factors which affect coloring rate at a preset voltage are:

1) Concentration of the conductive electrolyte,
2) Temperature of the electrolyte,
3) Concentration of the metal ion,
4) Ability of the metal ions to flow uniformly to the workpieces, and
5) Size of the film pore.

Conductivity of the electrolyte is directly proportional to the first three parameters listed. Increases in any one or all will increase the rate of color formation and decreases will reduce the coloring rate. These factors are easily controlled through chemical analysis and proper refrigeration. The voltages used, the current densities generated, and the time in the coloring tank are such that high refrigeration requirements are not necessary and close temperature control is readily obtainable.

Workpiece Distribution

The fourth factor has resulted somewhat in a confusion of the capabilities of the two-step coloring process. A common method of racking is the horizontal attachment of workpieces to vertical bars or splines (Figure 4.). In the case of integral color anodizing a certain spacing of the parts is necessary to achieve color uniformity. In the case of clear anodizing, parts are racked more closely together because the effects of non-uniform anodizing are not clearly visible nor are the specifications nearly as demanding for their particular applications (Figure 5). With the integral color system it is possible to rack double-spline loads, with parts evenly spaced on each side, in conjunction with an internal cathode which is used in the anodizing tank to divide it into two separate cells and assure that the current will flow uniformly from all exposed surfaces. With the clear anodizing system the racking may be several parts across using multiple splines, twist racks, or stack racks (Figure 6.). An internal cathode is not used and generally

the inside parts will have less film thickness than those parts at the outside.[4]

One explanation of the differences which can occur is simply that resistance increases with distance from the source, and the inner surfaces, which are farther from the cathode, pass less current and receive less oxygen for film production. The use of the internal cathode in the integral color system balances those distances. Another possible explanation is that the current travelling along the workpiece generates a field around it which, in proximity with another part generating a similar field, serves to shield the current from flowing uniformly between the parts, thus reducing film growth on opposing and inner surfaces. Attention to proper spacing of workpieces becomes important in both clear and color anodizing processes in order to comply with specific requirements for uniform film thickness and color in a given application.

Rules of workpiece distribution similar to those for integral color anodizing (Figure 7.) apply in the electrolytic coloring step in order for the metal ions to flow uniformly to all exposed surfaces, and in the clear anodizing step in order to develop a uniformly distributed film in preparation for the coloring step. Dense racking of parts, as used in clear anodizing, will meet with the same resistances in the color system as occur in the anodizing system with the color rate varying directly with the degree of exposure of workpiece surfaces to be colored.

Misunderstanding of the two-step process arises as a result of the first step, which requires clear anodizing, and the desire to follow the same racking practices. However, recognition that the anodize and color steps require the free flow of current around and between workpieces for uniform film quality and color (Figure 8.) will help to eliminate this confusion. With specific or limited product mixes, it is possible to develop racking techniques, electrolyte chemistries, and color programming to provide color uniformity without the use of internal cathodes, while with large product mixes it is necessary to use internal cathodes.

What Electrolytic Coloring Isn't

It is important to recognize that, although it requires control of conductivity parameters similar to those of good anodizing practices, it has no relationship to the principles and objectives of anodizing; that is, it is not intended to add to or take away from the aluminum oxide film or its qualities. The coloring step is programmed to respond to those film qualities which have already been determined in the clear anodizing step.

The Clear Anodizing Step

A brief description of anodizing is: The generation of an aluminum oxide film on an aluminum surface by the passage of a direct current between the part and a cathode (making the part anodic) in the presence of a suitable electrolyte. The aluminum oxide film adheres to the surface of the aluminum and protects it with a highly non-corrosive finish. The durability and protective qualities of the finish have led to a wide range of applications on aluminum products.

Another quality which the film has permits the addition of color to the final finish to make it more attractive. The quality is that of porosity. The pores in the film provide sites whereby color can be added, such as in electrolytic coloring. However, the film pore is not something which is

constant, but is very dynamic and changes with the conditions used to generate the anodic film. It is an understanding and control of those conditions that will lead to a programmable color response.

Since the electrolytic coloring step responds to the existence of pores in the film, it is necessary that those pores be distributed uniformly over those surfaces which are to receive color. The practices which will provide that uniformity have already been discussed in conjunction with Workpiece Distribution. This then leaves the fifth item to be considered which will ultimately affect current flow in the coloring step--size of the film pore.

Control of Pore Size

Generation of the pore is a direct result of the solubility of aluminum oxide in a strong acid electrolyte. The dissolution effect occurs in competition with film growth. Part of the dissolution occurs generally over the film surface as it develops and part of it occurs in the form of penetration of the cellular structure of the aluminum oxide such that each cell grows in thickness but retains a void area or pore at its center. This growth occurs as a network of cells and pores over the workpiece (Figure 9.). The pore does not penetrate all the way to the aluminum base metal, but it does extend to the film surface. The barrier layer at the base of the pore is solid aluminum oxide which is formed in the initial stages of the anodizing cycle and is not subject to the dissolving action of the electrolyte. It is very thin and represents only a small fraction of the total film. As a result, the depth of the pore is almost equal to the thickness of the film. The competitive actions of film growth and cellular dissolution and the factors which affect the mechanics of those actions have been studied in detail and a large body of information is available about them.[5,6,7,8]

The solubility properties of the electrolyte are principally controlled by temperature and acid concentration. Increases in either one or both will increase dissolution rate and enlarge the pore. Decreases will result in smaller pores. For instance, as early as 1932 it was determined that non-uniform electrolyte temperature resulted in non-uniform porosity of the film on a load of parts. The ones higher up had larger pores which would take dye faster than parts lower down. The heat generated during the anodizing cycle was rising to create a warmer solution near the surface increasing its solubility properties. This led to a patent[9] for a system of mixing the electrolyte to maintain a uniform temperature by the use of air agitation distributed through tubing laid along the bottom of the anodizing tank.

Formation of the aluminum oxide cells is a function of the flow of current which creates the oxidation reaction, but it is the force behind the current which determines the density of the aluminum oxide produced at the cellular level. That force is the voltage driving the current to overcome the resistances of the system. As the voltage increases the unit volume of aluminum oxide in the cell increases and the size of the pore decreases, and likewise, lower voltages will result in a larger pore. The forming voltage of the film is affected by temperature and acid concentration and will vary inversely with changes in the same two factors which directly affect solubility.

Therefore, increases in temperature and acid concentration will simultaneously increase solubility and reduce voltage resulting in increasing pore size. Decreases in temperature and acid concentration will simultaneously reduce solubility and increase voltage resulting in decreasing pore size.

Relationship of Electrolytic Coloring to Clear Anodizing Techniques

Since the depth of the pore varies primarily as a function of the thickness of the film, the principal change in the size of the pore due to solubility and voltage factors occurs in its diameter, which is the passageway for the movement of the metal ions in the electrolytic coloring step (Refer to Figure 1.). As discussed previously, the deposition of metal is a result of the migration of metal ions to the source of electrons at the base of the pore. Keeping in mind that this process is occurring at the chemical level and that the pore diameter is extremely minute, the size of the passageway for the flow of metal ions begins to have significance. If the passageway (the pore diameter) is large, the migration or flow of metal ions will be faster than if the pore diameter is small. Returning to the factors which affect coloring rate in the electrolytic coloring step, the rate will vary directly with the size (diameter) of the pore. Consistent control of the parameters of temperature and acid concentration in the anodizing step will produce an anodic film of consistent porosity which will result in a reproduction of color from load to load utilizing a specific color program.

The other factor which is controllable in the anodizing step with respect to pore size is the pore depth. Although not as significant as the pore diameter, experience has shown that there exists a relationship between film thickness and coloring rate. A variation in the film thickness will vary the length of the passageway (pore depth) and thus the time necessary for the metal ions to reach the pore base. Consistent film thickness is readily achievable by controlling the parameters of current density and time in the anodizing cycle.

High Current Density Anodizing

Current density is the amount of current passing through a unit of surface area at any instant of time and is normally expressed as amperes per square foot or amperes per square decimeter. In anodizing it is determined from the total amperes passing through a load of workpieces having a known total surface area. Current density is a rate factor. The formation of the aluminum oxide film is directly related to the amount of current available in a given unit of time. Therefore, if the amount of current available is increased per unit area (current density), there will be an accompanying rate increase in the buildup of the film, reducing the time in the anodizing cycle. Increasing the current density also increases the voltage because of increased system resistance, if the other factors are constant (surface area) or controlled (temperature and acid concentration). As discussed previously, an increase in voltage will result in a denser aluminum oxide layer and a smaller pore. These last two factors produce the qualities of hardness and abrasion resistance in the film, which are desirable in many applications of architectural finishes--both colored and clear. The integral color anodizing process has utilized the practices of high current density, high voltage, low acid concentration, and moderate temperatures for some fifteen years to produce durable, hardcoated, colored finishes.

Another result of the increase in current density and voltage is an increase in heat generation from resistances in the system and from the electrochemical reactions. Refrigeration and air agitation are designed to take care of the first, but the reactions take place within the pore itself. An investigation begun in the 1960s estimated that the chemical reactions

taking place within the film pore generated temperatures which exceeded the boiling point of water. A study of the effects of various chemicals which might assist in the oxidation step to reduce heat generation at the chemical level led to a patent[10] for a combination of certain organic chemicals, which could be added to the anodizing electrolyte for temperature control in the pore. This resulted in a system which could operate at higher current densities and voltages in a clear anodizing process to generate hard, abrasion-resistant films and reduce anodizing time.

Two-step anodizing processes have been in commercial use almost as long as integral color anodizing processes, but they have only been predominant in Europe. In recent years the cost of electricity has increased dramatically in the U.S. and pushed up the costs of integral color anodizing. As a result the two-step process, which operates with lower energy requirements, began to be introduced into the U.S. in the late 1970s as a viable alternative to the energy-intensive integral color process. However, this required that the high current density clear anodizing process be used as the first step as assurance that the resultant finish would have hardcoat properties, could be produced rapidly, and would be energy efficient.[2,3]

Interdependency and Independency

In order to understand the importance of the interdependency of the two steps, it is necessary to remember that the purpose of the process is not to produce an anodized product but a color-anodized product. With the emphasis on color, it becomes important to control the factors which affect color formation. One way to point this out is to consider what happens if the parameters of the process are not controlled. The result is, first of all, an anodized film of varying quality. The second is a color program which cannot provide the desired color from one load to the next. Color will develop, but in order to match color, the process reverts to the "eye-of-the-beholder" method of color judgement, which is difficult to reproduce, is very time consuming, and reduces productivity. The choice is a manual operation or control of the parameters which will provide a consistent and uniform anodized finish with a color which has been developed automatically and reproducibly.

The independency of the two steps can be recognized by remembering simply that the parameters for the anodizing step can be independently selected to produce a film meeting the required finish specifications for coating thickness, coating weight, hardness, and abrasion resistance, and then a color program can be generated which will reproduce the desired color for that finish.

Conclusion

Recognizing the parameters in the clear anodize first step which have an effect on the quality of the anodic film and which will ultimately affect the rate of coloring in the second step leads to an understanding of the relationship of electrolytic coloring to clear anodizing techniques and to the importance of control. If the parameters are controlled consistently, which is possible with present state-of-the-art technology, then the color process will respond consistently and uniformly according to the color program developed.

The flexibility of the process is realized in the same way. Because the anodizing step is independent from the coloring step, it is possible to

establish and utilize whatever parameters are desirable to produce a particular quality of finish or coating thickness. Once the parameters are established and a particular film is generated, it only requires that the voltages and times of a color program be determined for the color desired.

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2. A. J. Walsh, U. S. Patent No. 4,179,342

3. G. R. Darrow., U. S. Patent No. 4,180,443

4. A. W. Brace. and P. G. Sheasby., "The Technology of Anodizing Aluminium", Technicopy Ltd., England, 1979, Chapter 9, 128-129.

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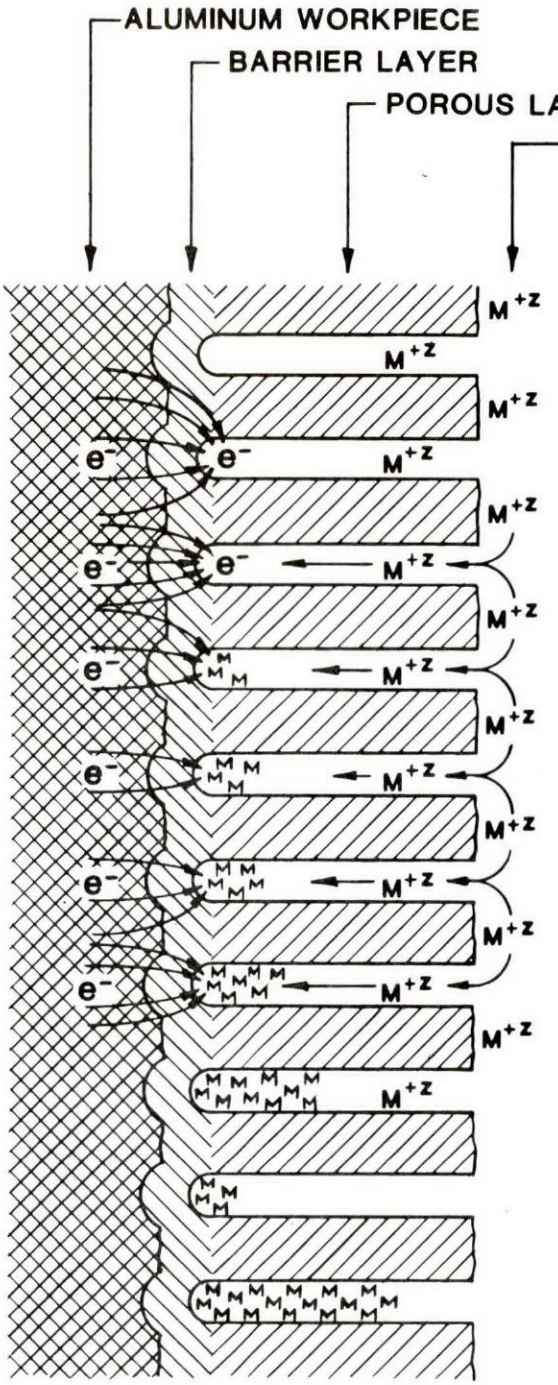
9. H. Bengston, U. S. Patent No. 1,891,703

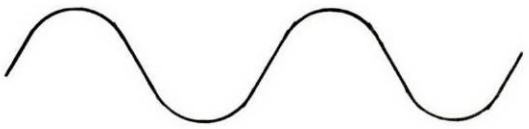
10. K. H. Dale, U. S. Patent No. 3,524,799



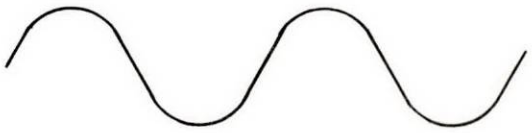
1. FILM PORE - ELECTROLYTE AND METAL IONS DIFFUSE INTO PORE.
2. <u>POWER ON</u> - ELECTRONS (e^-) FLOW INTO PORE AT BASE.
3. METAL IONS MIGRATE TO ELECTRON SOURCE.
4. METAL IONS PICK UP ELECTRONS AND DEPOSIT AS METAL (M).
5. RESISTANCE INCREASES TO ELECTRON FLOW. (INCREASE NEGATIVE VOLTAGE OVER POSITIVE VOLTAGE.)
6. POWER ADJUSTED - MIGRATION OF METAL IONS INCREASES.
7. AS METAL DEPOSITION CONTINUES COLOR INCREASES.
8. <u>POWER OFF</u> - FINAL COLOR IS ACHIEVED.
9. EXAMPLE - CHAMPAGNE
10. EXAMPLE - BLACK

THE ELECTROLYTIC COLORING STEP

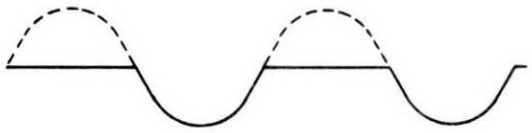
FIGURE 1.



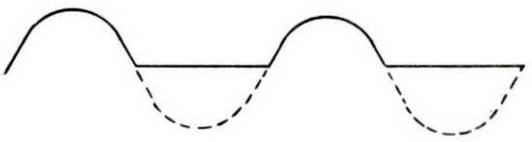
POWER LINE TO RECTIFIER.



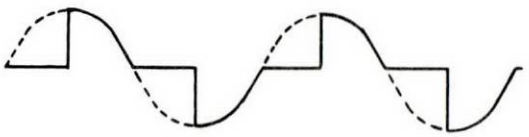
POTENTIAL SUPPLIED TO LOAD (AT FULL POWER).



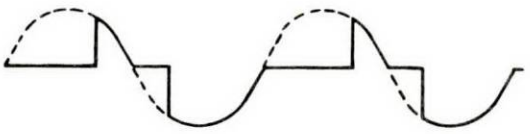
NEGATIVE POTENTIAL SUPPLIED TO LOAD.



POSITIVE POTENTIAL SUPPLIED TO LOAD.



INITIAL BALANCED (POSITIVE/ NEGATIVE) POTENTIAL SUPPLIED TO LOAD (AT PARTIAL POWER).



MODULATED (INCREASED NEGATIVE/REDUCED POSITIVE) POTENTIAL TO LOAD.

CONTROL OF ALTERNATING CURRENT

HALF - WAVE POTENTIALS

FIGURE 2.

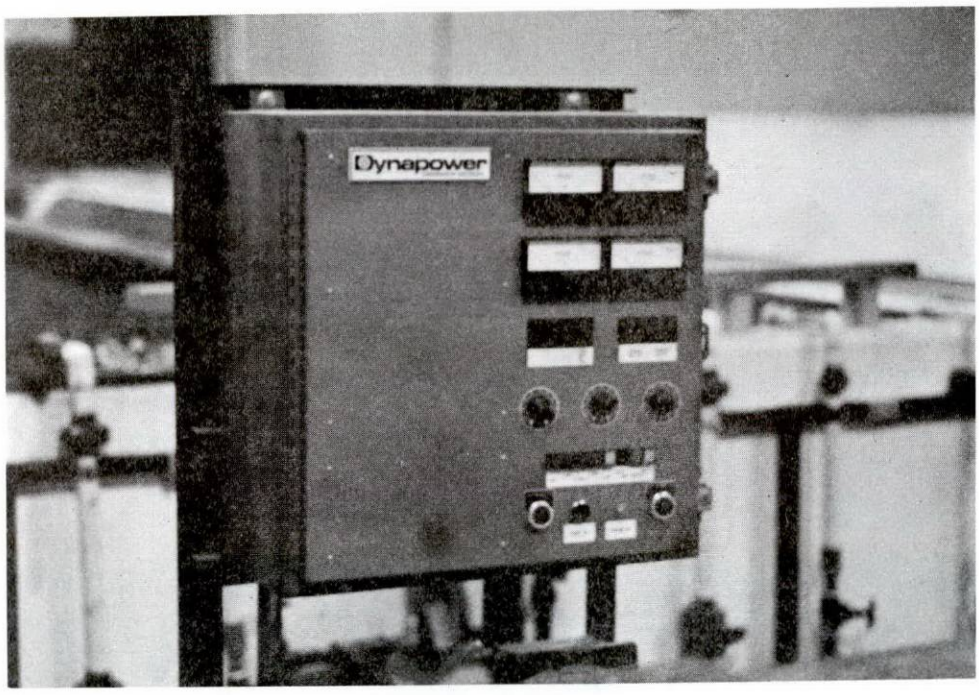


FIGURE 3.
Programmable Control Unit
For Electrolytic Coloring Power Supply

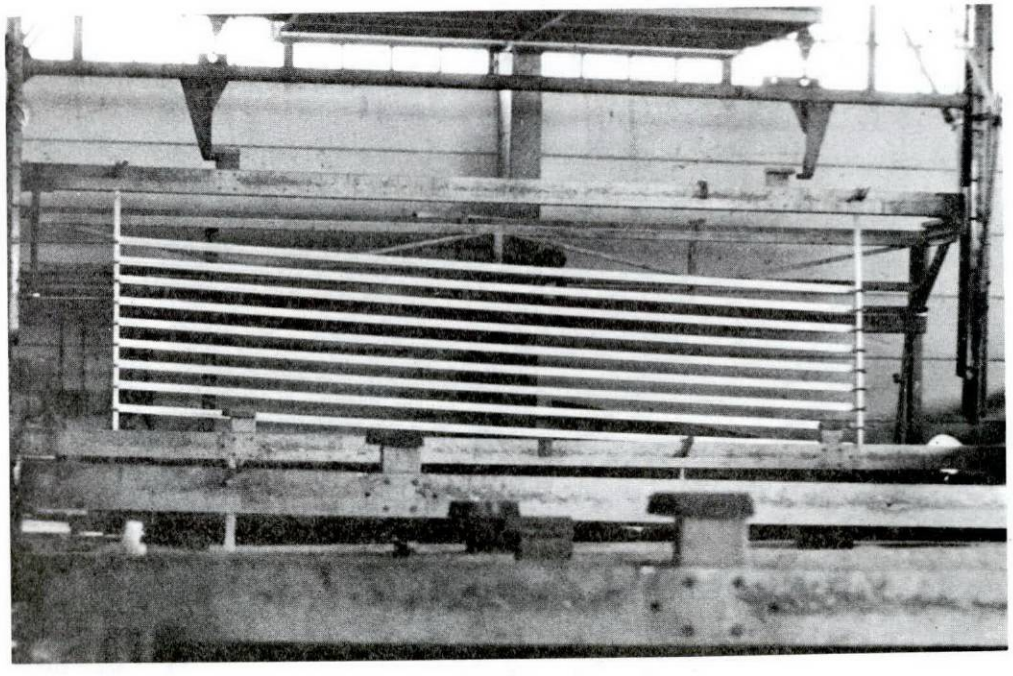


FIGURE 4.
Typical Method of Single-Spline Racking
For Color Anodizing

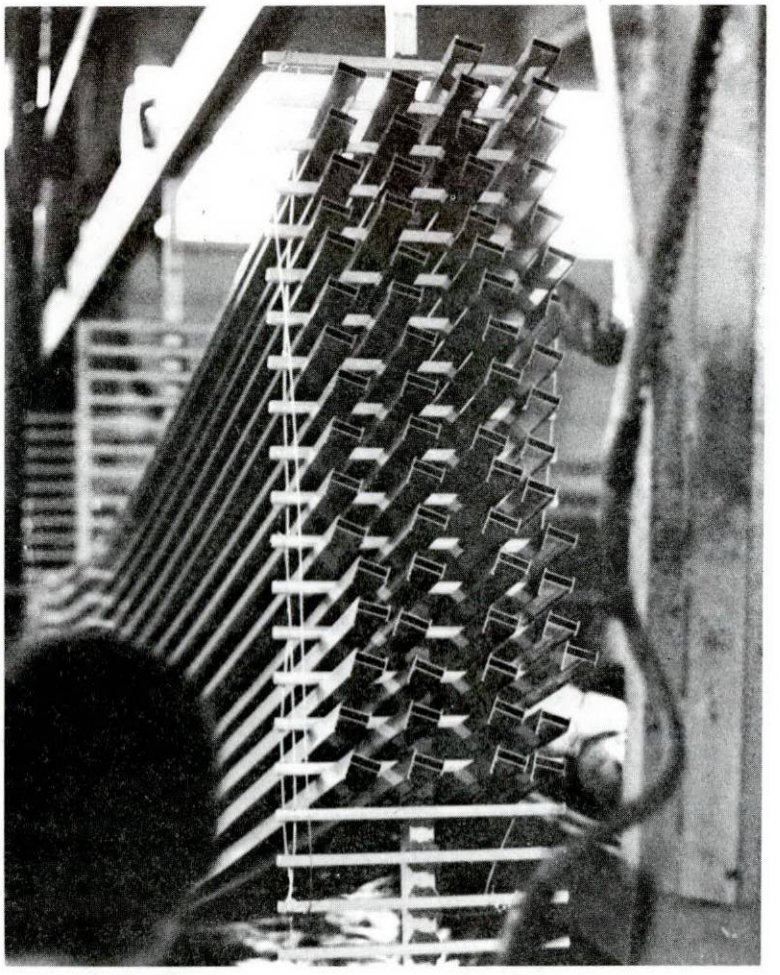


FIGURE 5.
Typical Method of Racking
For Clear Anodizing

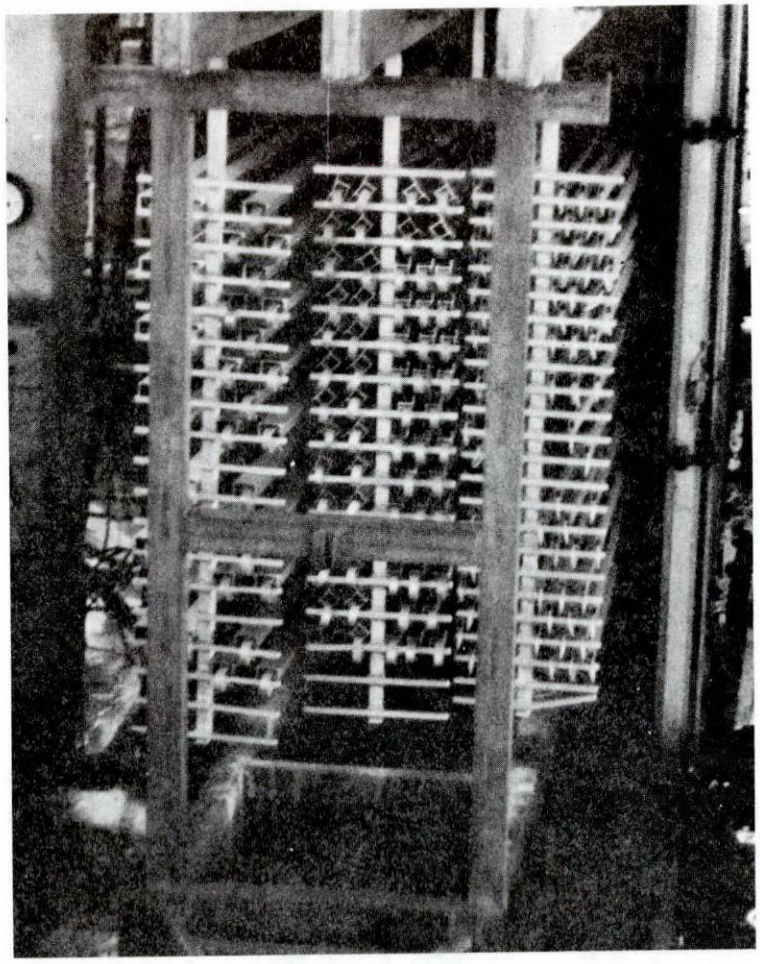


FIGURE 6.
Various Racks Showing Multiple Loading
of Workpieces for Clear Anodizing

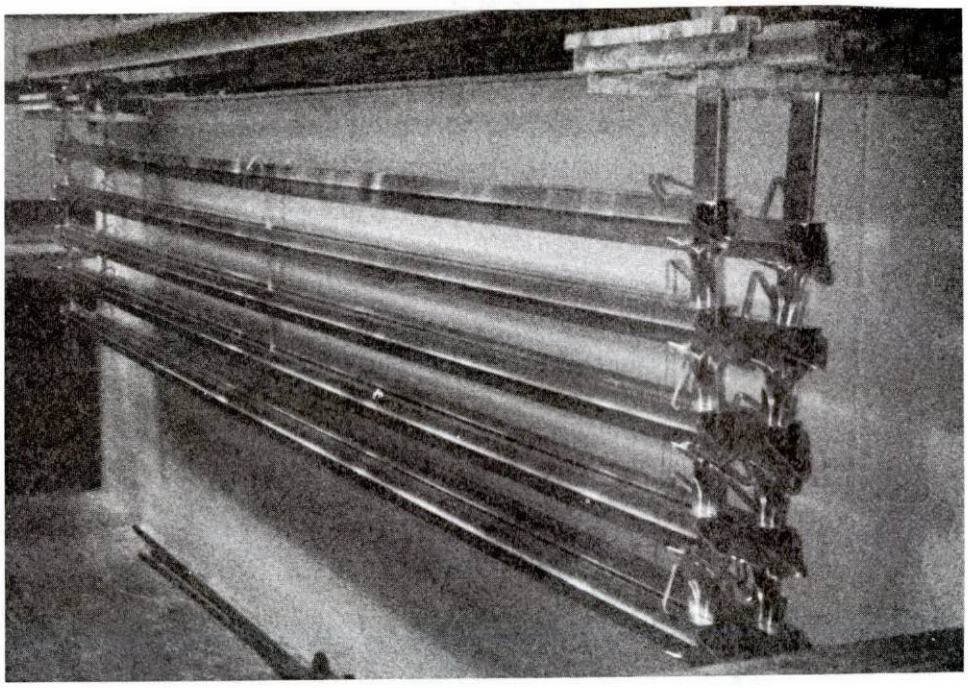


FIGURE 7.
One Method of Racking
For Electrolytic Coloring

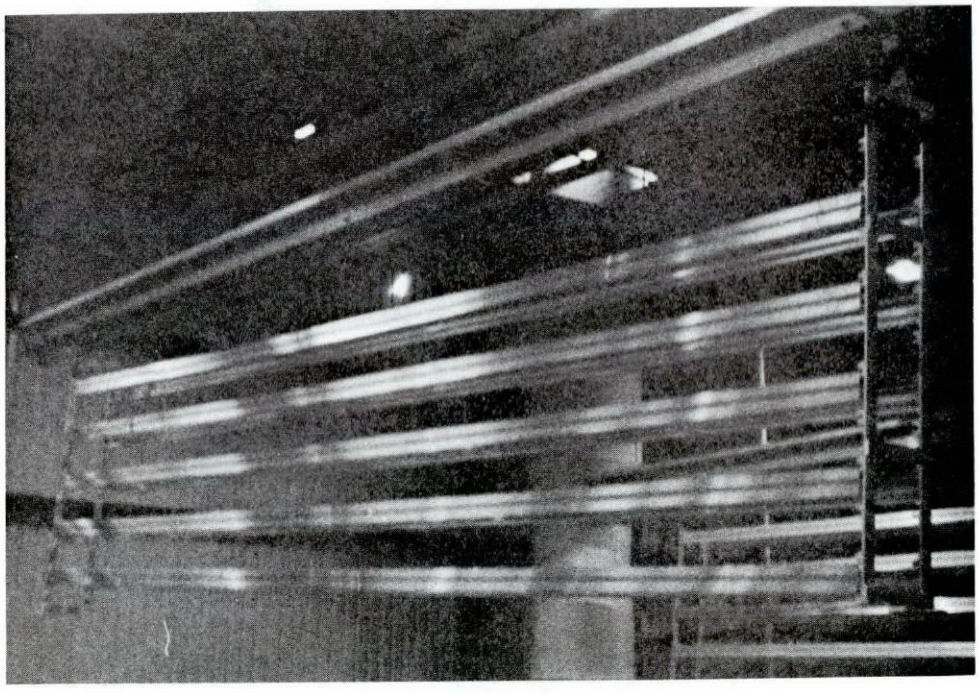
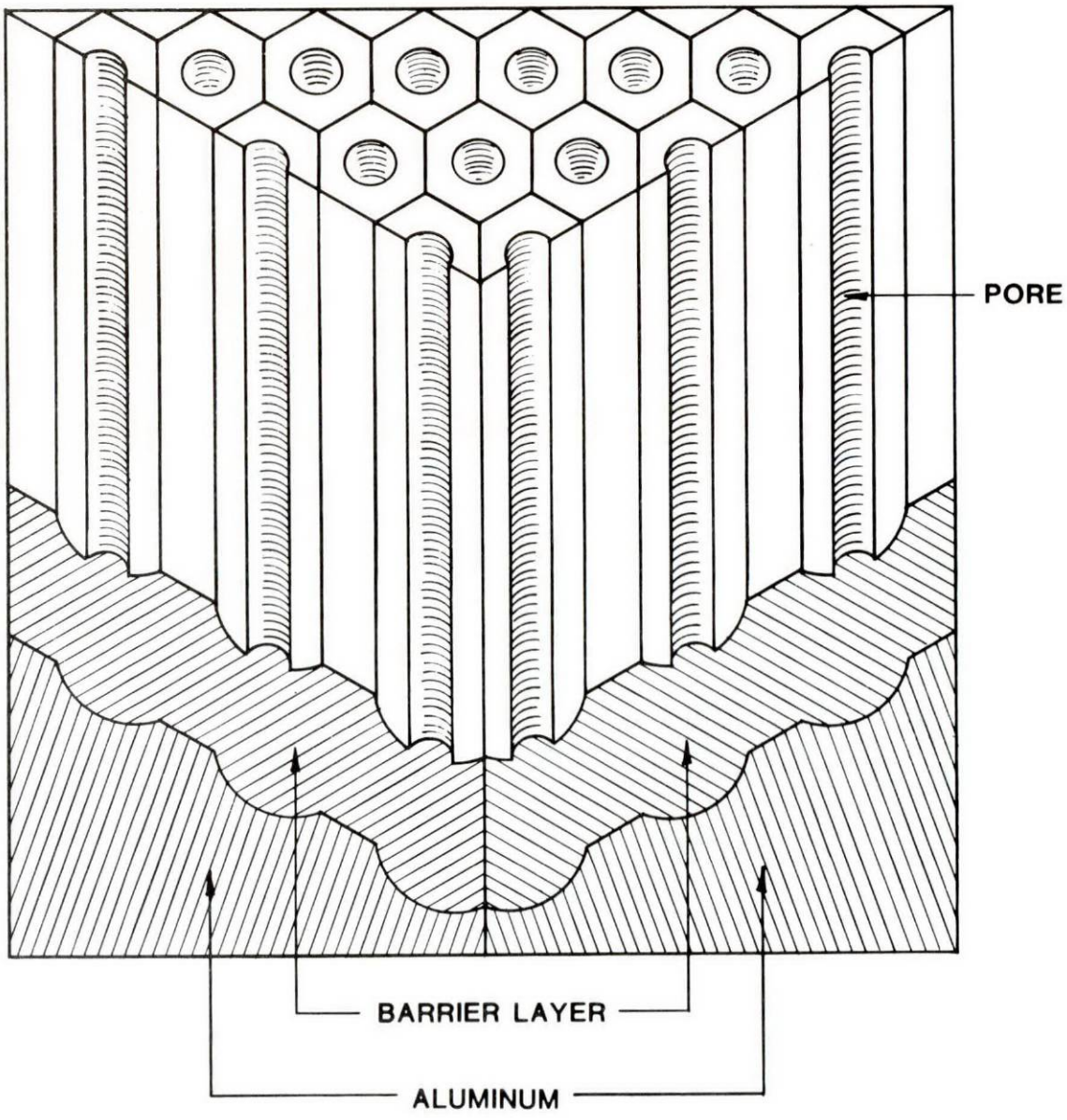


FIGURE 8.
Rack Load For Clear Anodizing
To Be Followed By Electrolytic Coloring



THREE - DIMENSIONAL SCHEMATIC OF ALUMINUM OXIDE FILM

FIGURE 9.

J-2

Light Metal Finishing I
Session J

The Production and Properties of Cobalt-Based Electrolytic Finishes

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THE PRODUCTION AND PROPERTIES OF COBALT-BASED ELECTROLYTIC FINISHES

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The paper describes the experience gained over a 12-year period in the production of cobalt-based electrolytic color finishes on aluminum. It gives indications of the equipment required and the operating costs involved, and describes the properties of the finishes produced, particularly their excellent light fastness and corrosion resistance.

THE PRODUCTION AND PROPERTIES OF COBALT-BASED ELECTROLYTIC FINISHES

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INTRODUCTION

Electrolytic coloring of anodized aluminum is now a well established production process that has been used in large-scale plants producing architectural finishes in many parts of the world since the late 1960's. Today electrolytic coloring processes are so strongly established in many areas that they have replaced the older integral-color anodizing processes. In contrast to integral-color anodizing, where color is developed during the anodizing process itself, electrolytic coloring is a two-step process involving first the production of a conventional clear anodic film, typically in a sulfuric acid electrolyte. The work is then transferred to a suitable metal salt solution and again treated electrolytically, usually under a.c., rather than d.c., conditions. This causes metal particles to be deposited at the base of the pores of the anodic film and these deposits act as scattering centers for light, in a similar way to the intermetallic particles present in integral-color coatings. The color and depth of shade produced depend on the metal being deposited and the coloring conditions used, but most metals produce a range of bronze shades and black. While many different metals and coloring electrolytes can theoretically give a variety of colors, in practice most industrial processes use electrolytes based on salts of nickel, cobalt or tin or mixtures of these salts[1,2]. In recent times electrolytes based on tin and tin-nickel mixtures have become used extensively and while outside Japan, the use of nickel-based electrolytes has become less common, cobalt-based electrolytes continue to be widely used, particularly in association with Alcan's ANOLOK* finishes.

Applications of Electrolytic Coloring

The major application of such finishes is in the architectural field where long-term durability is of prime importance. It is the ability of electrolytic coloring

*ANOLOK is a Registered Trademark by Alcan companies in many countries.

processes to provide this durability at a reasonable processing cost that has made them attractive to architectural finishers. In particular, the fact that in comparison with integral finishes they are relatively low-energy processes is now of considerable importance. This is mainly because the electrical energy used to produce an anodic film of a particular thickness in a sulfuric acid electrolyte is very much less than that required to produce a similar thickness in an integral-color process. Typically a 20 micron (0.8 mil) film produced in sulfuric acid requires about 2.2 kW hr/m^2 (0.2 kW hr/ft^2) and coloring of such a film in an electrolytic coloring process adds less than 0.2 kW hr/m^2 (0.02 kW hr/ft^2). In contrast an integral color anodizing process uses about 7.5 kW hr/m^2 (0.7 kW hr/ft^2) for a similar film thickness.

Another interesting aspect of electrolytic coloring is that the color is independent of the anodic film thickness, so the full range of colors can be produced with relatively thin films, say 5-10 microns (0.2 - 0.4 mil). This makes the finishes of interest for many other applications, especially for decorative trim components in the automotive field[3] where the ability to produce durable black finishes at a thickness of about 8 microns (0.3 mil) is of particular interest, as is the possibility of producing both high lustre or matte color finishes as required.

The Cobalt-Based Coloring Electrolyte

Electrolytes based on cobalt salts have been in widespread use since the early 1970's and their attractive features are the ability to produce a full range of bronze and black finishes, their relative insensitivity to contamination and the very high bath stability. Many baths of this type have been in continuous use for more than 10 years, and they normally need no filtration or regeneration procedures. Formulation of the electrolyte is important in order to cope with increasing aluminum content and to achieve an electrolyte with good throwing power, but properly formulated baths give excellent results. The pH of cobalt-based electrolytes is normally high (between 4 and 6) and this can be important, as highly acidic coloring electrolytes can cause some attack of the anodic film during the coloring operation.

The make-up cost for cobalt-based electrolytes is currently about 49¢/liter ($1.90/U.S. gallon). Typical consumption rates give a current operating cost of about 9¢/m^2 of surface colored (0.8¢/ft^2). It is important, however, to realize that more than 80% of the cobalt salts

used in a typical plant are lost through drag-out rather than deposition, so recovery of these salts from rinse waters can be an attractive proposition. Ion-exchange systems for doing this are available[4] and are in operation in a number of plants around the world. Use of such a recovery system can reduce chemical consumption costs to about 3¢/m^2 (0.25¢/ft^2).

Equipment for Coloring

The equipment required for electrolytic coloring with cobalt-based electrolytes is relatively simple and inexpensive (typically less than $40,000). It essentially consists of an appropriate tank, power supply and electrodes. The tank required is similar to that used for normal sulfuric acid anodizing operations, and is usually steel or concrete, lined with an acid-resistant plastic, fibreglass or rubber material. Air agitation of the electrolyte is necessary, but as the process operates at ambient temperature, means for cooling or heating the electrolyte are not normally required. Fume extraction equipment is also unnecessary. Rinsing between anodizing and coloring is important and this may necessitate an extra rinse tank at this stage.

The power supply is a continuously variable, single-phase, a.c. unit having a range of 0-25 V and a current capacity of about one-third the capacity of the anodizing rectifiers used. Appropriate controls to allow voltage or current/time programmes to be preset for particular shades of color are usually incorporated.

As the electrolytic coloring process is an a.c. process, current is passed between the work and suitable counter-electrodes. These are normally graphite or stainless steel and the use of appropriately spaced electrodes can be advantageous[5]. The electrodes are placed at the sides of the tank as in anodizing but, in addition, a central counter-electrode system is usually used to ensure good color uniformity throughout the load (Figure 1).

Properties of the Colored Finishes

In general, electrolytically colored finishes produced in cobalt-based electrolytes have properties that are similar to those of conventional sulfuric acid coatings, as the deposition of the metal within the pores of the film has little effect on the film structure itself. Thus properties such as abrasion resistance and sealing

characteristics are little affected by the coloring process.

The light fastness of the finishes produced is excellent, and even under very severe U.V. light conditions in the Microscal apparatus (I.S.O.6581:1980), the finishes have been shown to withstand more than 100 hours' exposure without change. Other work[6] has shown that 24 hours' exposure in this test is equivalent to 6-8 years' actual sunlight exposure.

In many applications corrosion resistance is the property that is most important, and the corrosion properties of cobalt-based electrolytic finishes are very good. This is borne out by their performance on many hundreds of storefronts, schools, hospitals and offices that were built throughout the United States during the last 12 years using only 10 micron (0.4 mil) thick anodic films (AA-Class II). Such finishes, with an anodic film thickness of 25 microns (1 mil), have also been exposed at our most severe industrial site in Sheffield (England) for more than 10 years, and are still in excellent condition with no pitting of the anodic coating. Other workers[7] have compared the performance of cobalt-based finishes with that of integral-color finishes at several exposure sites and have shown no significant difference in performance, all the finishes being in good condition after 5 years' exposure.

This good exposure performance is reflected in accelerated test performance in acidified salt spray tests (I.S.O.3769:1976 or ASTM Method B287-74), where the whole range of finishes, including the black, withstand more than 500 hours' exposure without significant pitting (anodic film thickness 25 microns (1 mil)). These good results are associated with the fact that cobalt, when deposited within the pores of an anodic film, is concentrated towards the base of the film and does not, even with black finishes, spread more than about 10 microns (0.4 mil) from the aluminum/aluminum oxide interface (this is not necessarily the case with all electrolytically colored finishes).

These, then, are the most important properties of cobalt-based electrolytic color finishes, and it is this combination of good properties and process economy that continue to arouse such widespread interest in these attractive finishes.

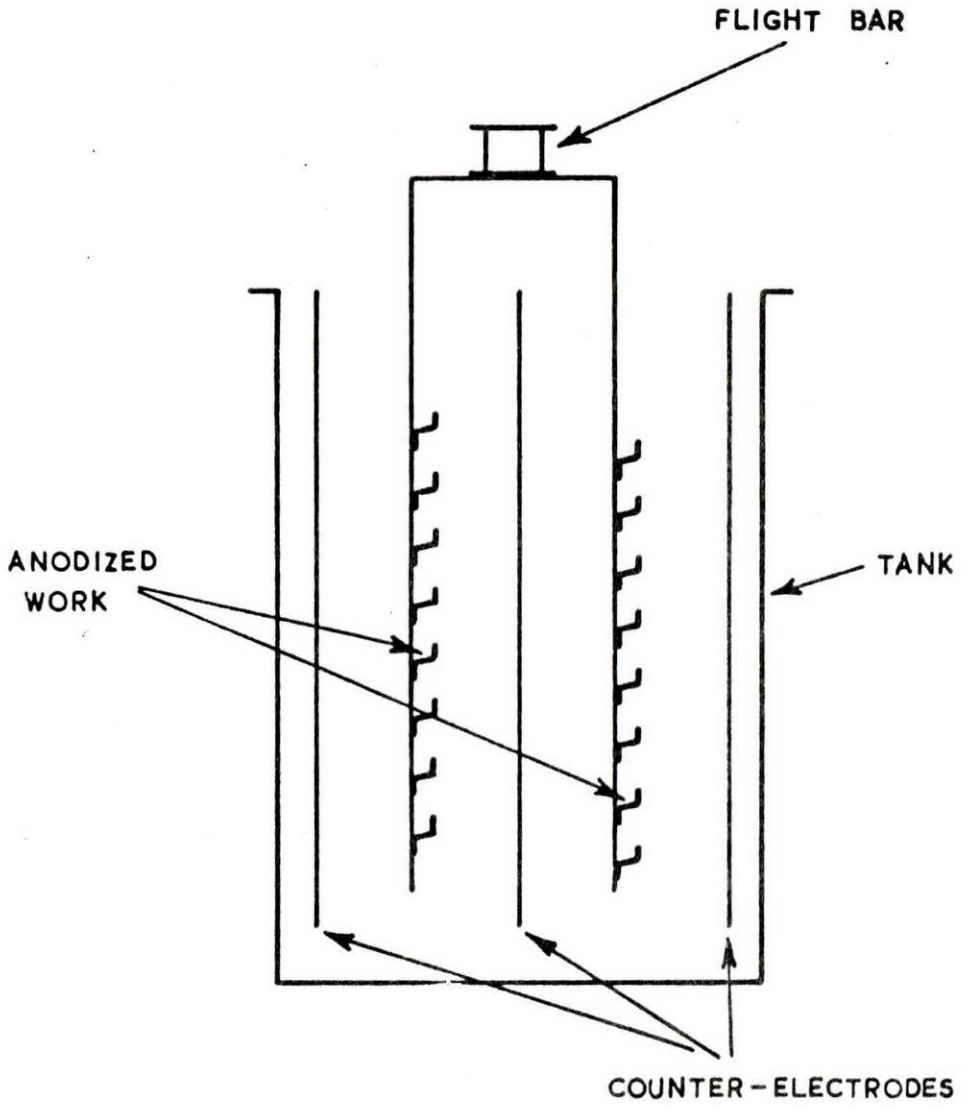

FIGURE 1. LAYOUT OF COUNTER-ELECTRODE SYSTEM FOR ELECTROLYTIC COLOURING

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J-3

Light Metal Finishing I
Session J

Electrolytic Coloring of Anodized Aluminum Using Tin Electrolytes

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ELECTROLYTIC COLORING OF ANODIZED ALUMINUM USING TIN ELECTROLYTES

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Comparison of Different Coloring Methods

Anodic oxide coatings on aluminum can be colored by one of three different methods which are distinguished by the nature of the coloring matter and its location within the oxide film (Fig. 1).

In adsorptive dyeing, organic dyestuffs or inorganic pigments are introduced into the openings of the pores in the oxide coating and are adsorbed in the region adjacent to the surface of the oxide coating. A wide range of colors with good uniformity and reproducibility can be obtained by adsorptive dyeing. Several dyestuffs exhibiting excellent lightfastness are currently available but their application under production conditions require much care and extensive controls in order to insure proper application and color matching. The problems of color control as well as earlier problems with lightfastness have led to the abandonment of this method of coloring in the field of architectural finishes in spite of the multitude of available color shades.

Integral color processes have dominated the architectural marketplace for many years. In an integral colored film, finely divided particles are situated inside the bulk oxide coating. These particles produce shades ranging from light bronze to black as a result of scattering of the incident light. These particles can be constituents of the base alloy, non-oxidized aluminum or decomposition products of the organic acids used in the color anodizing electrolytes. The depth of color produced is very dependent upon film thickness and alloy composition. The nature and location of the coloring particles make lightfastness a minor problem with the integral color process. Additionally, the high current densities and anodizing voltages employed in the integral coloring process result in the formation of an extremely hard,abrasion resistant oxide coating. These properties have resulted in the wide acceptance of integral colored finishes in the architectural field. However,a major drawback of the integral color processes is the extremely high energy consumption resulting from the high voltages and current densities required by the integral coloring process.

In electrolytic coloring, a clear anodized film is first produced. During a second step, small particles of metal are deposited irreversibly at the bottom of the pores of the oxide film by the application of an A.C. current in a metal salt solution. Most metals which can be electrodeposited from an aqueous solution may be used in electrolytic coloring but only some of them have gained practical importance. These are tin, nickel, cobalt and, to a lesser extent, copper. As in the integral colored film, the color is produced by light scattering phenomenon caused by the metallic particles. Therefore, the same range of light bronze to black color is obtained with all

metals except copper which produces red finishes if applied alone. The depth of color is determined by the quantity of metal deposited and is independent of film thickness and alloy composition within certain boundries. After initial uncertainties about the exact chemical nature of the deposits obtained, their metallic character has been proven independently by several researchers[1-3]. As with the integral color process, the nature and location of the coloring particles make lightfastness a minor problem with the electrolytic processes. Tin finishes, for example,have shown no fading after 2000 hours of cyclic Ultraviolet Weather-O-Meter testing.

All three coloring methods are still applied in the anodizing industry today. However, if we look back on the last 10 to 15 years of anodizing history, a clear shift in emphasis can be recognized, going from adsorptive dyeing to integral color processes and most recently to two-step electrolytic processes. Some of the factors used to assess the technical and economic value of a coloring method are: reproducibility of colors; uniformity of colors (throwing power); lightfastness of colors; corrosion resistance of colored finishes; ease of application; and cost per surface area. From these important considerations, the observed trend toward electrolytic coloring processes have their justification.

Compared to adsorptive dyeing, electrolytic processes provide greater color uniformity and reproducibility, as well as, improved lightfastness. Compared to integral color processes, electrolytic coloring produces equivalent color shades of greater uniformity and reproducibility on a wider range of alloy compositions. This fact coupled with the ability to obtain equal corrosion and abrasion resistance at much lower production costs have resulted in the rapid growth of two step coloring processes at the expense of the integral color process. By the introduction of an electrolytic coloring process, about DM 1.50 (about $0.62) in electrical cost can be saved per sq. meter. Therefore, it is not surprising that in Europe, integral coloring is continually being replaced by electrolytic coloring processes. This same trend is beginning to occur in the United States as demonstrated by the ever increasing number of anodizers installing two-step coloring processes.

As was mentioned earlier, the metals most frequently used for electrolytic coloring are tin, nickel and cobalt. Nickel based electrolytes, despite their low throwing power and sensitivity to contamination by foreign ions, are still widely used in Japan. Anodizers in Europe, on the otherhand, have demonstrated a clear preference for tin based electrolytes. These are relatively easy to operate, do not require expensive equipment, are insensitive to most contaminating ions and provide excellent throwing power. The following sections of the paper describe the method of operation of the tin based electrolytic coloring processes, the theoretical and practical problems originating in the relatively high acid content of these electrolytes, and the ways to overcome these potential problems.

Equipment and Coloring Procedure

Figure 2 shows a cross-section through a typical electrolytic coloring tank. The tank itself should be constructed from acid resistant material, preferably fiberglass or rubber lined mild steel. The most important feature

is the two sets of counter-electrodes running the length of the two long sides of the tank. In the case of tin based coloring electrolytes, the counter-electrodes are fabricated from stainlesss steel strips or tubes but carbon or tin can also be used. The counter-electrode system should have approximately the same surface area as the aluminum work load to be colored. The distribution of the counter-electrodes along the sides of the tank should be as uniform as possible. The fence-like construction visible in this drawing has given the best results in regard to color uniformity. The installation of a center counter-electrode, if the coloring tank is wide enough, will permit the processing of larger workloads. The center electrode should contain the same number of strips or tubes as the outer electrodes. The compressed air supply indicated in the drawing is used for mixing the coloring electrolyte after the addition of chemicals but times of air agitation should be kept as short as possible to prevent losses of divalent tin by air oxidation. The drawing does not show circulation and filtration equipment which can be installed to continuously remove any insoluble tetravalent tin compounds which may be formed during operation of the bath. The drawing also does not show any installation for heating or cooling. This equipment is only necessary if substantial deviations from the normal working temperatures of 18° - 24°C are to be expected due to climatic influences.

Normally, sinusoidal AC current with a frequency of 50 or 60 Hz is used for coloring. The transformer should have a maximum output of 25 volts with an amperage capacity corresponding to 75% of the anodizing amperage. Different attempts to improve the coloring efficiency have been made by employing solid-state thyristor based electrical equipment to control separately both the anodic and cathodic half cycles of the AC waveform. To date, these have not resulted in much benefit to the relatively easy-to-run tin coloring processes, making them, instead, unnecessarily complicated and extremely expensive to install.

The tin electrolytes used for coloring have a pH of 1.0 to 1.6. They normally contain between 8 and 10 g/L divalent tin as tin sulfate and between 16 and 22 g/L sulfuric acid. Organic stabilizers are often present to retard the air oxidation of divalent tin and to improve the throwing power of the process. Several proprietary stabilizers are available, some of which contain phenolic substances.

There are two alternative methods of producing a desired color shade. The coloring can be carried out for a constant time period using varying voltages, or the voltage can be kept constant and the time period varied. Normally, the second method is employed in most production facilities. To insure consistent color reproduction from load to load the anodizer must work with fixed coloring cycles. After anodizing, the rinsed parts are introduced into the coloring bath and are left there without voltage for about one minute. Following this immersion period the voltage is slowly increased from zero to a specific value between 10 and 18 volts within approximately one minute. This step must always be carried out in the same manner to insure color reproducibility. Coloring times range from 10 seconds for light champagne to 15 minutes for black. The current density at the beginning of the coloring process can be as high as 10 A/ft^2. Within 30 to 40 seconds it will drop to about 40% of the peak value and remain constant for the remainder

of the coloring time.

Influence of Coloring Voltage

Theoretically one would expect that the speed of coloring would be increased by increasing the coloring voltage. Surprisingly, this is only partly true as can be seen from Figure 3. In this figure the total reflection measured with a device similar to the PRS head[4] is plotted as a function of coloring voltage. The total reflection is given as a percentage of the reflection of a white barium sulfate plate. Using this method, the lower percentage figures represent darker shades. The two curves represent coloring times of 2 and 5 minutes in an electrolyte containing 10 g/L tin,20 g/L sulfuric acid and 20 g/L of proprietary stabilizer. It can be clearly recognized that the coloring speed is highest at about 15 to 16 volts. This is very important to know, particularly for the production of dark finishes, since the coloring time should be kept as short as possible.

The same test series was run at different concentrations of sulfuric acid. This was done to determine whether the position of the maximum coloring speed was influenced by the composition and the conductivity of the electrolyte. As can be seen in Figure 4, this was not the case. The two curves were obtained using a coloring time of 2 minutes. Darker shades were produced at all voltages with the lower sulfuric acid concentration of 15 g/L as compared to 30 g/L. The speed of coloring was highest at about 15 to 16 volts in both cases. A variation of the tin concentration leads to the same results.

We suggested, therefore, that the position of the maximum coloring speed might be influenced by the initial barrier layer thickness, which is a function of anodizing voltage. According to a previous work[5], the barrier layer thickness of oxalic acid films is reduced to a value which is determined by the coloring voltage and the acid concentration of the coloring electrolyte at the start of electrolytic coloring. It is certainly not wrong to theorize that similar changes will take place within a sulfuric acid film as well. Therefore, films of 20 to 21 μm were prepared with anodizing voltages ranging from 12 to 18 volts. These films were colored for a constant time of one minute in an electrolyte containing 10 g/L tin and 20 g/L sulfuric acid at 14, 16 and 18 volts. From the theoretical barrier layer thickness of 9 A°/V for d.c. anodizing and 10.9 A°/V (peak) for a.c. anodizing, an increase of the barrier layer thickness during coloring ranging from 54 to 170 A° was calculated. However, no correlation between these changes and the depth of color could be detected. Figure 5 shows that the darkest color was obtained at a coloring voltage of 16V independent of anodizing conditions.

One possible explanation for the fact that the voltage of maximum coloring speed is not influenced by the composition of the electrolyte or the properties of the anodic oxide coating can be given. In the first part of the curves, between 10 and about 14 volts, the speed of metal deposition increases linearly, similar to electroplating, whereas at still higher voltages the redissolution of tin during the anodic half-cycle of the a.c. wave becomes increasingly noticeable.

Contamination of the Coloring Electrolyte

It has been mentioned earlier that nickel based coloring electrolytes are extremely sensitive to contamination by foreign ions, especially sodium and potassium. This is not the case with tin based processes. However, no quantitative data has been published concerning the maximum permissible concentrations of impurities. In order to fill this gap, increasing amounts of chemicals normally encountered in an anodizing facility were added to a tin based coloring electrolyte. The electrolyte employed contained 10 g/L tin and 20 g/L sulfuric acid. The changes in coloring efficiency, that is the depth of color obtained after a fixed coloring time of 2 minutes, were observed. The ions investigated were sodium, potassium, calcium,magnesium, ammonium, nitrate, chloride, borate and oxalate. The tin is precipitated by phosphate ions, therefore they will not build up to a significant concentration. The influence of trivalent chromium ions and silicate ions were also investigated.

The results for sodium, potassium, nitrate and chloride are shown in Figure 6. The depth of color obtained after 2 minutes at 16V is plotted as a function of the concentration of the contaminating ion. It can be seen that sodium and potassium ions show an effect only at concentrations above 2 g/L. The coloring current density showed a significant increase at potassium ion concentrations above 5 g/L. Presumably such concentrations will rarely be attained by simple carryover from other pretreatment baths. Nitrate ions, on the other hand, reduce the coloring efficiency at concentrations as low as 0.2 g/L. In the presence of 1.5 g/L nitrate, no color was obtained. It might be concluded from the graph that chloride ions had no influence whatsoever. However, at a concentration of about 2 g/L chloride, the total film started to separate from the base aluminum. Simultaneously, the current density showed a tremendous increase. Chlorides, therefore, must be included among the dangerous ions, especially if the concentration approaches 1 g/L.

The other ions investigated are shown in Table I. Their influence on coloring efficiency is rather small. Very slight fading was observed with ammonium, borate, silicate and magnesium ions when their concentrations exceeded 5 to 10 g/L. Oxalic acid precipitated the tin and calcium was precipitated as calcium sulfate at rather low concentrations. Trivalent chromium was added in the form of a 1% solution of chromium-III sulfate. Only low concentrations were studied in order not to dilute the coloring electrolyte. No detrimental effects were observed to the maximum 0.8 g/L studied.

As a whole, these results confirmed the high tolerance of tin based coloring electrolytes toward contamination by foreign ions. Only nitrate and chloride proved to be dangerous at concentrations below 1 g/L. All other ions showed an effect only at much higher concentrations. Due regard has to be given to the quality of the coloring chemicals since chloride is a frequent contaminant of commercially available tin salts. Additionally, the chloride content of the make-up water must also be considered.

The Problem of Spalling

A local chipping off of the anodic oxide coating during the electrolytic coloring, called 'spalling' was a severe problem during the early development of electrolytic coloring processes. This phenomenon can occur with all electrolytes, independent of their acidity and the metal used for coloring. Possible reasons are too high coloring voltages and too fast an increase in voltage at the beginning of the coloring cycle. Spalling seems to occur at lower voltages in the less acidic nickel and cobalt electrolytes than in the more acidic tin electrolytes. Recently it has been recognized that the composition of the alloy is another important factor. Sheet alloys containing more than 1.5% magnesium proved to be especially susceptable to spalling.

Film Quality and Corrosion Resistance

The predominant point of dispute in comparisons of different electrolytic coloring processes has been and continues to be the question whether or not the relatively high acid content of tin based electrolytes is harmful to the quality of the anodic oxide coating. Conclusions have been drawn from purely theoretical considerations that, due to the high redissolution of the oxide film, tin finishes should show reduced abrasion resistance and inferior corrosion protection properties. The question of how much metal must be deposited or, in other words, how far the pores must be filled in order to obtain a dark color, has gained some importance in regard to the corrosion resistance problem. Electron microscopic investigations[6] have indicated that new pores are formed inside the original barrier layer due to reanodizing during the a.c. treatment in acidic electrolytes. This phenomenon is thought to increase the danger that the deposited metal might come into contact with the substrate aluminum thereby reducing the corrosion resistance.

In the following sections an attempt will be made to provide answers to all these questions. All the experimental variables involved in anodizing, coloring and sealing were closely controlled in order to be able to make a judgement on the basis of samples with defined properties.

Alterations of the Barrier Layer

Electron microscopic investigations on the structure of sulfuric acid anodized films are extremely difficult since the thickness of the barrier layer and the cell walls is only 100-150 A° if normal anodizing voltages are applied. Therefore, films anodized in oxalic acid or phosphoric acid at voltages ranging from 50 to 80V have been preferred for this type of work. Only under these conditions could the formation of branched pores under the original barrier layer during electrolytic coloring in acid electrolytes and the deposition of metal inside these new pores be demonstrated[5,7]. Simultaneously, a thinning of the barrier layer to a value corresponding to the much lower coloring voltage was observed. According to a Japanese work[8] on the structural changes inside the barrier layer produced by a sudden voltage

drop during anodizing, a strong branching of new pores is only to be expected if the voltage is reduced to less than two-thirds of the original anodizing voltage. In all other cases the new film grows uniformly below the original barrier layer. Conditions are even more favorable in the case of anodizing in sulfuric acid and subsequent electrolytic coloring. Since the coloring voltage is generally higher than the anodizing voltage, the thickness of the barrier layer is actually increased. This should make corrosion originating from a contact of the deposited metal with the aluminum substrate less probable.

Salt Spray Tests and Outdoor Exposure Results

An investigation into the corrosion resistance of tin based finishes was performed using different color shades. The samples were anodized in an electrolyte containing 200 g/L H_2SO_4 at 18°C using a current density of 15 A/ft^2 to a film thickness of 20 microns (0.8 mil). The coloring electrolyte contained 10 g/L tin and between 15 and 30 g/L sulfuric acid. The color shades produced were light bronze, medium bronze and black. All samples were sealed for 3 min/micron in boiling deionized water at a pH of 5.8. Fig. 7 shows the black samples after 1500 hours of exposure in an acidified salt spray test[9]. The upper test sheets were merely rinsed after leaving the test cabinet. The lower ones of identical pretreatment were cleaned with a slightly abrasive cleaner. The salt spray caused some greyish discoloration and only very slight pitting. No correlation between the number of pits, the depth of color and the sulfuric acid concentration could be detected. This becomes obvious from Table II which gives the number of pits observed on the cleaned samples having a surface area of 50 cm^2. Pits situated directly at the cut edges of the samples were not considered in the evaluation. The black sheet colored with the highest sulfuric acid concentration showed the largest number of pits. However, the medium bronze sample prepared using the same pretreatment did not develop any pits at all. The black test specimen colored with the next lowest sulfuric acid content also did not develop any pits. Therefore, the differences noted must be attributed to statistical variations. Furthermore, the pits which did develop had a very small diameter (less than 0.3 mm). This means that even in the worst case, only 30 ppm of the total surface area was covered with pits.

These very favorable results are in accordance with outdoor exposure tests carried out in France[10] and Germany[11]. In the latter country a comparison between dark tin based finishes and integral colored finishes was conducted in maritime, industrial and mixed maritime/industrial climates. No differences in corrosion resistance could be observed on samples with a minimum film thickness of 20 microns when evaluated after 5 years of exposure. A conclusion might be drawn from these results that the concentration of the sulfuric acid in the coloring electrolyte is of no importance whatsoever. This is certainly not entirely true. It has been shown previously that the acidic coloring electrolytes do not reduce the abrasion resistance of the anodic oxide coating if the anodizing is carried out under proper conditions[12]. This is demonstrated by Fig. 8 in which the thickness reduction in the abrasive wheel test is plotted as a function of the number of double movements with a constant contact pressure. It can be seen that the same curve is obtained for clear anodized, electrolytically colored and the organically dyed

sample if anodizing is performed at 18°C. Figure 9 shows, however, that a small increase in anodizing temperature of only 3°C produces a significant reduction in abrasion resistance if the film is colored in an acidic electrolyte. These differences have been explained as indicating that the coloring step will show a harmful effect only if the outermost zones of the anodic oxide coating have already been weakened or softened during anodizing.

Anodizing temperature is only one factor affecting the hardness of the anodic oxide coating. Another factor is the current density, by which the porosity of the film and the contact time in the anodizing bath are determined. It is known that extended anodizing times and elevated film thicknesses will result in an oxide coating with reduced strength and wear resistance especially in the outermost zones. Samples were anodized at current densities of 12 and 15 A/ft^2 to a film thickness of 25 microns to determine whether the resistance to an acidic coloring electrolyte is reduced by these effects. One set of the test samples were colored black in a cobalt electrolyte. Two other sets were colored to a dark bronze and a black shade in a tin electrolyte containing 20 g/L H_2SO_4. The film quality was determined after sealing by means of the chromic-phosphoric acid weight loss test and the abrasive wheel test and compared to that of clear anodized samples produced under identical conditions. The results summarized in Table III show only very slight effects of current density and coloring treatment on the acid resistance, though the weight losses of the cobalt colored samples tend to be somewhat higher. The influence of current density on the abrasion resistance is more distinct. A significant reduction, especially in the case of the black tin finish, is observed if the current density is lower than 15 A/ft^2. It can be concluded from previous work by one of the authors[12], that under the test conditions used, all thickness reductions below 4 to 5 microns must be regarded as satisfactory. Abrasion resistance can be obtained with black tin finishes which come close to that of integral colored films if the current density is further increased to 24 A/ft^2. In these cases, however oxalic acid must be added to the anodizing electrolyte in order to avoid the negative effect of local overheating (burning) of the film.

Metal Distribution Inside the Pores

The dark bronze and black samples on which the location and amount of metal inside the pores were determined had not been prepared in the laboratory but were taken from the production of an anodizing plant. The scanning electron micrograph in Fig. 10 shows the cross-section of a 20 µm film colored dark bronze in a tin electrolyte. The line scan with the electron microprobe was run along the white line and the tin concentration profile in the pore is given by the dotted curve. It can be clearly recognized that the maximum of this curve is situated at the oxide/metal interface and that only the lower 25% of the pores are filled with tin. Identical results were obtained on a sample colored to the same shade using a cobalt electrolyte with the only difference being a slightly narrower distribution.

More metal must be deposited in the pores for the production of a black finish. This becomes obvious from Fig. 11 which shows the tin distribution inside a black 20 micron thick film. The deposited metal extends about 10 microns into the coating leaving the pore openings free for sealing. Its

absolute concentration decreases steadily from the barrier layer in the direction of the film surface. The corresponding distribution of cobalt is somewhat different (Fig. 12). Here again the pores are about half-filled with metal. The concentration profile, however, shows a much sharper increase as compared to tin and a plateau with a width of about 5 µm where the pores seem to contain the maximum possible amount of cobalt. These results are in accordance with the observation that over-coloring, that is, overfilling the pores with metal; is more likely to occur with tin than with cobalt. On the other hand they also prove that this possibility is by no means an unavoidable characteristic of tin based coloring processes. It can be overcome and therefore avoided by limiting the coloring times to the minimum necessary to produce the required shade. Admittance measurements provide a fast and accurate means of determining whether or not the pores have been overfilled with metal. The coloring parameters and admittance values of different dark tin finishes are summarized in Table IV. A black film with an admittance of 77 µS was obtained after 8 min. coloring at 16 Volts. The Table shows that an extension of the coloring time to 15 min. did not bring about any change in color but caused the admittance to rise in increments to 200 µS. It is advisable, therefore, for an anodizer to establish internal standards defining maximum permissible admittance values for dark finishes.

It has been claimed[10] that the deposition of nickel inside the pore is able to enhance the corrosion resistance of the anodic oxide coating. Occasionally, therefore, mixed tin/nickel coloring electrolytes are used adjusted to a pH of about one. Fig. 13 shows the nickel distribution inside a film colored to a dark shade according to one of these processes. There is only a very small amount of nickel present at the bottom of the pores which presumably has been co-precipitated together with the tin. No nickel at all could be detected in other areas of the same sample. Significant amounts of nickel can only be introduced into the film if the pH of the coloring electrolyte is raised to a value more favorable for the electrodeposition of this metal. This change requires special means for preventing the precipitation of tin salts as well as bringing about a remarkable decrease in throwing power.

Conclusions

Tin based electrolytic coloring processes are predominant in Europe for the production of bronze to black architectural finishes due to their high throwing power, ease of operation, low cost and high tolerance to contaminating ions. More than ten years of field experience have given proof of the excellent lightfastness and corrosion resistance of tin colored films. The tin based electrolytic processes are very rapidly becoming the standard choice of anodizers in the United States for the same reasons stated above. Tin based coloring processes have achieved this wide acceptance in spite of the relatively high acid content of the coloring electrolytes.

Possible negative effects of the acid concentration can be avoided by controlling the anodizing conditions and by applying as short as possible coloring times. Anodizing should be carried out at a maximum temperature of 19°C and at current densities not much lower than 15 A/ft^2.

The preferred coloring voltage is 15 to 16 V a.c., since in this region maximum speed of coloring is obtained. The pore must be almost half filled with tin in order to produce a black color on a 20 μm Class I architectural film. Production of black Class II work will require anodizing to approximate 12 μm to insure that empty pore space is available for adequate sealing. The dangerous overfilling of the pores which can occur at extended coloring times can be detected by means of the admittance test.

Samples anodized and colored under conditions quoted above and sealed for 3 min./micron in deionized water showed excellent results after 1500 hrs. of acidified salt spray testing. The test results were independent of the color shade and a wide variation in acid concentrations in the coloring electrolyte.

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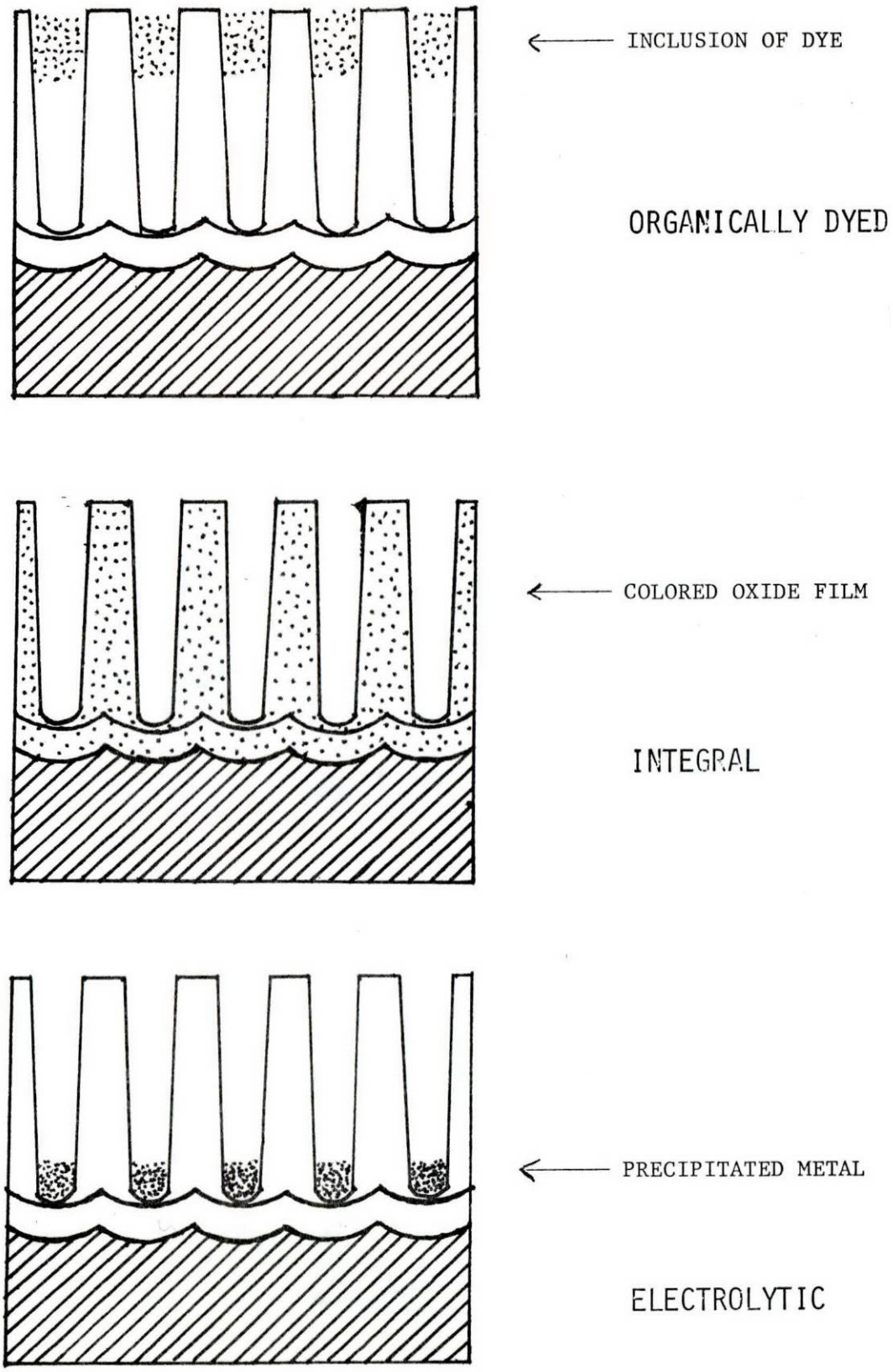

Fig. 1 Comparison of Various Methods for Coloring Anodized aluminum.

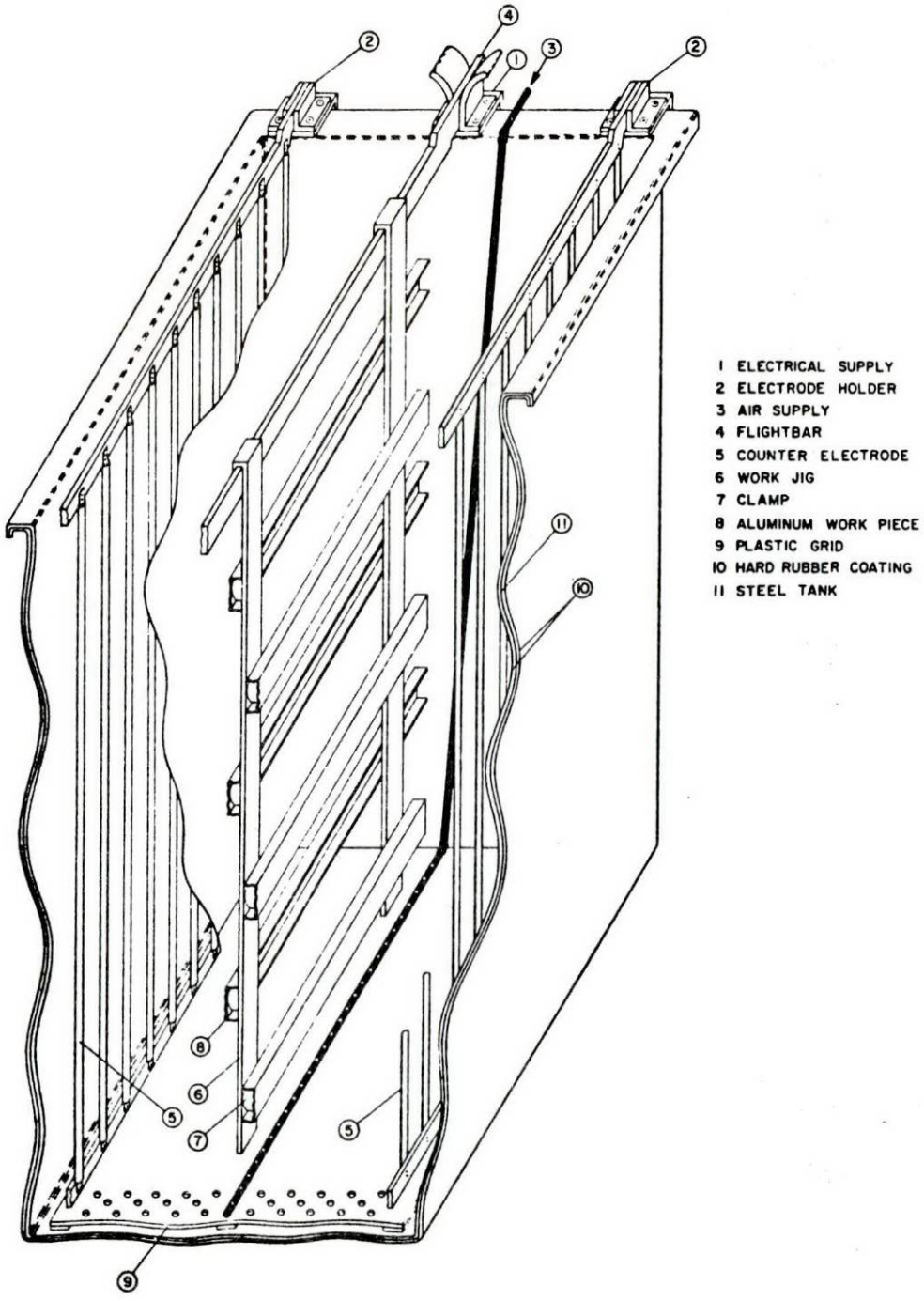

Fig. 2. Schematic drawing of a typical electrolytic Coloring Tank

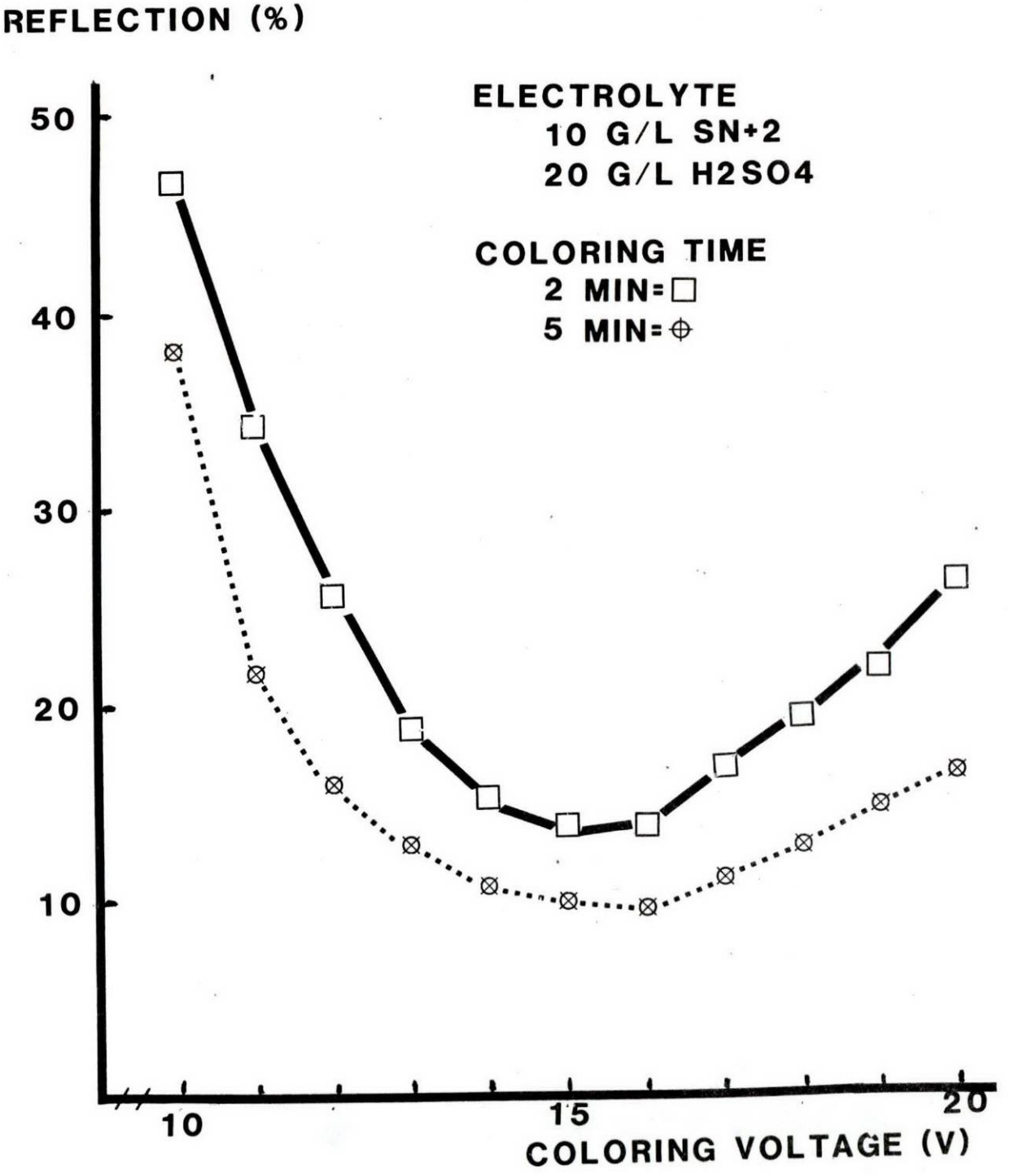

FIG 3. INFLUENCE OF COLORING VOLTAGE ON COLORING TIME

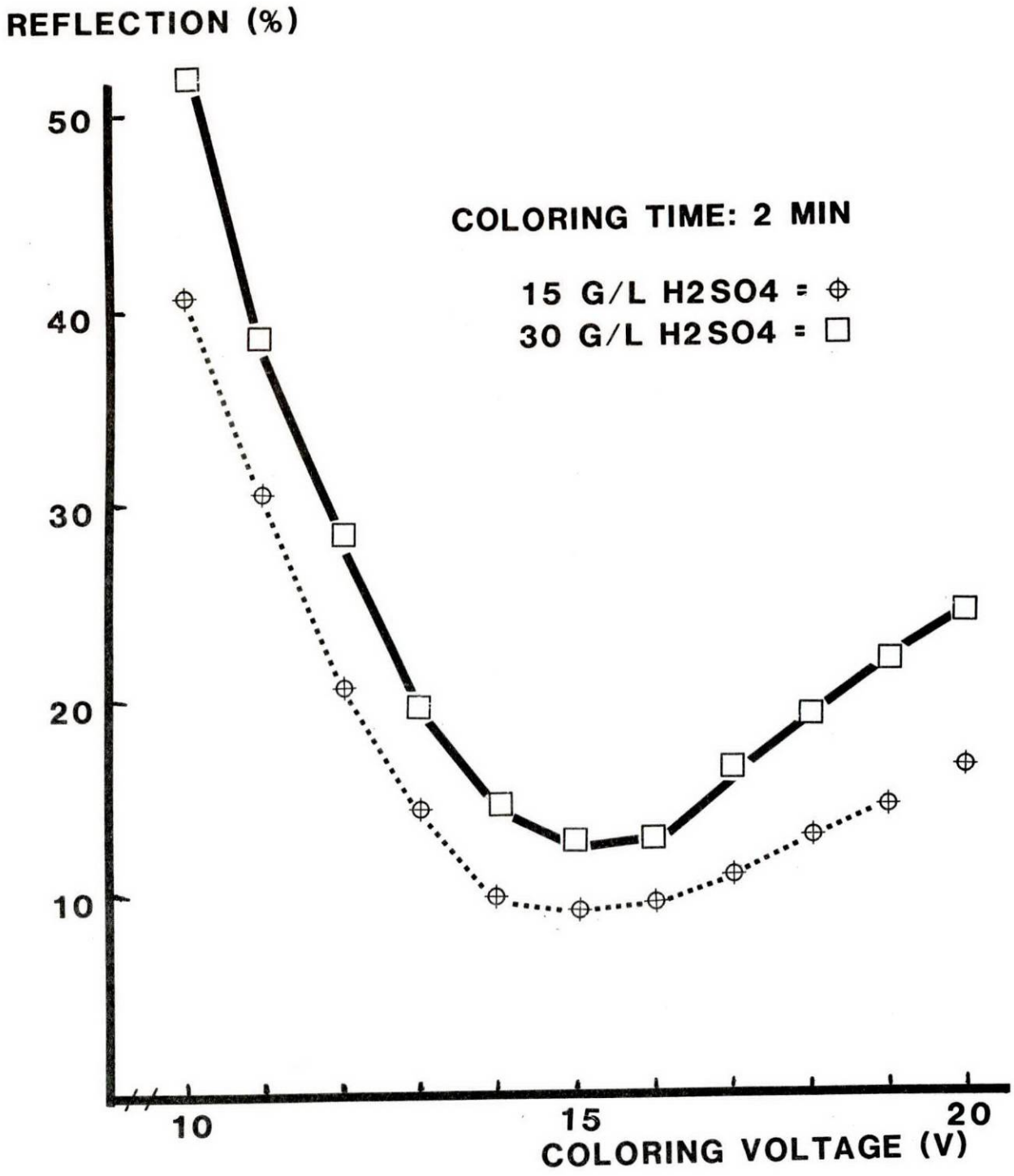

FIG 4. INFLUENCE OF SULFURIC ACID CONCENTRATION AND VOLTAGE ON COLORING SPEED

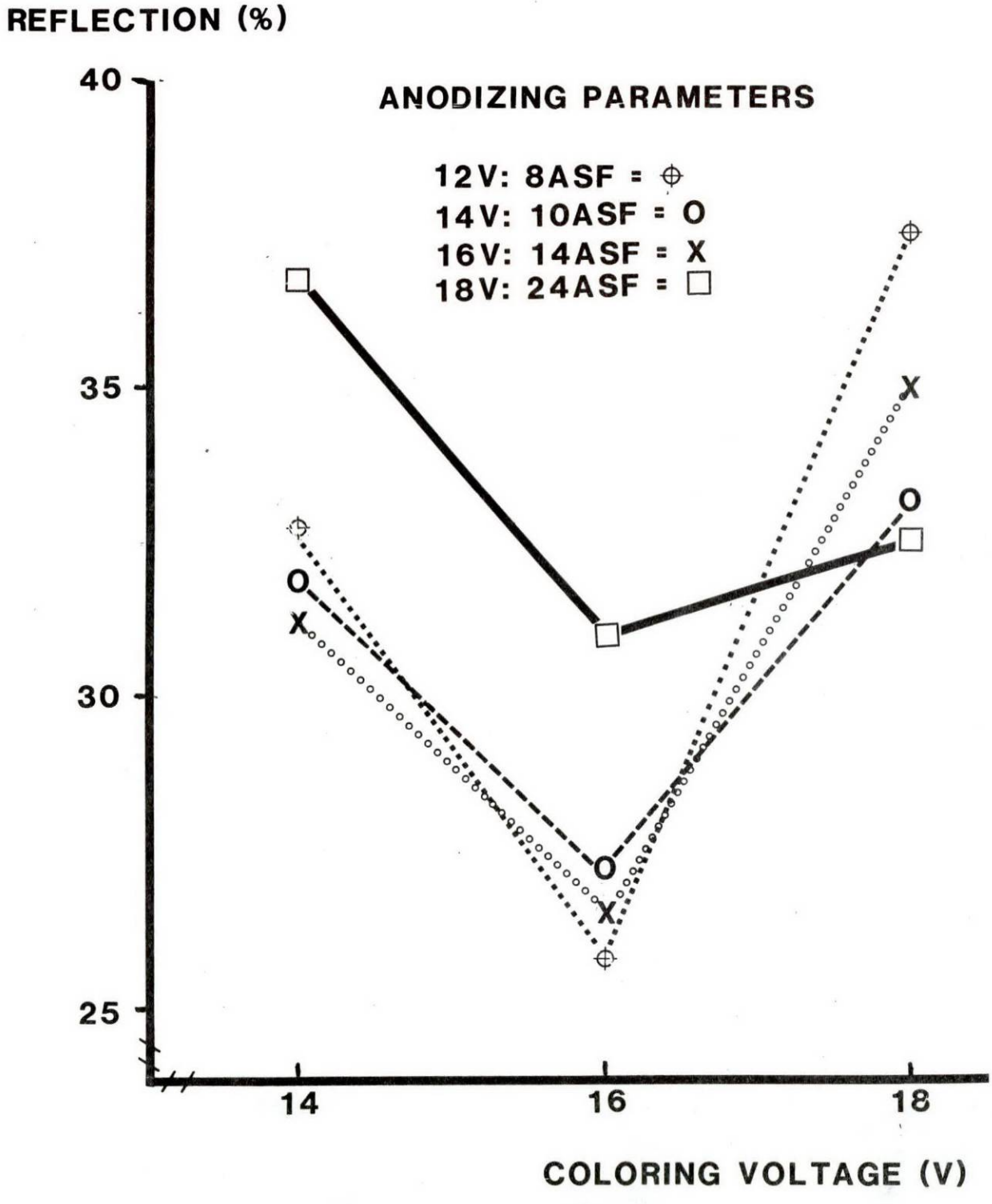

FIG 5. INFLUENCE OF ANODIZING AND COLORING VOLTAGES ON COLORING SPEED

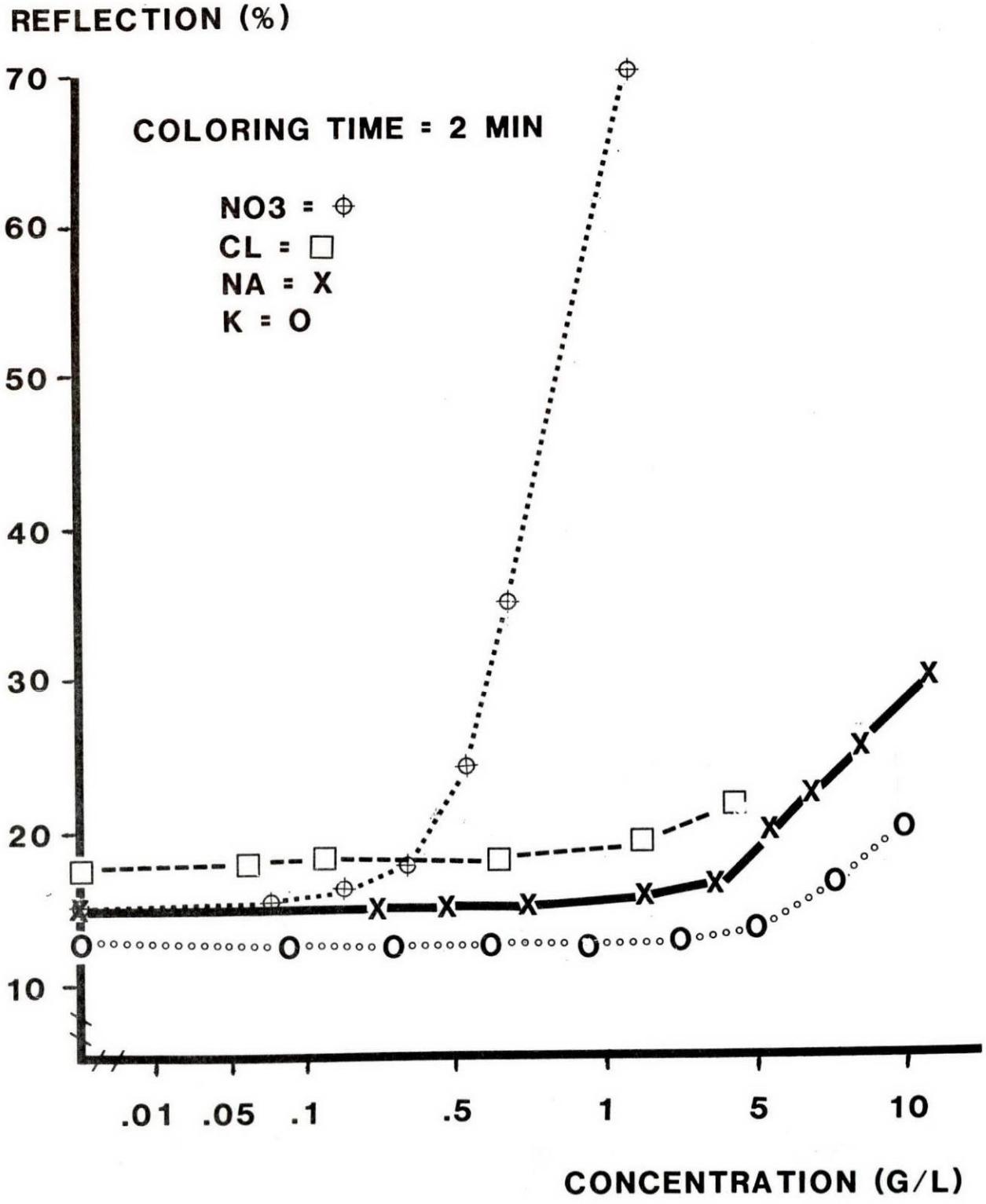

FIG 6. EFFECTS OF CONTAMINATING IONS ON COLORING EFFICIENCY

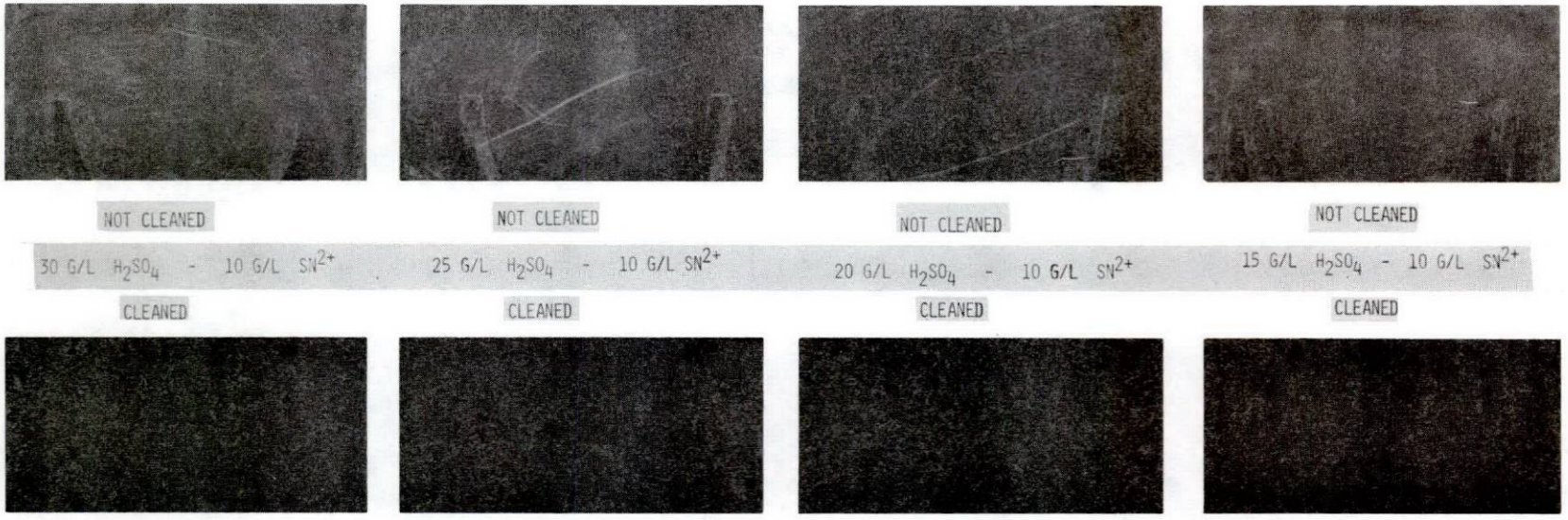

Fig. 7: Black Tin Colored Samples After 1500 hrs. Acidified Salt Spray Test

TABLE II PITTING CORROSION ON DIFFERENT TIN FINISHES AFTER 1500 HRS ACIDIFIED SALT SPRAY TEST

Sample No.	Coloring Electrolyte	Color Shade	Number of Pits
2	10 G/L SN^{+2} 15 G/L H_2SO_4	Light Bronze	0
4		Medium Bronze	2
6		Black	2
8	10 G/L Sn^{+2} 20 G/L H_2SO_4	Light Bronze	5
10		Medium Bronze	1
12		Black	3
14	10 G/L Sn^{+2} 25 G/L H_2SO_4	Light Bronze	1
16		Medium Bronze	0
18		Black	0
20	10 G/L Sn^{+2} 30 G/L H_2SO_4	Light Bronze	6
22		Medium Bronze	0
24		Black	9

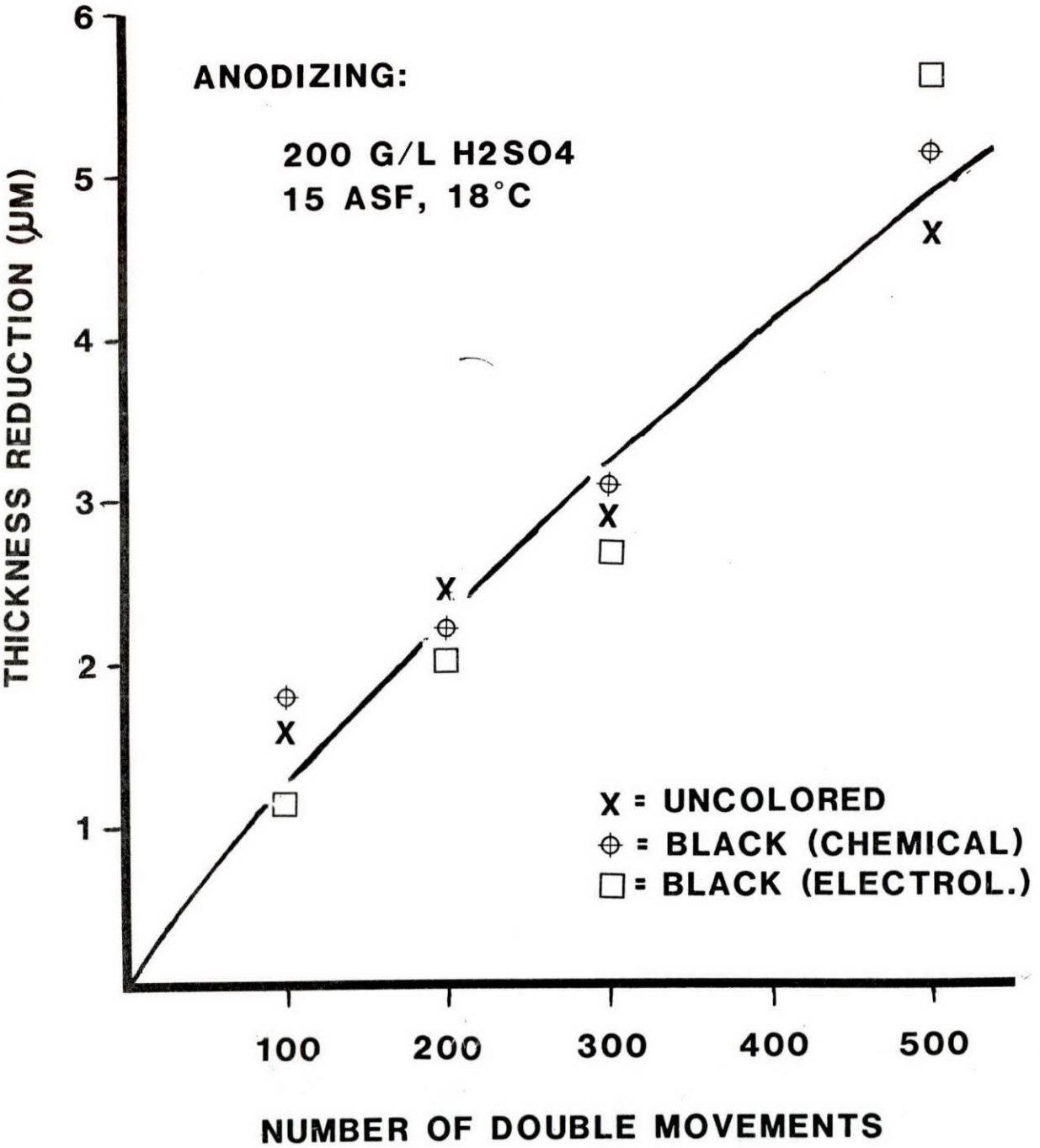

FIG 8. INFLUENCE OF CHEMICAL AND ELECTROLYTIC COLORING ON ABRASION RESISTANCE

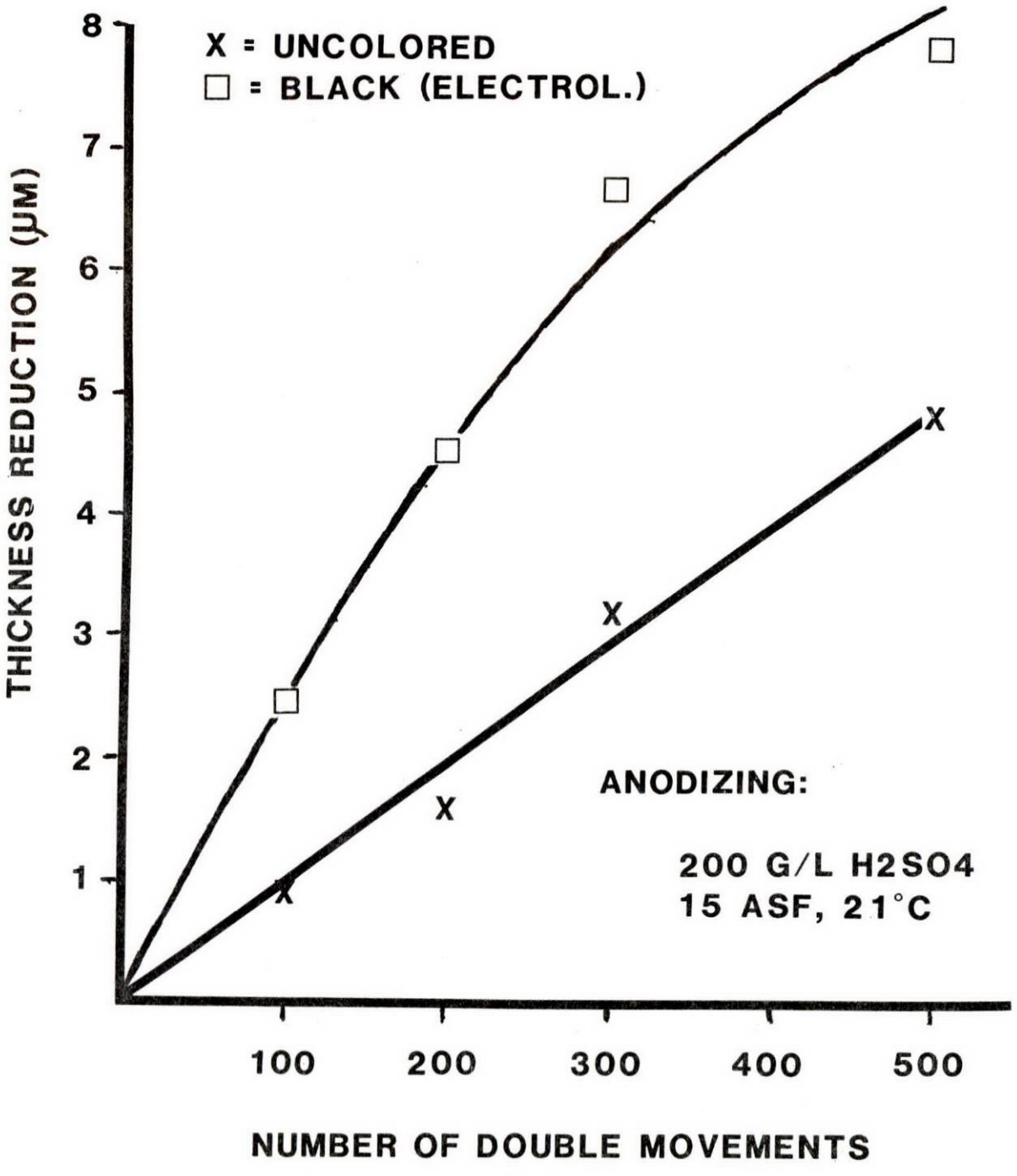

FIG 9. INFLUENCE OF ANODIZING TEMPERATURE ON ABRASION RESISTANCE

TABLE III INFLUENCE OF ANODIZING CONDITIONS ON TIN AND COBALT FINISHES.

Finish	Anodizing Conditions (ASF)	Acid Dissolution Weight Loss Test (Mg/ft^2)	Thickness Reduction Abrasive Wheel Test (um)
Uncolored	12	1.5	3.4
	15	1.3	1.7
Sn^{+2}, Black	12	1.5	3.7
	15	1.3	2.6
Sn^{+2}, Black	12	1.6	10.7
	15	1.4	2.7
Co^{+2} Black	12	1.8	3.0
	15	1.4	1.8

Anodizing Electrolyte: 160 g/L H_2SO_4; 7 g/L AL^{+3}; 19°C

Film Thickness - 25 um

Sn^{+2} Coloring Electrolyte: 10 g/L Sn^{+2}; 20 g/L H_2SO_4

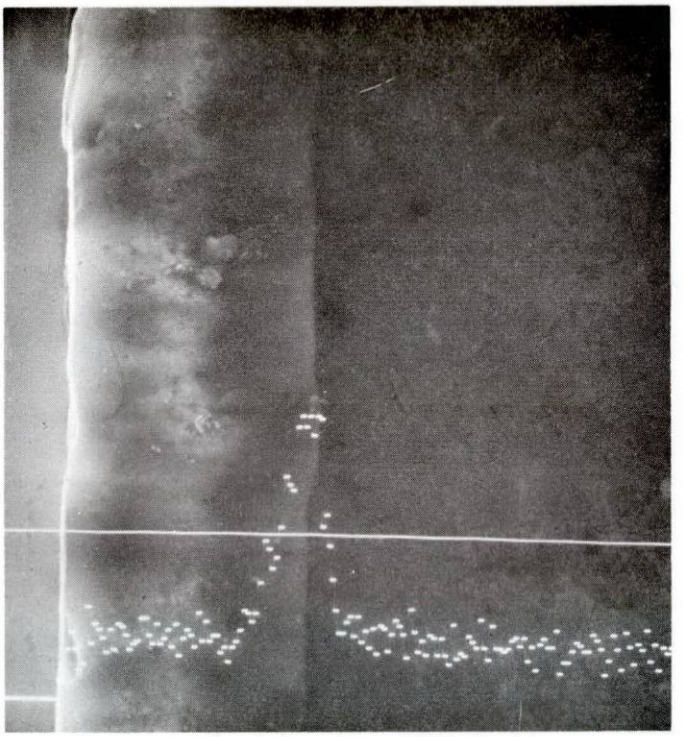

Fig. 10: Tin distribution inside a dark bronze film

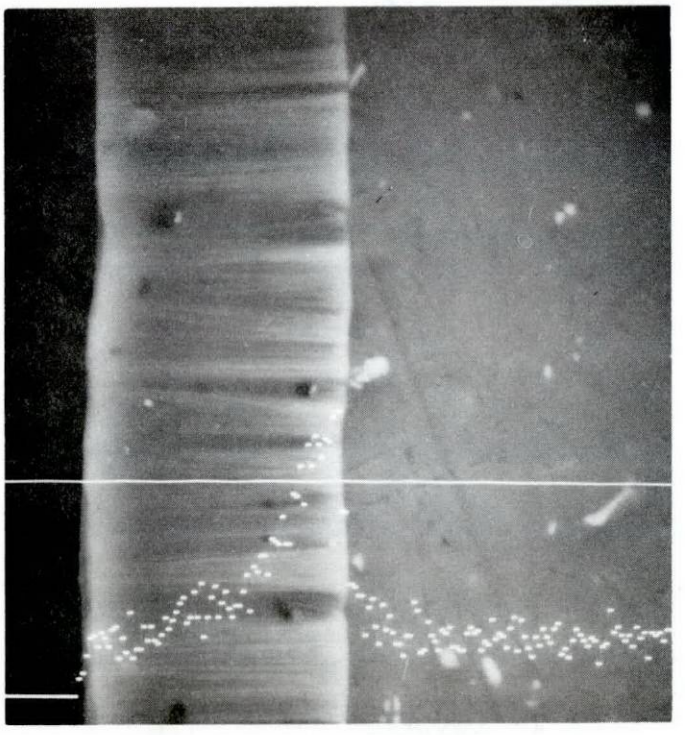

Fig. 11: Tin distribution inside a black film

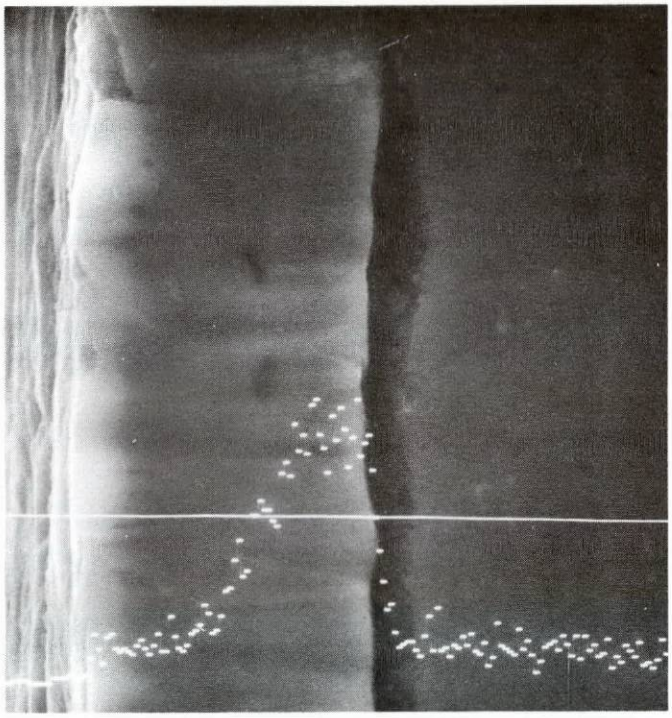

Fig. 12: Cobalt distribution inside a black film

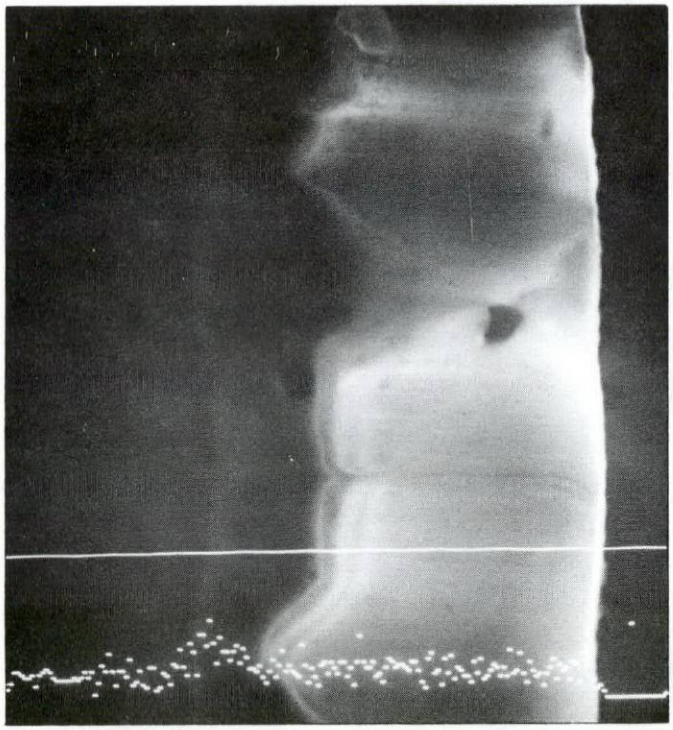

Fig. 13: Nickel distribution inside a dark bronze film
Colored in a mixed Sn/Ni bath at pH = 1

TABLE IV ADMITTANCE VALUES OF DARK TIN FINISHES
AS A FUNCTION OF COLORING TIMES

Color	Coloring Conditions		Admittance Y_{20} (μS)
	Voltage (V)	Time (T)	
Dark Bronze	16	4	23
Black	16	8	77
Black	16	9	100
Black	16	10	130
Black	16	15	200

Anodizing: 200 g/L H_2SO_4; 8 g/L AL^{+3}; 15 ASF; 18°C; 19 μm

Coloring Electrolyte: 10 g/L Sn^{+2}; 20 g/L H_2SO_4; 20 g/L additive

Sealing: 3 min/micron in Deionized water.

J-4

Light Metal Finishing I
Session J

Electro-Coloration of Anodized Aluminum: Evolution of these Processes

Michel LeGrand
Cegedur Pechinery
Montreuil-Juigne, France


AMERICAN ELECTROPLATERS' SOCIETY