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Session A

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Light Metals Finishing
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Color Measurement of Electrolytically Colored Anodized Aluminum

A.W. Brace
Metal Information Services
Stonehouse, Glos., England

Color Measurement of Electrolytically Colored Bronze Anodized Aluminum

A W Brace

Metal Information Services, Stonehouse, Glos., England.

Abstract

The paper initially discusses color theory and the response of the eye to color. Results are then given for color measurements made with three different instruments on specimens of electrolytically colored (2-step) bronze finishes on anodized aluminum, produced in industrial anodizing plants. Three proprietary processes were used - two based on tin electrolytes and the third employing cobalt salts. One of these instruments was considered superior to the others and was used to record color limits for standard shades, to investigate the effect of etching and to resolve color matching disputes.

Introduction

The use of color in architectural anodizing first became commercially significant in the 1950's, which saw the introduction of integral coloring processes towards the end of the decade. During the next 20 years these processes were widely used, such that toward the end of that period they had largely replaced the adsorbtion dyeing which had previously dominated the market, particularly for the production of gold or bronze shades and black. For past seven years has seen integral coloring largely superseded by electrolytic coloring processes (often referred to as '2-step').

Some years ago Gardam published a paper [1] in which he posed the question "Why do we need to measure color ?" - to which he gave the following answers:

1. Standard colors arrived at visually are liable to show color drift, i.e. samples produced over a period to match original standards do not always reproduce the original shade and the color drifts away if the matching is purely visual.

2. Color measurement show up process factors which affect the color.

3. The need to resolve contractual disputes when work from an anodizer is rejected by a customer for not being within color limits.

Gardam used a reflectivity attachment on a spectrophotometer in conjunction with a 30-ordinate method [2] to obtain values which could be plotted on the color triangle using the C.I.E. method of measuring color [3]. This involves 30 separate measurements which have then to be integrated with the help of an electronic calculator or computer. Although the accuracy of the method is high, it is not a practical method for routine use in an anodizing shop.

Over subsequent years there has been a continuing need to find a technique of color measurement which could be used for routine color checking by anodizers to obtain good color matching, as well as to resolve dispute situations. The paper that follows represents work carried out by the author in an attempt to meet these objectives, as well as trying to keep the cost of such equipment below £2,500 (US$ 5,000).

Factors affecting the Perception of Color

The response of the human eye to color depends upon the subjective response of any individual to the light reflected from the surface being viewed. An image is received by the retina of the eye, which transmits a signal to the brain. The interpretation of this signal is affected by the ability of each individual to perceive color, but the ability of the individual to perceive small differences in color varies widely. According to Wright [4], some 8.1% of the male population, but less than 0.5% of the female population, have inherent color vision deficiencies. These deficiencies are less in young men but become higher with age. Whilst color (like beauty) may be in the eye of the beholder, there is a high probability that no two beholders will see the same color.

Color Theory

According to Maxwell's theory, any visible color is made up from three primary colors - red, green and blue, plus brightness this latter can be regarded as equivalent to adding various amounts of white to black. This also implies that white contains equal amounts of these three primary colors, whilst black is the absence of color. Any color can be expresses numerically in terms of the proportion of these primary colours present, plus what is known as the "Luminance factor". This can be considered as representing the level of brightness of the color, in that a theoretical black has no luminance and hence no color, whilst the maximum luminance theoretically possible for any primary color is 100%. If these primary colours are mixed in equal amounts the result is white.

On the basis of this theory it should be possible to define any color by the amount of the three primary primary colors present, plotted on an equilateral triangle whose vertices are R (red), G (green) and B (blue), which is known as the Color Triangle (Fig. 1). However, the colors seen by the human eye do not correspond to this theory, since only those colors bounded by the line BR and the curve RB can be seen by the human eye. In other words, an observed color has to be specified as if it lies within a triangle whose vertices are a red that is redder than the deepest red that can be seen by the human eye, and similarly for green and blue.

The most accurate way of measuring the color of a material is to obtain reflectance readings at 100 Å intervals over the range 4000 Å to 7000 Å. The procedure for converting these readings into the equivalent of the three primary colors, whose wavelengths are taken as 7000 Å for red (X), 5461 Å for green (Y) and 4358 Å for blue (Z), are given in reference. [3]. However, the color can only be fully specified if its brightness (luminance) is also measured, since this has a significant effect of the color perceived by the eye.

The values so obtained are converted to C.I.E. values, which are referred to as x, y, and z values, although once the x and y values have been obtained there is no need to calculate the z values. In fact, for the Color Triangle, any two values automatically defines the third. The conversion of the X, Y and Z values to x, y and z values is obtained as follows:

$$x = X/(X + Y + Z) \qquad y = Y/(X + Y + Z) \qquad z = Z/(X + Y + Z)$$

The values X, Y and Z are the reflectance values obtained either from the conversion of spectrophotometer readings to primary color values, as described above, or from reflectance values obtained using red (X), green (G) and blue (B) filters.

The luminance R = the reflectance value (%) obtained through the green filter.

Low Cost Instruments for Color Measurement

After a survey of low cost instruments available in the United Kingdom for color measurement, it was decided to investigate the three instruments described below:

The Lovibond Flexible Optic Tintometer Mk 3 *

This instrument (Fig. 2) directs a beam of light via a flexible glass fibre optical leads on to the surface to be tested. Normally the transmitted light is directed on to the surface at 45° and the light reflected at 90° is received by a fibre optic receptor, whose end is parallel to the surface being measured. This feeds back the light received to the measuring system in the instrument. It is possible to reverse the leads so that the incident beam is at 90° and the reflected light is then received at 45°.

In the instrument itself a field is seen in the eyepiece which is split into two halves. The left hand portion consists of light reflected from the specimen into the eyepiece and the right hand portion consists of light which is transmitted through colored glass filters. The color can be matched by putting a succession of filters into place and adjusting the brightness until a match is obtained. This requires some experience and an operator with good color perception. The results obtained can remain as Lovibond units, as shown on the dials on the instrument, or they can be converted by a nomogram into C.I.E. values. However, where this instrument is in routine use this latter conversion requires the data to be handled using a micro-computer program which the manufacturers will supply.

Tri-Stimulus Reflectometers

Basic these instruments employ color filters which allow a band of light to be transmitted whose peak value and spread are known. Normally, these will have peak transmission values near the wavelength which corresponds to the red, green and blue primary colors which are used to obtain C.I.E. values. Two instruments were investigated: (1) the Sheen Miniature Colorimeter ** and (2) Diffusion Systems Reflectance Spectrophotometer Mk.III - Model II ***. The peak values of the filters used in these instruments is as follows:

Instrument	*X (Red)*	*Y (Green)*	*Z (Blue)*
Sheen Instruments Ltd	6600Å	5200Å	4800Å
Diffusion Systems Ltd	6300Å	5300Å	4300Å

The two instruments differ in detail, since the filters of the Diffusion Systems instrument cover a greater span of wavelength and the Z (Blue) filter is closer to the specified wavelength of the C.I.E. system than that of the Sheen instrument. Further, the Sheen instrument uses a 45° reflectance head (Fig. 3), whilst that of Diffusion Systems is a 90° head (Fig. 4).

With both of these instruments there is a set-up procedure to standardize the instrument readings for each of the three filters. The results are initially recorded as reflectance values and then converted into C.I.E. values using the formulae given above. It must be appreciated that it is possible for tri-stimulus reflectometers to give identical C.I.E. values on specimens that may exhibit different spectrophotometric curves. This can happen with paint pigments, but is less likely to be found on electrolytically colored anodized surfaces. For a given material and process it was considered probable that the readings would reveal small but significant color differences where these exist.

* The Tintometer Limited, Salisbury, SP1 2JY, England. ** Sheen Instruments Limited, Richmond, TW9 2JL, England.
*** Diffusion Systems Limited, London, W7, England.

Experimental

To evaluate these instruments, samples of flat 6063 extrusions were anodized to a thickness of 25μ (1 mil) in production plants which operated three commercial electrolytic coloring processes - 2 of which were based on tin salts but of different composition (identified as "AL" and "MX" respectively and the other ("AN") based on cobalt salts. In each of the plants the specimens were produced to cover the range of bronze shades regarded as standard by the plants concerned. Some black samples were also prepared. Although specific anodizing and coloring conditions were not disclosed, the sulphuric acid electrolyte concentration was understood to have been in the range of 160-190 g/l and the temperature within the range 15 - 20 °C (60 - 68°F, with a current density of 1.7 A/dm^2. The coloring processes were operated using suppliers recommendations.

Measurements using the Lovibond Flexible Optic Tintometer Mk.3

A series of measurements were made on a set of panels produced to a set of internal color standards set by the anodizers operating the various proprietary processes. In the first of these measurements were made on the same series of panels, identified as panels P1 - P5, with the light source from the instrument directed at an angle of 45° to the surface of the specimen and the reflected light measured at 90° to the specimen surface. The results are shown in Table 1. The leads to and from the instrument were then reversed so that the light reaching the panel surface was at 90° and the reflected light was measured at 45°. The effect of these variants on the C.I.E. color values obtained are shown in Tables 1 and 2.

Table 1: Lovibond Flexible Optic Tintometer readings on standard colours produced by the "AL" (tin) process - geometry 45°/90°.

Specimen	Instrument Readings			C.I.E. values		
Identification	R	Y	Density	*x*	*y*	R%
P1 T*	0	0.2	0.24	0.314	0.323	57.3
L**	0	0.3	0.31	0.315	0.326	48.7
P3 T	0.9	1.4	0.68	0.341	0.358	18.2
L	0.8	1.3	0.8	0.339	0.348	14.0
P5 T	2.1	1.3	0.80	0.373	0.371	9.5
L	1.9	2.8	0.89	0.368	0.368	7.9
P7 T	2.6	2.7	1.05	0.377	0.365	6.2
L	2.3	2.5	1.20	0.372	0.364	4.6
P9 T	1.3	0.7	1.54	0.334	0.328	2.4
L	1.2	0.6	1.70	0.331	0.325	1.7

* T = transverse direction ** L = longitudinal direction

It was found that the latter arrangement reduced the difference between the values obtained in the longitudinal (L) and transverse (T) directions. However, it was found that the principal limitation to the instrument was that it required an operator whose eyesight has good color discrimination, since the instrument requires the color in the two halves of the eyepiece of the instrument to be matched visually and then the values on the dials of the instrument read and converted to C.I.E. values. This was considered to be likely to limit the usefulness of the instrument as a routine color measuring device, so that further work was not carried out with this

instrument. However, the small size of the measuring head was an advantage when carrying out measurements on extrusions with only a limited flat surface.

Table 2: Lovibond Flexible Optic Tintometer readings on standard colours produced by the "AL" (tin) process - geometry 90°/45°.

Specimen	Instrument Readings			C.I.E. values		
Identification	R	Y	Brightness	*x*	*y*	R%
P1 T*	0	0.4	71	0.317	0.329	55
L**	0	0.4	73	0.317	0.329	49
P3 T	1.1	1.7	86	0.348	0.356	17
L	1.1	1.7	88	0.348	0.356	15
P5 T	2.2	3.3	90	0.380	0.379	9.5
L	2.7	3.3	92	0.380	0.375	8.0
P7 T	2.7	3.3	94	0.386	0.375	6.0
L	2.4	1.3	99	0.375	0.367	5.3
P9 T	1.7	1.3	99	0.348	0.341	2.5
L	1.7	1.1	101	0.345	0.336	2.0

* T = transverse direction ** L = longitudinal direction

Tests with the Sheen Miniature Colorimeter

This instrument consists of a measuring head containing a photo-electric cell and a holder, within which filter wheels could be rotated. Light from a tungsten filament lamp is directed at 45° through the color filters on to the specimen surface. The reflected light is measured by a photocell in a measuring head also at 45° to the horizontal, so that the angle between the incident and reflected light was 90°. The aperture in contact with the specimen is approximately 35 x 25 mm. The light source used corresponds to C.I.E. Illuminant A, which approximates to a north light and is slightly yellower than Illuminant C, which is the normal illuminant for very precise measurement of C.I.E. values. Readings were taken in turn with the X, Y and X filters in position. In each case the instrument was standardized to give a 100 reading on the galvanometer, using a magnesium carbonate block as standard.

Table 3: Reflectivity and C.I.E. color readings with the Sheen Colorimeter of panels electrolytically colored sheet specimens by the "MX" (tin) process

Color ref.	X%	*x*	Y%	*y*	Z%	*z*
MX1	32.1	0.349	31.2	0.339	28.7	0.312
MX2	22.9	0.363	21.8	0.346	18.3	0.290
MX3	15.6	0.374	14.7	0.352	11.4	0.274
MX4	7.0	0.354	7.4	0.374	5.4	0.272
MX5	2.4	0.276	3.9	0.448	2.4	0.276
MX6*	0.4	0.085	2.9	0.617	1.4	0.298

* Black

Measurements were made on extrusions colored two of the proprietary process and are reported in Tables 3 and 4. These results would appear to indicate that the specimens produced by "MX" process (Table 3) are broadly consistent with increasing depth of shade, but with a tendency for the MX5 sample to be slightly greener, whilst MX6 is effectively black.

It is useful to remember, when considering the values reported in Tables 3 and 4 that the value Y% is that obtained using the Y (green) filter and approximates to the average eye response, the value recorded being that of the "brightness" or "reflectivity" of the surface. It can be seen that these values are very low for the darker bronze and black shades.

The results obtained on the "AN" series (Table 4) show rather significant differences in the readings obtained in the longitudinal and transverse directions. The author considers that these are not surprising in view of the geometry of the measuring instrument, but are too great for the equipment to be considered satisfactory for routine use.

Table 4: Reflectivity and C.I.E. color readings on extrusions with the Sheen Colorimeter on extruded sections electrolytically colored by the "AN" (cobalt) process.

	Longitudinal						Transverse					
Color ref.	X%	*x*	Y%	*y*	Z%	*z*	X%	*x*	Y%	*y*	Z%	*z*
A541	55.5	.414	44.5	.332	34.1	.254	46.7	.371	37.7	.300	41.4	.329
A543	40.1	.453	28.6	.323	19.8	.223	33.1	.407	24.4	.300	23.9	.294
A545	18.6	.522	10.9	.306	6.1	.171	14.5	.457	10.0	.315	7.2	.227
A547	4.0	.526	3.2	.421	0.4	.053	3.0	.454	2.8	.424	0.8	.121
A549	1.8	.375	2.7	.562	0.3	.062	1.3	.382	1.4	.412	0.7	.206

A practical problem found when using this instrument was that the large measuring aperture of the instrument tended to let in light unless particular care was taken to exclude it, especially is the extruded surface was not quite flat. It also required a flat surface of greater than 25mm (1 inch) for a measurement to be made.

Measurements made with Diffusion Systems Ltd. Reflectometer Mark II - Model 2

This instrument is based on a reflectivity head developed for measuring the reflectivity of gloss paints, but this version has a color filter wheel inserted between the light source and the specimen being measured. However, the arrangement is such that the light from the tungsten bulb is directed to and reflected from the surface at an angle close to 90°. An annular photocell measures the light reflected from the specimen surface after it has passed through the required filter. A rotatable wheel contains three C.I.E. filters which are inserted between the beam of light from the lamp and the specimen. The output from the photocell is fed into a galvanometer, which is standardized against a magnesium carbonate block. To correct for equal energy response, the X filter should give a reading of 100, the Y filter 90.8 and the Z filter a value of 32.3.

Measurements were made initially on the "MX" series of specimens and as these seemed promising the "AL" and "AN" series were also measured. The results obtained are summarized as plots on the C.I.E. color triangle (Figs. 5, 6 and 7). These results are interesting, in that although the color range and hue observed seemed similar for the three processes, each had a different range of C.I.E. values. The "AL" series give the classic characteristic of lying on a straight line, thus showing a simple increase in depth of hue. The "MX" series show a much closer bunching of values, but again they lie on a straight line.

The results obtained from the "AN" series does not appear to conform to the expected relationship, in that the values for the 543, 545 and 547 specimens tend to increasing redness, but the 547 and 549 specimens have moved towards the blue-purple. This set of measurements has not been repeated on a second series of specimens similarly prepared, so it it not possible to state whether this behaviour is typical of the process.

Since the results from the Diffusion Systems instrument appeared to be the most promising, this was used exclusively for the measurements reported below.

Effect of Etching

It is well known that the luminance (reflectivity) of the specimen surface affects the color seen by an observer. Since etching is generally employed as a pretreatment prior to anodizing, it was decided to measure the effect of etching time on reflectivity and C.I.E. values. A set of small flat extrusions in 6063 alloy were etched in a proprietary caustic-gluconate etchant of 70 g/l concentration and operated at 60°C. for times up to 20 minutes. The effect of etching time on reflectivity for specimens anodized only is shown in Fig. 8, whilst its effect on C.I.E. values for specimens etched at the same time and electrolytically colored by the "MX" process to give a medium bronze shade (MX3) is shown in Table 5.

It can be seen that the effect of etching time is particularly critical for up to 12 minutes etching time, so that for good color matching long etching times seem essential.

Table 5: Reflectivity and C.I.E. values for samples etched for varying times and anodized only using the same conditions as for the electrolytic (tin) MX2 colored extrusions measured with the Diffusion Systems Reflectometer

Etching time (mins)	X%	*x*	Y%	*y*	Z%	*z*
0	31.6	0.454	29.2	0.420	8.8	0.126
4	30.0	0.452	27.9	0.421	8.4	0.127
8	28.7	0.453	26.5	0.419	8.1	0.128
12	26.9	0.454	26.2	0.423	7.6	0.126
16	27.5	0.455	25.6	0.424	7.4	0.121
20	27.3	0.454	25.5	0.425	7.3	0.120

Checking Color Drift on Standard Color Samples:

Most architectural anodizers produce a set of color standards for customers to use as reference samples. These are usually matched against standard samples retained in the laboratory or quality manager's office. When a stock of samples is at an end, new ones are prepared by a visual match against the originals. Gardam[1] has previously demonstrated that 'color drift can occur from such a procedure, as a result of very small differences in match. This is often made worse by the fact that original samples can be lost and the match is not against the original standards.

To check the possibility that this was happening two sets of standard colors were checked, the first being ones prepared nearly two years after the original ones. The results are shown in Table 6. It can be seen that although the reflectivity values are reasonably close, there is a perceptible difference in instrumental values, particularly the *X* values, so that color drift cannot be ignored in practice.

Table 6: Reflectivity and C.I.E. values - measured by the Diffusion Systems Reflectometer for two sets of standard samples produced by the "AL" (tin) process after a time interval.

	First set					Later set			
Color ref.	X%	*x*	Y%	*y*	Z%	*z*	X%	Y%	Z%
AL1	63.9	0.451	57.4	0.405	20.3	0.143	64.4	58.2	19.5
AL3	27.4	0.457	25.1	0.418	7.5	0.125	29.0	25.4	7.3
AL5	11.5	0.422	11.2	0.431	3.3	0.127	12.8	11.7	3.2
AL7	6.4	0.386	7.6	0.458	2.6	0.157	8.6	7.5	2.5
AL9	2.3	0.237	5.1	0.526	2.3	0.237	4.1	4.4	2.3

Establishing Color Limits:

For practical purposes the C.I.E. values can be ignored once they have been recorded for the color range in use. For routine quality control purposes the *X, Y and Z* values are all that are needed for test purposes.

Samples were obtained of color samples offered showing the top and bottom limits within which the color would be produced for AN 547 and AN 549. The following were the results obtained:

Table 7: Reflectivity and C.I.E. values - measured by the Diffusion Systems Reflectometer for top and bottom limits of AN 547 and AN 549 standard color.

Color reference	X %	*x*	Y%	*y*	Z%	*z*
AN 547 - top limit	7.5	0.412	7.8	0.429	2.9	0.159
AN 547 - bottom limit	3.4	0.333	4.6	0.451	2.2	0.216
AN 549 - top limit	1.0	0.164	3.0	0.492	2.1	0.344
AN 549 - bottom limit	0.5	0.098	2.6	0.510	2.0	0.392

These colors are the two darkest bronze shades produced, so that the reflectivity readings are low and the most difficult to measure. However, it is considered that these values show that it can be used to carry out control tests on color matching.

Color Measurements for Referee Purposes

Having established these figures the author was called on to carry out referee testing in a dispute involving extrusions produced to the AN 547 color. Table 8 shows the results obtained:

It can be seen that the work rejected gave values which lie outside the reference sample limits. The instrument thus confirmed the inspector's visual inspection, although there were about 2% of the lengths tested which had been rejected that were just within limits. Since carrying out this initial work the author has used this instrument on a number of occasions to resolve disputes on color matching and has found it to be an acceptable instrument for this purpose.

Table 8: Use of Diffusion Systems Reflectometer for resolving dispute on color limits on AN 547 (cobalt process) bronze color extrusions.

Color reference	Reflectance %	*x*	*y*	*z*
AN 547 - top limit	7.8	0.412	0.429	0.159
AN 547 - bottom limit	4.6	0.333	0.451	0.216
Work accepted (typical)	6.6	0.389	0.443	0.168
Work rejected (typical)	9.0	0.438	0.448	0.114

The instrument has also been used to resolve disputes over color matching on electrolytically colored bronze anodized finishes obtained using tin electrolytes. Table 9 shows some typical results obtained:

Table 9: Use of Diffusion Systems Reflectometer for resolving dispute on color limits on MX 3 (tin process) bronze color extrusions.

Color reference	Reflectance %	*x*	*y*	*z*
MX 3 - top limit	14.1	0.490	0.370	0.130
MX 3 - bottom limit	12.8	0.517	0.380	0.120
Work accepted (typical)	13.8	0.490	0.370	0.130
Work rejected (typical)	12.1	0.480	0.360	0.140

Here it can be seen that the main reason for lack of color match is the heavier etch which has been given to some of the work produced. This confirms the results reported in the series shown in Table 5.

Discussion

To inspect color anodized aluminum parts for color matching it is useful to have an understanding of the basic theory of color. Apart from an appreciation that any color can be defined as a mixture of the three primary colors, it is also necessary to appreciate that the luminance (reflectivity) of the surface also affects color. In the course of using the Diffusion Systems Ltd. instrument over several years, it has been found that variations in the degree of etch can be a significant contributor to variability in color. This points to the need to institute a routine check on the degree of etch by reflectivity measurements after etching.

It is not intended that the above results should imply that the instrument used is the only one available that will be suitable for checking color match. It was the best available at the time within the price constraints which were imposed. It has proved to be quite a useful instrument for the purpose required. However, there is one inherent problem, in that careful setup and operation of the instrument is required because the reflectivity values which are recorded for the darker bronze shades are very low, so it is essential to recheck all reading to ensure they are repeatable. The author feels that the problem with some of the instruments currently available is not only their cost, but the fact that it requires a skill above and beyond that of the average quality inspector to use them.

It is also necessary to remember that the measurement can only be made on a flat surface, or nearly so. If steps are taken to exclude stray light entering the reflection head, it is not essential for the surface to be absolutely flat. It is also necessary with any instrument to check for directionality effects. The above work has shown that this is affected by the geometry of the measuring head. It would appear that one useful line of development would be to use fibre optic technology to replace the present conventional system.

Acknowledgements

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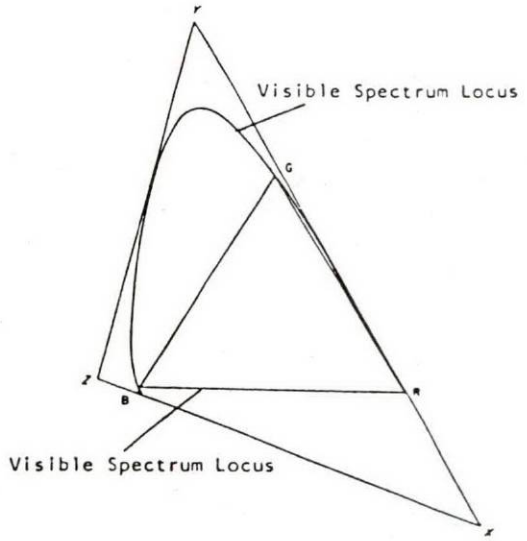


Fig. 1: The Color Triangle showing the Visible Spectrum Locus.

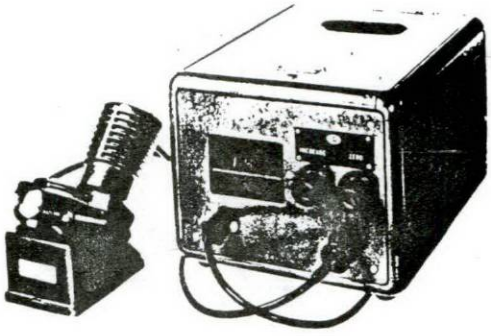


Fig. 2: The Lovibond Flexible Optic Tintometer Mk. 3.

Fig. 3: The Sheen Miniature Colorimeter.



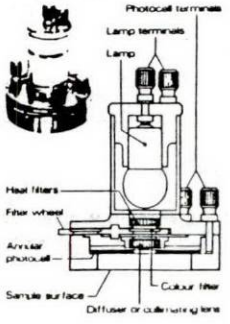




Fig. 4: Diffusion Systems Reflectance Spectrometer Mk. 3, Model II (left) used in conjunction with the DS29 Digital Galvanometer.

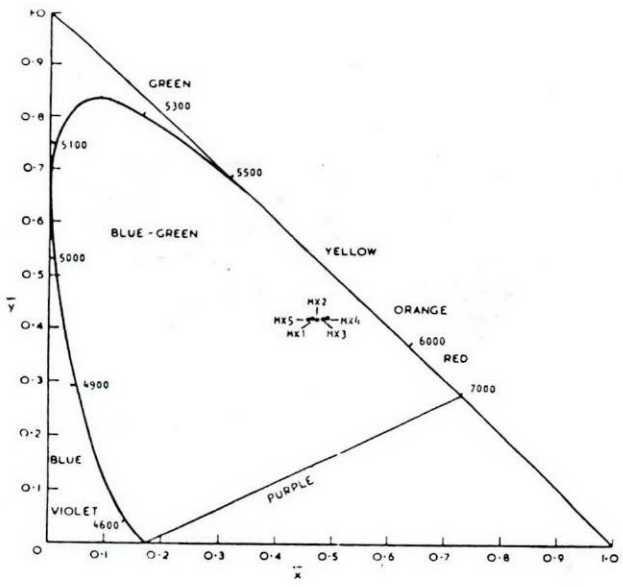


Fig. 5: C.I.E. values for the MX series of standard colors.

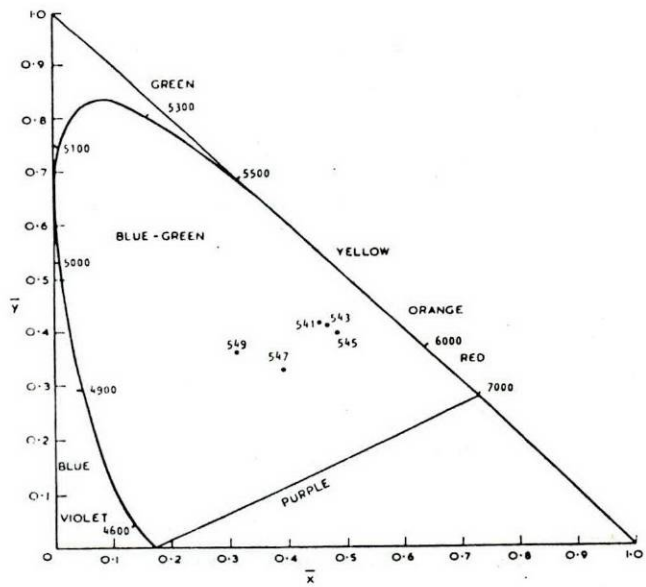


Fig. 6: C.I.E. values for AL series of standard colors.

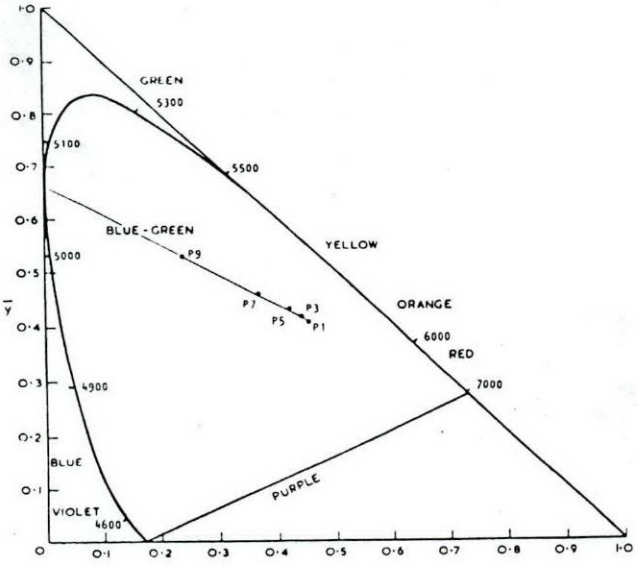


Fig. 7: C.I.E. values for the standard AN series of standard colors.

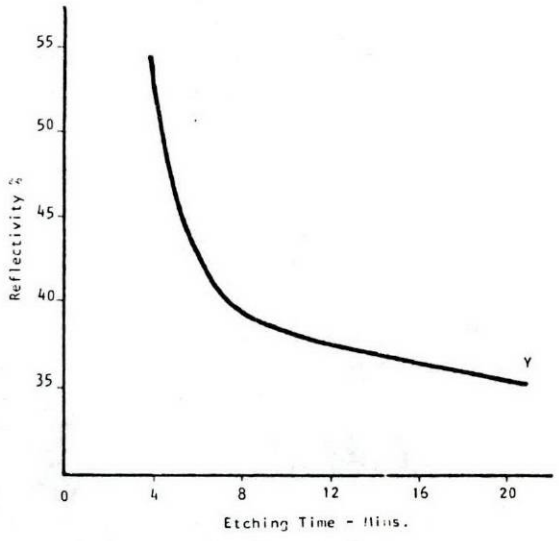


Fig. 8: Effect of etching time in a proprietary caustic gluconate etchant operated at 60°C, on reflectivity at anodized extrusions.

A-2

Light Metals Finishing
Session A

Developments in the Coloring of Anodized Aluminum

Dr. G. Tscheulin
Sandoz Ltd.
Basle, Switzerland

DEVELOPMENTS IN THE COLORING OF ANODIZED ALUMINUM

(Dr. G. Tscheulin, Sandoz Ltd., Basle, Switzerland)

In recent years various systems have been developed for the production of colored anodic coatings on aluminum. The coloring processes now available include the following:

- Inorganic chemical coloring
- Integral or one-step coloring
- Electrolytic or two-step coloring
- Adsorption coloring with organic dyes
- Combination coloring (electrolytic coloring followed by overcoloring with dyes)

The common feature of all five processes is that:

- The coloring system, whether based on organic dye molecules, organic sulfo derivatives or inorganic substances, is either directly bonded to the metal or deposited in the pores of the anodic coating.

- The hard, anodic colored coating is inseparably bonded to the aluminum. This is quite different from other coloring methods such as color coating.

. The colored anodic coatings are characterized by very good resistance to fading and corrosion.

. The metallic character of the aluminum is retained after the coloring process.

In my talk today, I will concentrate on two processes, adsorption coloring with organic dyes[1] and combination coloring[2].

Anodizing

In the electrolytic oxidizing process, it is known that:

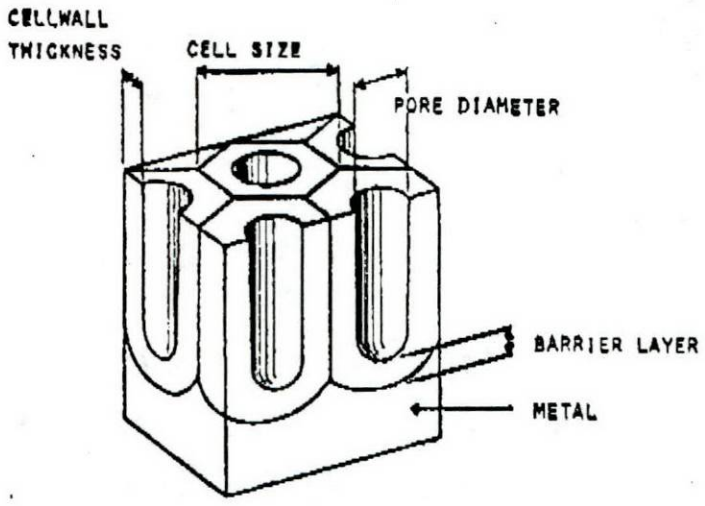
. First a very thin (< 1 um), nonconductive coating (barrier layer) is formed consisting of amorphous or microcrystalline aluminum oxide.

. After the barrier layer has been formed, the anodic coating continues to grow. The coating always grows from the metal outwards,

(1) SANODAL®: Trademark of Sandoz Ltd., Basle Switzerland

(2) SANDALOR®: Trademark of Interoxyd AG, Altenrhein, Switzerland

i.e., at the aluminum-aluminum oxide interface. The first layer formed constitutes the outer surface.

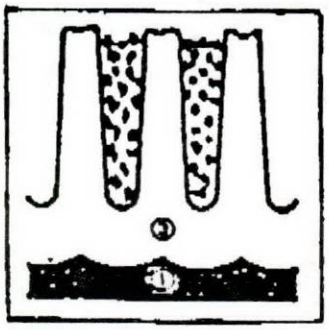


The anodic coating consists of a multitude of hexagonal cells, aligned perpendicular to the metal surface. Each cell contains a pore in it's center. There are about 10^{10} pores per square centimeter of surface, each having a diameter of about 100 Å and a length of several hundred thousand Å.

The pores of these films:

- exhibit large adsorption capacity
- improve hardness and abrasion resistance
- make it possible to color the aluminum with organic and inorganic dyestuffs.

Adsorptive Dyeing Process



Adsorption of organic dyestuff by the pore system by immersion.

When anodized in H_2SO_4, the metal surface becomes positively charged with the bisulfate anion (HSO_4^-) acting as a counter ion. Anionic dyes are mostly used in this dyeing process. Their adsorption is mainly based on the exchange of the bisulfate counter ion with dye anions (e.g. $-SO_3^-$. $-PO_3^{2-}$, $-CO_2^-$) which are covalently bonded to dye molecules.

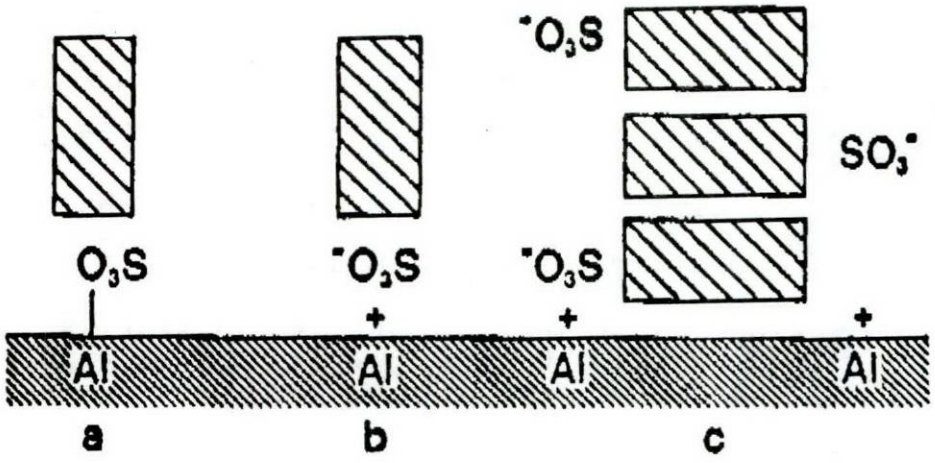
$$Al\ \ HSO_4^- + Na^- O_3S\text{——}F \rightleftharpoons Al\ \ {}^- O_3S\ \ F + NaHSO_4$$

Where F represents the dyestuff molecule.

By increasing the concentration of hydrogen ions in the dyebath, the positive charge of the metal surface is increased, thus improving the capacity for adsorbing acid dyes. The bonding of the ions can be supplemented by additional bonding forces such as Van der Waals and hydrogen bridging. However, these forces

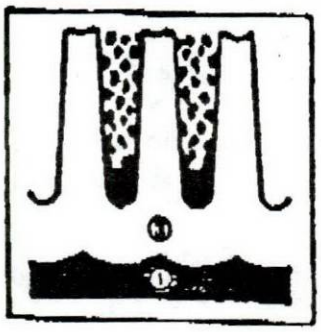
are much less in evidence here than in textile dyeing, probably due to the fact that the surface is very rigid as compared with cellulose and protein substrates.

The dye molecule can be bonded either covalently or ionically by either ion exchange with dye anions or with anionic micelles of dye.



- Diagram of probable nature of dye-alumina bonds with sulphonated dyes on the anodic film: (a) Covalent bond; (b) ion exchange with individual dye anions; (c) ion exchange with anionic micelles of dye.

Combination Process (Overdyeing)



Electrolytic coloring combined with adsorptive dyeing.
This method is a successful, more recent development for the production of weather-fast colorations in spectral colors on anodized aluminum. The method consists in first coloring the anodic coating electrolytically in a light to dark bronze tone and then overdyeing directly with the highly lightfast, organic dyes in the second bath. Two different coloring substances - precipitated metal and the dye molecule - are layered in the anodic coating and do not affect one another. the coatings are as hard as those of electrolytic colorations alone.

With the combination process, the color palette is considerably richer than with any of the other coloring methods listed at the beginning of this talk. With this combined coloring technique, any desired muted shade and depth - from curry yellow to black can be produced.

This combined coloring technique offers a real alternative to color coating since in the combination process there is:

- No chalking of the surface, and
- No separation of the color coat since the hard colored coating is inseparably bonded with the aluminum.

Moreover, the metallic character of the aluminum is retained even after the coloring treatment.

Analytical Methods

To investigate the dyeing kinetics and equilibrium, methods must be available for determining the amount of dye adsorbed on the coating. One possibility is by means of desorption of the dyes from the unsealed anodic coating using tartaric acid + sodium hydroxide solution and then determining the dye content spectrophotometrically.

With an electron microprobe it is possible to determine not only the amount of the dye but also its distribution in the coating. Here heavy metals of metal complexes contained in the dye are determined. The following diagrams show very clearly that the dyes diffuse down into pores.

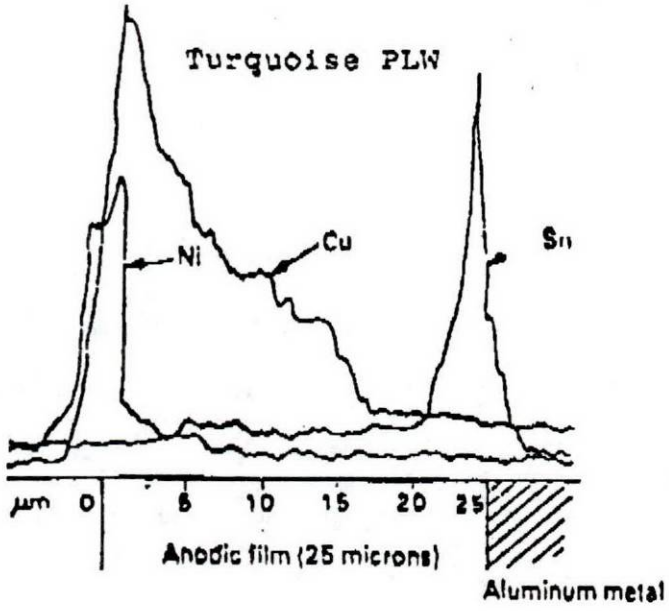
Electron micro-probe

electrolytic bronze (tin)

dyed (copper)

nickel seal (nickel)

metal traces



I would now like to mention a number of test results, which should make clear the quality level of aluminum colorations produced by this process.

Light and Weather Fastnesses

A number of long-term weathering tests were carried out in the

- Xenotest 450
- Weather-Ometer (Atlas 600 WRC)
- Open-air weathering stations in different countries.

The results show that only gold colorations in heavy shades suffered a 30% loss in intensity.

In all the other shades the loss of color intensity is much lower, 10% on average, which can hardly be detected by the eye. The results also make it clear that combination colorations are at least as weatherfast as corresponding organic dyeings.

Sealing Quality and Corrosion

Parallel tests with uncolored aluminum, electrolytically colored aluminum, organic dyeings and combination colorations have shown that all these processes produce practically the same results with respect to corrosion.

CORRELATION OF SEALING QUALITY TEST METHODS

In principle, three different sealing mechanisms are distinguished: Water sealing , sealing with nickel salts and cold sealing . When dyeing with aluminum dyes however, only nickel salt sealing is used since only this type of sealing will prevent bleeding of the dyestuff.

On testing the quality of sealing, three ISO norm tests are now generally employed in industrial practice.

- Weight loss
- Impedance
- Dye stain

The question thus arises whether these 3 tests lead to results which can be correlated, or under what conditions would a different picture of the quality of the seal be obtained. Investigations were carried out with oxide films produced by various methods and sealed:

- with demineralized water

. with the addition of so-called sealing inhibitors (phosphates, silicates, fluorides)
. with the addition of a sealing smut suppressant
. in a typical Ni sealing bath

The results provide the following picture:

1. The three sealing quality tests correlate only in the case of demineralized water. In the presence of a sealing inhibitor however, the three methods lead to quite different assessments of the quality of the sealed test samples.

2. Hot water sealing with and without a suppressant is very heavily influenced by PO_4^{3-} ions.

3. Weight loss values become distinctly poorer in the presence of even small amounts of PO_4^{3-} ions.

4. Impedance tests, on the other hand, still show excellent results even with higher concentrations of PO_4^{3-} ions.

5. The dye stain test correlates with the weight loss test and provides comparable values.

6. Ni sealing reacts much less sensitively to the presence of PO_4^{3-} ions. Even at relatively high phosphate concentrations, good results are still obtained.

These statements apply both to oxide films produced by different processes and to dyed and undyed samples.

A Possible Reaction Pattern

How then can these differences in results be explained?

Sealing inhibitors such as phosphates, e.g. due to their complex-building properties, may accumulate at reactive sites on the aluminum oxide particles on the pore walls, and thus impair hydration. The sealing process is then delayed or even rendered impossible. The depth of penetration however remains limited, since during the pore-filling phase the sealing proceeds rapidly from the metal toward the outside. The pore-filling mass should still be penetrable by water but not inhibitor ions. For this reason, the hydration process is only hindered at the outermost region of the anodic coating, whereas the reaction process in the pore itself can proceed undisturbed.

Based on these statements, the following conclusions can be drawn:

1. In the weight loss test only the state of the outermost region of the oxide film (0.5 um) is assessed, while the layers below it are not affected. Assessment is therefore made of the outer layer only, which explains why PO_4^{3-} ions can cause the values to go so much lower.

2. In the case of the impedance test, the quality of the entire oxide coating is assessed.

   This value depends on the
   - . sealing time
   - . sealing temperature
   - . pH value
   - . film thickness,

   which clearly shows that "weak spots" in the outermost layer of the film do not weigh so heavily in the values obtained.

3. In the case of the dye stain test, the quality of the outermost layer is assessed, in a similar manner to that of the weight loss test. In the dye stain test, the sealed oxide film is pretreated with an acid, after which a drop of dye solution is place on the surface, and in this manner the adsorptivity of the coating is determined. Depending

on the quality of the sealing, greater or lesser staining of the surface occurs. It is therefore understandable that the results of the dye stain and weight loss test are roughly parallel.

When sealing is carried out with nickel acetate, nickel hydroxide precipitates in the outermost region of the pores of the coating immediately after the sealing process begins and this seals the pores very rapidly. In this manner the diffusion of dissolved substances such as PO_4^{3-} ions into the coatings is suppressed. Trials have shown that at boiling temperature, the nickel hydroxide deposit into the pores is already complete after 1 minute. With longer sealing there is no further uptake of nickel hydroxide.

Conclusion

If the results of only one test are considered, the sealing quality of a production sample may not always be correctly assessed. A much more realistic picture of the actual sealing quality is given by the combined results of the three methods discussed.

COLD SEALING

Cold sealing or impregnation processes are all based on solutions of nickel salts, most commonly nickel fluorides, and in some cases using alcohol solutions to facilitate the deposition of the nickel as its hydroxide. The treatment temperatures are from 25 - 35°C and the treatment times range up to 20 min. Investigations permit the supposition that nickel hydroxide is the principal pore-filler and the aluminum fluoride complexes are formed.

Cold Sealing Quality

Various cold sealing products were compared with conventional nickel hot water sealing in terms of the aforementioned three ISO norm tests. Light fastness and corrosion (Cass and Kesternich) tests were also performed.

Both natural-coloured aluminum as well as coatings electrolytically bronze-coloured and dyed with organic dyes were investigated.

The conclusions to be drawn from these comparative tests on cold-sealed products are as follows:

1. Accelerated laboratory tests indicate that impregnation processes made shortly after treatment lead to high, unacceptable apparent impedance measurements. These values, however, are found to become acceptable with time.

2. The weight loss values are for the most part already acceptable at the beginning, but improve appreciably with time.

3. The stain test shows no difference between impregnation and conventional sealing.

4. The Kesternich test leads in certain cases to corrosion.

5. In the salt spray tests, the impregnated specimens show more traces of corrosion than with conventionally sealed ones. The differences are not great.

6. After heat treatment (70°C for 3 h), very clear evidence of crazing of the oxide occurs. Test specimens treated in this manner also corrode.

7. A hot water dip at 70°C for 5-10 minutes improves the results decisively.

8. After 3 years outdoor exposure in an industrial atmosphere there is not much difference between hot-sealed and cold-sealed samples.

When the sealing treatment has been carried out to full effectiveness, the aluminum coating or dyeing attains optimum corrosion, light and weather resistance, because the dyes absorbed by the film are sealed into the correct sealing procedure. This is of decisive importance for the quality of the finished aluminum particularly for dyeings on aluminum.

However, here as with all anodized aluminum, smut formation on sealing and on exposure to weather are problems not yet fully solved.

Sealing and Weather Smut

In water sealing, we now know that sealing smut differs from weathering smut, and that the former may play a role in the formation of the latter.

Although the sealing smut problem has been partially resolved with a number of proprietary products, the weathering smut problem has not yet been solved - but is currently undergoing intensive investigation.

May I conclude my talk by showing you some of the colored buildings. Today worldwide, about 700 buildings using organic or combination colored aluminum have been constructed. The oldest among them are now over 17 years old and are in Australia. Their condition is described as very good.

A-3

Light Metals Finishing
Session A

Coil Technology from Japanese Patent

Teruo Mori
Mori Metalfinishing Consultant Office
871-3 Daitoh-Cho, Fujieda, Shizuokaken 426 Japan

COIL TECHNOLOGY FROM JAPANESE PATENT

MORI METALFINISHING CONSULTANT OFFICE
TERUO MORI
871-3 DAITOH-CHO FUJIEDA SHIZUOKAKEN 426 JAPAN

(1) SUMMARY

Plate mass-production is better coil than batch treatment. Coi treatment gives us high productivity and high constant quality. It uses for producing color anodizing plate, presensitized plate, electro plating. Thire proccess usually has three main processes. They are chemical, mechanical and electro chemical process. Most important process is electro chemical process .

This report describes a lot of device points for electro chemical equipment from Japanese patent between 1910 and 1985.

In electro treatmet , there are six type treatment structures.

(2) COIL-TECHNOLOGY FROM JAPANESE PATENT

Electorolyte solution is put through between coil and electrde, and it is started to turn on electorotritic current coil and electrode. In this world, we must study high-speed electroplating for mass production and saving energy for cost down.

If we want much more mass production, we must run coil faster, so we usually face the following subjects.

1) Big current introducing
2) Uniformity of coating weight of width direction

There are strecture and film producing efficiency investigation in the big current introducing, it includes current distribution, electrode structure, pumping system supplement equipment. We have to get uniformed coating film, and saving energy including one-side, local electroplating subject. Fig 1 shows those deatiled subjects.

(3) HISTORY OF CONTINUOUS ELECTORO PLATING TREATMENT ON PATENT

In Germany, it was written on patent 1942 DLS 71895. Fig 2 showed this patent. It is possible to treat coil face to electrode in Fig 2. This structure is very simple water rising room devide into feeding tank and plating tank. And it is useful for them.

UK's first patent about coil treatment is 1936 and Japanese patent is also 1936. Continuous coil treatment become popular in the ninety-forties.

(4) TYPICAL STRUCTURE OF ELEMENT ON PATENT

4, 1) CLASSIFACATION OF TYPICAL STRUCTURE

Fig 3 shows typical coil plating structure. First classificatiuon was devided with typical or suportsystem for coil, Secound classifacation is devided with path pattern.
Third classification is devided with others.

4. 2) (DRUM +CONTACT) STYLE

This structure makes coil run along ronnd of big drum surface. The most bnifit point of this point is that this style can take very easy simple structure. This structure has a good another point to be able to set bearing upper electrolyte solution. So this structure is independent techniqu and corrosion of bearing.

If gas stays under bottom surface long time, it induces rainbow pattern, because plating film is not uniformly produced by gas. So it get bad visual appearance and get no good quality.

Engineer has another reason to select this structure, it is able to get perfect one side plating. This structure is able to reduce 25-30% current compared with flat bed type bath.

Fig 4 shows typical drum-contact structure. Coil(1) comes and dips electrolyte bath along the drum-style roller(2). Electrode(5) is set up against coil(1) after filling electrolyte in the bath. It is turnned on coil(1) and electrode(5).

This Fig 4-1 is standard style process. Round-electrode style Fig4-2, 4-3 has a bigger round electrode square compared with standard style(1).

Electrode has also a function to be bath wall. It is able to move electrolyte quickly. And flow rate is easily controlled with pump-through out. This structure has some quality defect to induce ununiform flow rate and temparature distribution.

Spray style Fig4-3 has a strong point flow rate compared with round electrode style. This structure get good qualities, because coil surface is refreshed with spray. It is not suitable to turn on big current, because it has a small electrode-square.

Fig4-1~4-3 has a common point which is defect feeding system. Direct feeding method (Metal contact) is that Metal/Metal contact resistance is big, so it seem to induce coil-strain, stain, and spark with heat and contact defect. In order to improve those points some time liquid contact (Indirect feeding method) is adapted for coil treatment.

Liquid contact type Fig4-4 has a liquid contact and electrode. It is possible to feed big current but automatically voltage is bigger. This structure has better points not to be defect of metal-metal contact. Fig 4-4 liquid contact decide on bath into 2 room , first room is liquid contact , and last room is plating section. If liquid contact is too small sommtime it is possible to arrenge liquid contact cell serially.

4.3) (DRUM NON-CONTACT) STYLE

Fig 4 group has a significance to ccontact roller and coil. Fig 5 shows drum-noncontact style. In this structure , coil doesn't contact roller. There is a big fixed roller with a lot of holes on surface. Electoryte is sprayed out from the hole and this spray pressure makes narrow distance between roller and coil, this disdance indicates electorolysis distance.

This equipment has non contact system between coil and drum, so there is no scrach. This system has one side perfect plating and high speed flow rate, so it is possible top get bigger current density plating. This equipment is the best methode to get maxium current density compared to other methods. This method has a defect that coil condition on running is vibrated for vertical direction, so hole number, pattern, distribution is studied for coil runing ballance. This method is thought the best plating system, because it's higher flowrate make to get rid of reaction gas easy and get nice surface finishing. Electoro -coil distance is short , so this is useful for saving energy.

4.4) (HPRIZONAL+DIP) STYLE

There is a diffect point to keep electorolyte solution on plating the previous system. We can keep it in a tank with roller for running. This is very useful for plating system. Fig 6 shows those plating equipment.

Fig 6-1 indicates standard style . Help roller makes a coil dip in the tank. There is 2 room deviding by isolated plate , those each has independent electorode and cathode.

Standard style has some defects for plating and otrhefers. There a small leak current anode and cathode , because this srtructure has not enough to isolate. Multi type Fig 6-2 has plural isolate plates, but it is still perfect. This leak is called as short cut current or bipath current.

Fig6-3 perfectly cut off it. Air feeding style is not suitable for bigger current electo plating because coil will get warp with jule heat . Separate type Fig 6-4 cut off leak current perfectly, it auto matically increase voltage. This style eventualy must dip coil surface and back face in electrolyte, so it is very difficult to plate only one side about 30~50% current will reach unexpectedface.

(4. 5) (HORIZON+SPRAY) STYLE

Fig 7 (HORIZON+SPRAY) style has some defect.

1) It is impossible to make a perfect one side plating .
2) It is beggerIRdrop between coil and spray
3) It is diffcult to get quality for wide direction

To get rid of those deffect, coil surface put reaction side, and coilback face put feeding side. This is call verticalcurrent electrolysis This method the most current effective plating method theoritically.

But there are some difficultpoint for adapting plating electolyte and feeding electorolyte. It is leak current causing to contact reaction electrolyte and feeding electorite,

Now we can not get success to separate their electorolyte solution .

We can supply electoro with spray for surface it has a problem spray electorode is has only several metal, so it is not so long life even if it is so expensive.

(4, 6) (HORIZON+FLOW) STYLE

If we dip coil surface and back face, automatically coil both side fase is treated. If we treat only one side fase we only supply electoryte one side face.

Fig 8 show (horizonal + flow) type. Surface electolyte is isolated with in the tank. It always needs to get red of reaction gas immedately, if it appearance becomes rainbow color and get stain.

Bottom electorolyte coil must suport the all wight of electolyte , so it needs to set hight tension handling or back up rolle.

(4, 7) VERTICAL STYLE

Fig 3~8 shows reveal or horizonal but fig 9 show verticalline plating , spray type and dipping type.

Spray type Fig 9-1 is that coil line set vertical direction and put multi spray power sorce contact spray and rolle spraied solution drop for down direction, so it is very easy to change surface solution and it's very effiency to exchange coil, it is possible to operate a small amounts

Fig 9-2 shows vertical line style and it is narrow style, it is easy to plate both side because each sidee has some condition about gas temperature.

We can adapt metal contact or liquid contact for the system in any case. If coil is explored on air, it's easy to appear stain on coil surfase.

5) CONCLUSION

I studied fundimental structure of continuous coil treatment with Japanese patent and others.
Mane subjects of those patent are

1) High current density plating

2) Saving energy plating

They are six type of fundimental structure of continuous coil treatment to get mass production and cost down.

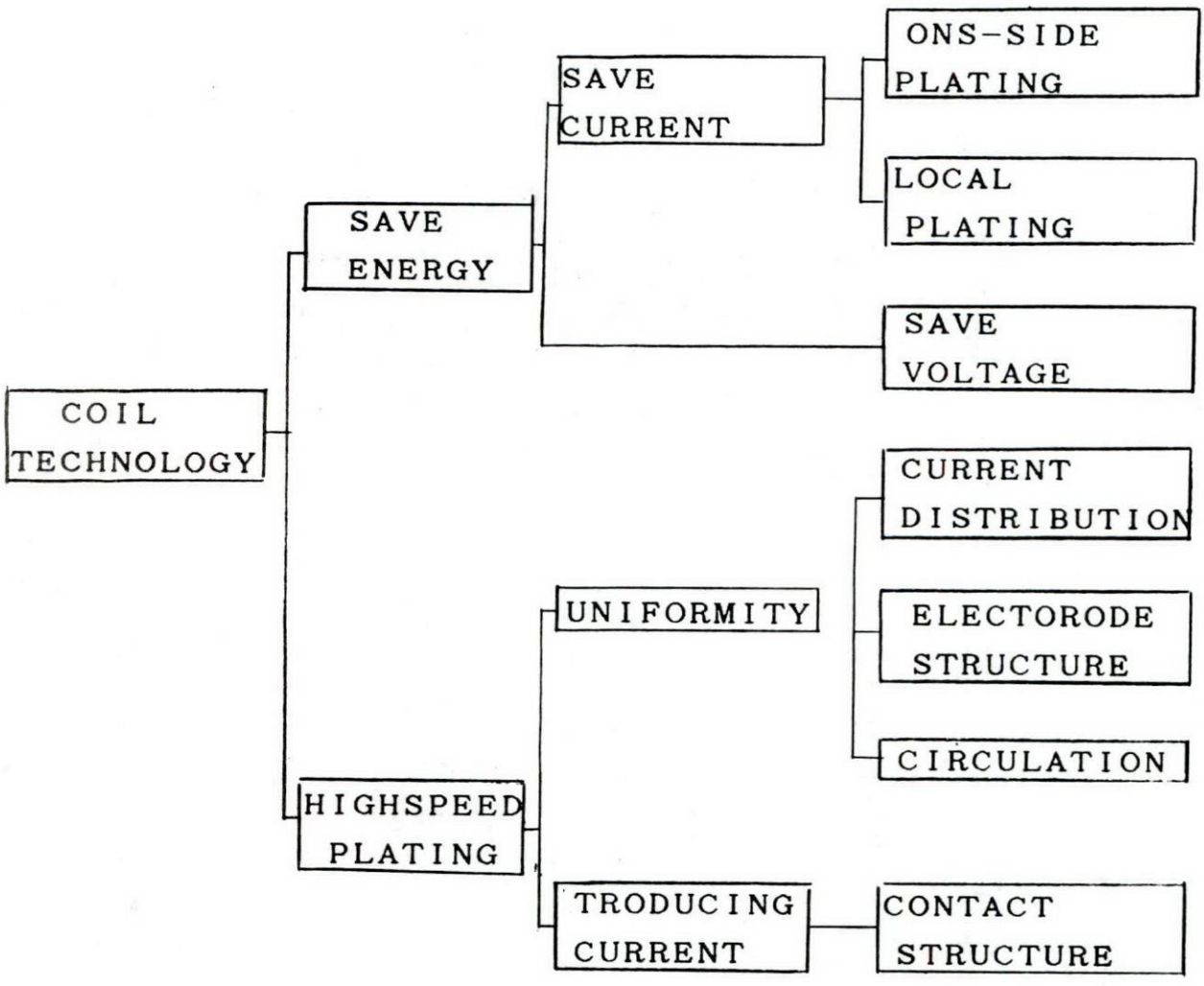
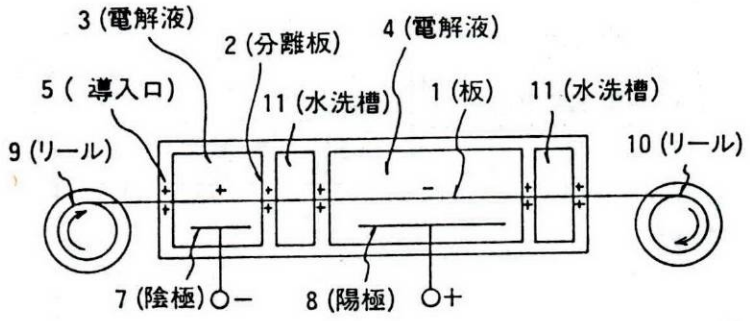


FIG 1 COIL PLATING SUBJECT FROM PATENTS



1	COIL
2	SERARATER
3, 4	ELECTOLYTE
5	INPUT
7	CATHODE
8	ANODE
9, 10	COILER
11	WASHING TANK

FIG 2 DLS 718975 (1942)

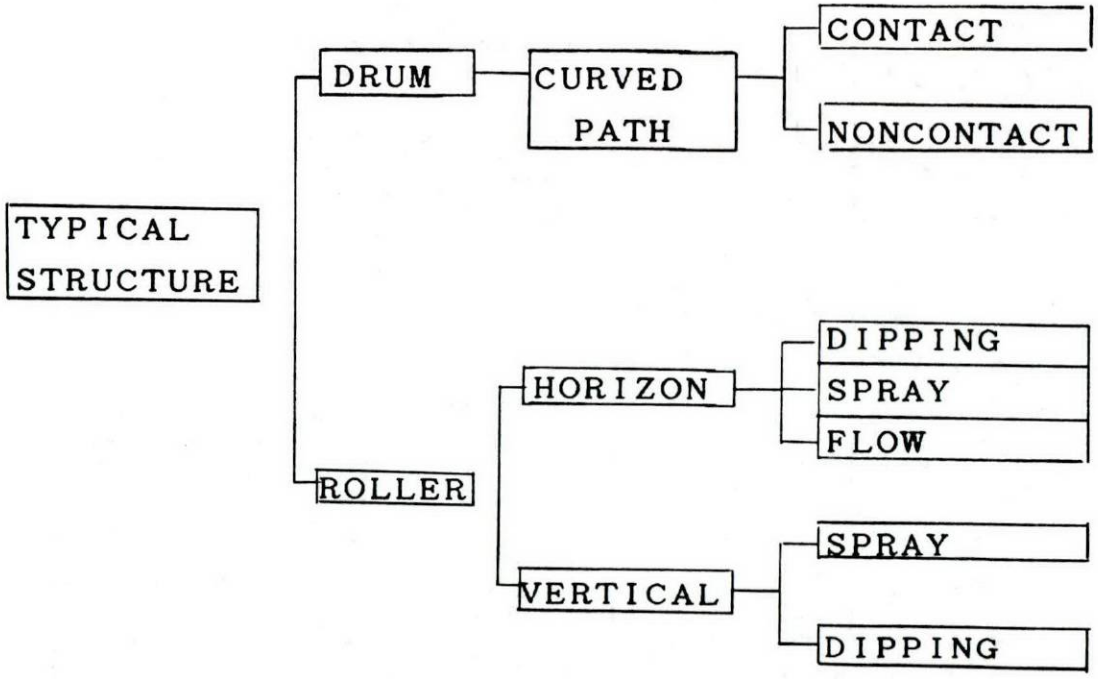
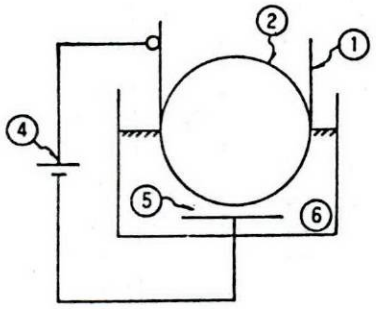
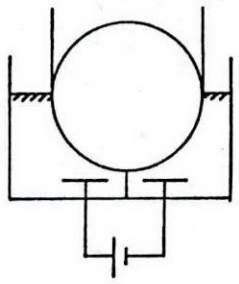


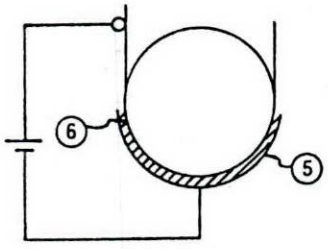
FIG 3 TYPICAL COIL PLATING STRUCTURE



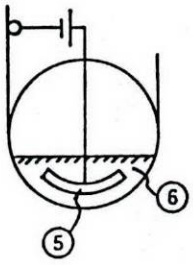
(1) STANDARD



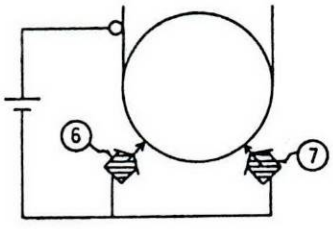
(4) LIQUID



(2) ROUND ELECTORODE



(5) INSIDE REACTION



(3) SPRAY

FIG 4 (DRUM+CONTACT) STYLE

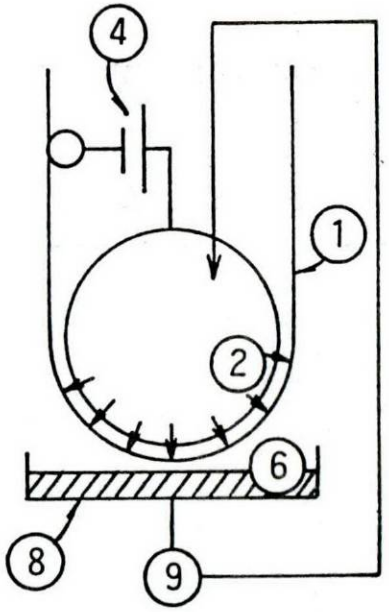


FIG 5 (DRUM+NONCONTACT) STYLE

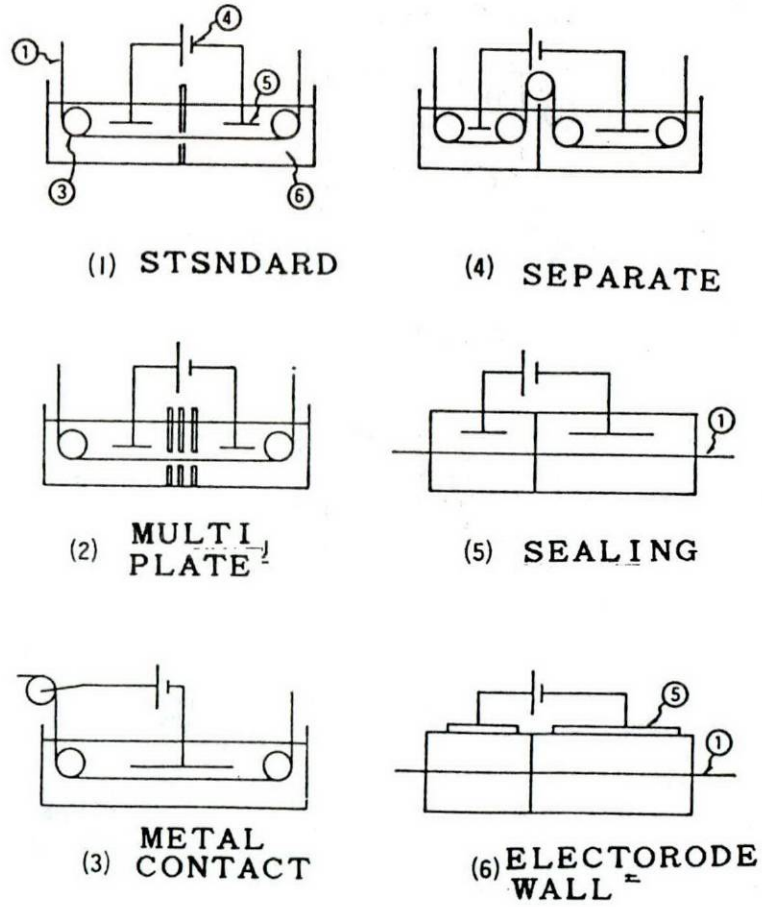


FIG 6 (HORIZON+NONCONTACT) STYLE

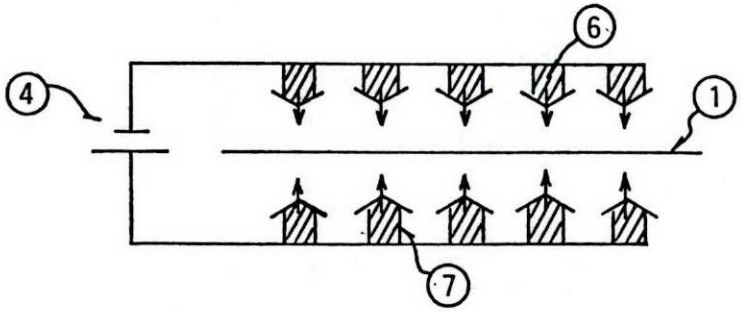


FIG 7 (DIP+SPRAY) STYLE

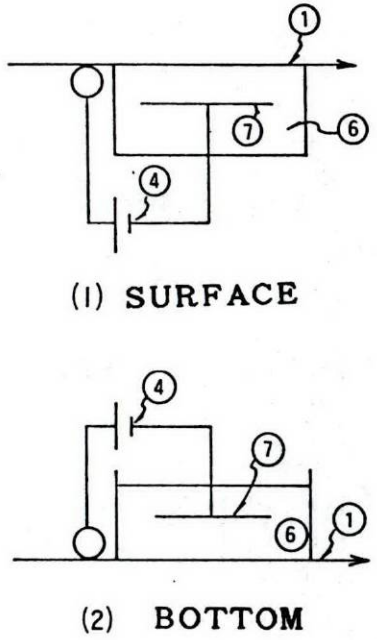
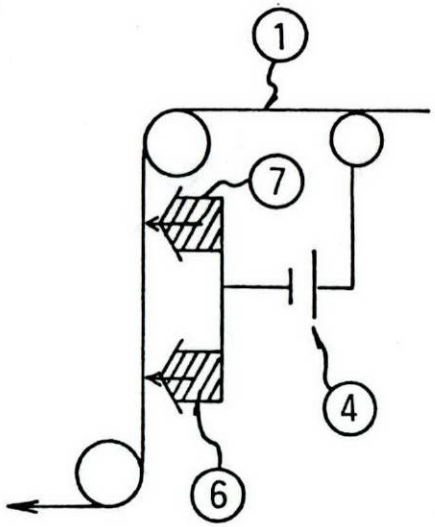
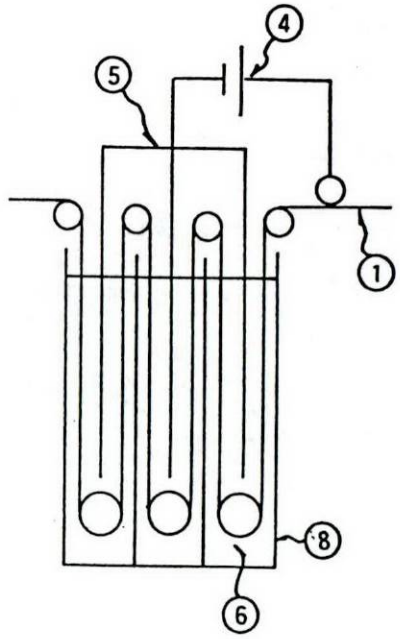


FIG 8 (HORIZON+FLOW) STYLE



SPRAY STYLE



DIPPING STYLE

FIG 9 VERTICAL STYLE

A-4

Light Metals Finishing
Session A

Meeting Military Specifications for Chromate Conversion Coatings on Aluminum

Allan H. Reed
Electrochemicals
751 Elm Street
Youngstown, OH 44502

Meeting Military Specifications For Chromate Conversion Coatings on Aluminum

by
Allan H. Reed
Electrochemicals
751 Elm Street
Youngstown, Ohio 44502

Aluminum and aluminum alloys are widely used in today's diverse economy because of their desirable characteristics of light weight, high strength, low cost, and ease of fabrication. However, since aluminum is attacked by many substances in the environment, some type of corrosion-resistant surface finish is generally required to protect it from corrosion and pitting. In many cases, paint is the most obvious and economical choice of finishes. Paint, however, will not adhere directly to an aluminum surface, even when a primer is used, because of the thin, naturally-occuring oxide which is always present on aluminum.

In order to obtain an adherent coating of paint on aluminum, a chromate conversion coating must first be applied to the surface of the aluminum prior to the application of paint or primer. These conversion coating are the subject of two Military Specifications:

MIL-C-5541C (14 April 1981) gives the requirements for conversion coatings on aluminum alloys and MIL-C-81706 (30 June 1970) covers the chemical materials used to produce the coatings. Both of these specifications describe the performance requirements that the conversion coatings must meet.

For most metal finishers, MIL-C-5541C is the pertinent specification. It describes two classes of coatings.

Class 1A - For maximum protection against corrosion for surfaces to be painted or left unpainted.
Class 3 - For protection against corrosion where low electrical resistance is required.

The only requirement in MIL-C-5541C for the chemical coating is that it be produced from a solution conforming to MIL-C-81706. These requirements are directed specifically toward military applications; however, chromate converstion coatings have many commercial applications and any coating that meets military requirements will certainly provide adequate commercial performance.

The government maintains a Qualified Products List (QPL) for MIL-C-81706 as well as for many other specifications. A QPL lists products that have been tested by the government and have been shown to meet specification requirements. By maintaining such lists, the need for much duplicative testing by government agencies and contractors is eliminated. Thus, the proprietary chemical processes for producing chromate conversion coatings listed on the QPL for MIL-C-81706 have all been shown to produce coatings that meet the requirements of MIL-C-5541C. Therefore, a user can be assured, without further testing, that any product on this list, when properly applied, will produce coatings that meet the requirements of the specification.

Considerable testing is required to qualify a product for inclusion on a QPL. First, a manufacturer must determine by actual tests that the product meets all the requirements of the specification. Second, a report of the test data must be submitted to the government agency responsbile for the specification. (In this case, the Navy Department). Third, the manufacturer provides two samples of material, each sufficient to prepare a 10-gallon bath. Fourth, the government agency uses one sample to prepare panels for testing according to the specification. If the panels pass all tests, the product is placed on the QPL. The second sample of material is used to prepare another set of panels for testing after the material has been stored for a specified period of time to determine its storage stability. All testing is done using 3 inch by 10 inch by 0.032 inch thick aluminum alloy panels.

Description of Coatings

Chromate films on aluminum are generally thought to be a hydrated gel containing aluminum, hexavalent chromium, water, and other film-forming ions from the chromating solution. Chromating solutions, while usually proprietary in nature, contain chromic acid, other compounds whose ions contribute to the structure of the film, and ions to increase the rate of film formation. The chromate film, when first formed, is soft and easily damaged. However, it "cures" in about twenty-four hours. It is important not to heat the coatings to accelerate this "cure" since the structure and corrosion-resistant nature of the film will be destroyed if water is driven off from the gel structure of the film.

The color of chromate conversion coatings on aluminum varies from almost clear to an iridescent yellow or brown depending on the specific chemical nature of the chromating solution and the composition of the particular aluminum alloy. In

general, colored coatings are preferred since their color makes visual inspection for defects easier. Since the films are very thin and somewhat soft, they have only limited abrasion resistance. Normally, they will withstand moderate handling and careful cold-forming operations without significant damage to the films. In some instances, minor scratches in the coating are self-healing because the ions in the gel-like film can react with the exposed aluminum in the presence of moisture to reform the chromate film.

Performance Requirements

The performance requirements to be discussed are those of MIL-C-81706 which all chromating materials must meet in order to be placed on the QPL for this specification.

Materials used to produce Class 1A coatings are evaluated on aluminum alloys 2024-T3 and 7075-T6, while materials used to produce Class 3 coatings are evaluated on aluminum alloy 6061-T6.

The Class 1A coatings produced by these materials must meet the following requirements:

1. **Corrosion Resistance.** Chromated aluminum test panels must show no evidence of corrosion after 336 hours of 5-percent salt spray testing.
2. **Paint Adhesion (knife).** Paint applied over a primer to chromated aluminum test panels must not flake or separate when scored in a cross-hatch pattern.
3. **Paint Adhesion (tape).** Peeling of tape applied to the scored areas of the panels from the previous test must not cause a separation between the primer and the chromate coating or between the chromate coating and the aluminum substrate.
4. **Coating Weight.** The coating weight must be at least 40 milligrams per square foot as determined by weight difference when the coating is stripped in nitric acid.

Class 3 coatings produced by these materials must meet the following requirements:

1. **Corrosion Resistance.** Test panels must show no evidence of corrosion after 168 hours of 5-percent salt spray testing.
2. **Paint Adhesion (knife).** Same as for Class 1A panels.
3. **Paint Adhesion (tape).** Same as for Class 1A panels.
4. **Contact Electrical Resistance.** The contact electrical resistance of the coatings must not be greater than 5,000 microhms per square inch after application nor greater than 10,000 microhms per square inch after exposure to the 168-hour salt spray test.

Evaluation of Test Panels

1. **Corrosion Resistance.** After salt spray, the test panels are examined visually with a naked eye. Bleaching or other changes of the iridescent color of the panels is not cause for rejection as long as there is no evidence of corrosion pits.
2. **Paint Adhesion.** Painted panels are evaluated visually after knife cross-hatching and again after tape is peeled from the scored area. No evidence of flaking or separation beyond the scored areas should be seen.
3. **Coating Weight.** After weighing, the panels are immersed in a freshly-prepared solution of nitric acid at room temperature for 60 seconds. The nitric acid solution is made up of equal parts by volume of concentrated nitric acid and water. The panels are then rinsed, blown dry with clean, oil-free air, and reweighed. The weight of the chromate conversion coating is calculated in milligrams per square foot as

$$\Delta W \times 2.4$$

   where ΔW is the difference between initial and final weights of the panels in milligrams. Table I shows the weight of chromate conversion coatings applied to the three different aluminum alloy test panels. These weights are averages of triplicate determinations. All of the coating weights significantly exceed the minimum of 40 milligrams per square foot specified for Class 1A coatings on 2024-T3 and 7075-T6 alloys. There is no specified minimum weight for Class 3 coatings.
4. **Contact Electrical Resistance.** The electrical resistance of Class 3 panels is measured before and after salt spray testing. Ten measurements are made on each of five panels. The panels are clamped between flat copper electrodes under a pressure of 200 psi. The average contact resistance must not exceed 5,000 microhms per square inch before and 10,000 microhms per square inch after salt spray testing. Individual readings not greater than 20 percent in excess of these maximum values are acceptable as long as the average of all ten measurements does not exceed the maximum values.

Table II shows the averages of ten contact resistance measurements on each of five chromated Class 3 panels before and after salt spray testing for 168 hours. The averages (as well as all of the individual measurements) are well below the specified limits.

Process Description

The key to obtaining an acceptable chromate conversion coating on aluminum is the same as that for obtaining any other satisfactory surface finish: namely, proper surface preparation. The following sequence of steps has been demonstrated to

produce chromate conversion coatings that meet the requirements of both Class 1A and Class 3 coatings. Thorough rinsing must follow each step.

1. **Solvent Clean (Optional).** This step removes loose grease and marking inks.
2. **Soak Clean.** Use a mild alkaline cleaner especially formulated for cleaning aluminum. Such cleaners contain no caustic soda and therefore do not etch aluminum. A typical cleaner is operated at a concentration of 4 to 6 ounces per gallon and a temperature of 140 to 160°F.
3. **Etch (Optional).** An etch prior to chromating is often used to increase paint adhesion. A solution containing 6 ounces per gallon of caustic soda at 160°F can be used to produce a suitable etch. The time required to produce the etch depends on the particular alloy and the degree of etching desired.
4. **Desmut.** Etching of aluminum alloys, particulary those containing high copper concentrations, leaves a loosely-adherent smut on the surface. This smut can be removed in a solution of 50 percent nitric acid or a mixture of 2 to 3 parts concentrated nitric acid to one part 70 percent hydrofluoric acid. These desmutting solutions dissolve the smut and activate the surface by removing any aluminum oxide left on the surface. The best choice of desmutting solution will depend on the particular aluminum alloy being treated.
5. **Chromate.** Most chromating solutions are run at 75 to 85°F and require an immersion time of one to two minutes to produce a satisfactory conversion coating. Specific operating instructions for particular proprietary solutions should be followed carefully. Following chromating, parts should be thoroughly rinsed to remove all traces of the chromating solution. Final rinsing in warm (120- 140°F) water facilitates drying. When air is used to blow the parts dry, only cool (120-125°F) air should be used so that the coating will not be damaged by excess heat.

A bright aluminum pickle process can be used as an alternate to the etch and desmut steps described above. This process, based on sulfuric acid and hydrogen peroxide, will lightly etch, deoxidize, and desmut in one step. This process is usually operated at about 120°F. In addition to shortening the process sequence, it also has the advantage of eliminating the use of the hot caustic solution and the nitric or nitric- hydrofluoric acid solution, all of which are hazardous and expensive to operate.

Chromate conversion coatings offer many advantages in preparing aluminum surfaces for painting. They provide the best known method for obtaining paint adhesion as well as ease and speed of application, a fairly wide range of process parameters, and a coating that can be readily stripped and reapplied if a mistake is made.

TABLE I
WEIGHTS OF CHROMATE CONVERSION COATINGS ON ALUMINUM

ALLOY	WEIGHT, mg/sq.ft.
2024-T3	98.5
7075-T6	118.7
6061-T6	51.7

TABLE II
AVERAGE CONTACT RESISTANCE OF CHROMATED ALUMINUM

	Resistance, Microhms/sq. inch	
Panel Number	Before Salt Spray	After Salt Spray
1	1831	1955
2	2140	2403
3	702	2704
4	988	1915
5	1071	2332
Grand Average	1346	2262

A-5

Light Metals Finishing
Session A

Hard, Thick, Smooth and High Dielectric Strength Anodic Oxide Films

Setsuo Tomita
Tomita Electrochemical Research Laboratories
Koda City 444-01

Sakae Tajima and Shigeyoshi Morisake
Electrochemistry Lab
Tokyo City University and
Environmental and Resources Research Institute (NRI)
Tokyo University of Agriculture
Tokyo

Yoshio Hirayama
Nikkei Giken Research Center
Kambara City 421-32

HARD,THICK,SMOOTH AND HIGH DIELECTRIC STRENGTH ANODIC OXIDE FILMS

Setsuo Tomita(Tomita Electrochemical Research Laboratories,Koda City 444-01)
Sakae Tajima and Shigeyoshi Morisaki(Electrochemistry Lab, Tokyo City Univ. and Environmental and Resorces Research Inst.(NRI), Tokyo University of Agriculture,Tokyo) and
Yoshio Hirayama(Nikkei Giken Research Center, Kambara City 421-32)

Abstract

Hard,thick,lustrous,high dielectric strength and high thermal resistance anodic films on aluminum have been developed from organic acid based electrolytes in rather short time.. Dielectric strength 3000-4000 V(50 micron thick), 5000 V up (100 micron thick), DC (AC gives lower value), Hv 450 up, were attained at 20 ± 1°C , C.D. 2-5 A/dm^2 in 40- 80 min. for nearly all wrought alloys except some cast alloys, 2024 and 7075. Al-Mg(5052) and 3 N Al give excellent results. The films are smooth and crack-free with naked eyes and lustrous. Fewer corner effects are noted by not so strong shocking. Abrasion resistance is generally superior . Further ca. 500 micron(0.5 mm) thick films,still lustrous, reddish brown to brown colored, will be shown together with SEM picture. Detailed data will be given particularly for breakdown voltage. These data are the results from the comparison with the conventional sulfuric acid hard anodizing. The quality may be still improved by further efforts.. For presentation,slides,OHP(SEM and thermal analysis) and real samples will be used.

Introduction

Early in 1904, F.Fischer(5) reported that 300 micron thick anodic oxide film could be formed on Al-tube in 24% sulfuric acid by passing cold water through the tube. A.Miyata(1,2), Th.Rummel(1,2,3,4) ,G.Elssner(1,2,3,4),during 1930-1940, obtained thick films in oxalic or sulfuric acid. However,N.D.Tomashov(7) seems the first who applied these thick films as hard and abrasion resistant films for engineering purposes. Thereafter, practical hard anodizing became popular. The process proposed by Tomashov is briefly outlined as follows:

Electrolyte 200 g/l, 1-3°C.
Voltage 23-100 V, 240 min.
Film thickness 130-170 micron
Porosity 20 % for 1010 Al, 35 % for 2018.

M.M.Lerner of the Sanford Process Corp. in US seems the successor of this tradition. However, as to the high dielectric strength and accordingly high thermal resistant films, the research interest had not been so intensive,it seems. At one time, the breakdown voltage measurement was used as a measure of anodized film thickness. A.Miyata(2) who pioneered in "sealing"(by steam ,5-6 kg/cm^2 in an autoclave) and also first proposed the"barrier + porous" duplex structure, was originally an electric engineer who, of course , had an interest in "breakdown"voltage both in wet and dried states. But it seems,he had more interest in the former,i.e. pure barrier utilization for electrolytic capacitors. The barrier layer grows in,e.g., borate solutions by 10-14 Å/V and the maximum breakdown voltage is ca.700 V(equivalent to ca. 1 micron thick).

For oxalic acid duplex type film, 30 micron, Miyata obtained 10.3 kV/mm(10.3 V/micron), 14,5 kV(14.5 V/micron) for steam-sealed film,by applying AC(50 cycles). Miyata stated that the electric resistance of as-anodized film is nearly equal to the value of the same thickness of "air" and concluded that barrier layer is only playing a rôle of "separator". Since the pure barrier film is so thin that the engineering and mechanical use can not be expected.

Measurement of Breakdown Voltage in Dried States(1,2,3)

In order to determine the electric breakdown voltage,particularly of anodic aluminum oxide films,,there exist the two typical test methods. The one is the "Probe test" which uses graphite or stainless steel rod as counter electrode and the other electrode is,of course, basis aluminum plate. The other method is "Mercury pool" or "Evaporated silver" as counter electrode. However,there exist numerous complex factors such as degree of humidity, and vacuum,the rate of voltage rise,use of DC or AC and the cyles, the permissible leakage current,roughness of the surface and existence of cracks,, impressed presure of the counter electrode etc and no general definite methods seem exist.. The reports in this field seem to use the method of their own choice. Usually DC gives higher values than AC. At any rate, the hitherto reported data : 10-20 V/micron seems the average value.

The maximum dielectric strength hitherto attained (4) seems ca. 2000 V.

ASTM B-110(Probe test)	100-125 micron	1800 V for 2024-T3
		6061-T6
Mercury pool method	"	below 600V for 2024-T3

by R.F.Hafer quoted by J.Machlin et al(7).

From these not a big amount of data, it is known that the values of dielectric strength is rather fluctuating.

For comparison, the data for some synthetic plastics are shown:

PVC	1000-1200 V/100 micron
Polyethylene	1200-1400 V/100 micron
Vinyl carbasol	3000-4000 V/100 micron

From these data,the value of dielectric strength , apart from the original properties,is dependent how thick, compact and smooth the mamaterial is.

Classification of Hard Coatings

As seen in the last Paragraph, the high dielectric films must be thick and smooth in order to secure good contact between dielectrics and the counter-electrode, while thicker films mean hard coatings in the case of anodic aluminum oxides. One of the authors,Tajima(3,8,9) defined hard coating(except corrundum coating(3,4,10) as the "semi-barrier" type coating,i.e.,the intermediate between "pure barrier film" and "barrier + porous-layered film(duplex type). The duplex film usually after reaching maximum thickness(ca.25-35) finally disappears (3) by temperature rise and induced strong solvent action of the electrolyte.

The semi-barrier type films can be classified into 3 types as shown in Table 1. It is to be noted that the anodic oxide and the anion content in the electrolyte and in the film is ,so to say, in a dynamic balanced state,i.e.,the concentrations are nearly the same. Sulfuric acid coating contains nearly similar amount of sulfate. The high potential gradient produced by low temperature leads to the "coloring potential" or "excited state potential" causing excess Al° in the film(18,11,8) or "excited carboxylate ions" in the case of oxalic acid films etc, causing EL(electroluminescence) in the dark ,finally ends in the tarry products(yellow through reddish brown to brown). Excess Al° in sulfuric acid film causes light brown through brown to black color(so to say, dirty gem).

Formation of Hard,Smooth,High Corrosion Resistance and High Dielectric Strength Films

Table 1. Classification of Hard Coatings

	So-called Hard Coating	Integral Color(A)	(B)
Electrolyte	Sulfuric acid 1-30 % (basic acid)	Sulfonated aliphatic or aromatic acid + sulfuric acid	Oxalic acid or other mixtures
Temperature	-5-20 C	20-30 C	5-40 C
C.D. A/dm^2	≒ 3	1-2	1-5
Thickness, μm	below 200	normally up to 40 for architectural	500 or more
Type	Semi-barrier	Semi-barrier	Semi-barrier
Composition	Al_2O_3 + sulfate + Al^o + some sulfur	Al_2O_3 + sulfate + Al^o	Al_2O_3 + organic polymerized tarry products
Color	light brown, grey to black	light, deep brown to black	light yellow, gold, reddish brown
Origin of color	excess Al^o + some S in the film	excess Al^o in the film	excited carboxyl radicals(and polymerized tarry products)
Smell	deposited S, H_2S at low temp. or when too thick	--	--
Coloring potential	above 20 V	above 15 V	7V especially AC
Luminescence	--	--	EL, PL by UV
Roughness	becoming rough with thickness	rather smooth	smooth and lustrous
Cracks and corner effect	many and brittle	many micro-cracks	apparently few. long streaks above 250 micron
Hv	≒350	≒400	above 450
Dielectric strength	not good (detailed in other Tables)	permissible	excellent

As shown in Table 1, we presumed that the most promising coatings may come from the Integral color(B). Incidentally the electrolyte composition is similar to that proposed by P.Lelong, R.S.Segond and J.Herenguel(12), followed by E.Lichtenberger and co-workers(13,14) as rapid anodizing. According to Lichtenberger and Hollo,at the formation voltage up to 50 V, the barrier thickness may be up to 540 Å(by the Hunter method) and the coatings are substantially less porous,e.g. 1-2 x 10^8 pores/cm^2. The cell diameter is correspondingly larger, which will be shown later by our SEM picture. In this connection, Lichtenberger and G.J.V.Raja(13) reported the breakdown voltage as 1000-1200 V at anodizing voltage at 55 V DC for 10-12 micron film. Oil uptake 0.002-o.0006 g/dm^2 is described. But no mention is made on the method of breakdown voltage and as-anodized or after oil-uptake.It seems they examined no thicker films than about 50 micron due to excessive heating of the bath.

Now we shall describe our proposed conditions. As mentioned before, the electrolyte is similar to those of Lelong et al. and Lichtenberger et al. However, we made a unique and creative designing in the bath construction, electrode materials and improvement of anode throw and way of cooling, and cleared at least 5000V per 100 micron or more and Hv above 450.

Electrolyte	Oxalic acid	80 g/L	Initial voltage is 60 V as
	Formic acid	50 g/L	compared with 20-30 V of
Temperature	5-40 C		Lichtenberger,perhaps due
Counter cathode	graphite sheet, C.D.2-6A/dm^2		to our strong cold jet stream.

Very smooth, lustrous,hard,hard,thick,lustrous,reddish-brown films are obatained with less crack up to 300 micron and up to 500 or more with few but long stretched streaks. We think that the reason of the difference in appearance,feature of cracking and smoothness from those of sulfuric acid hard coating is due mostly to the tarry products in the film as mentioned in Table 1. Al-oxalate complex had been extracted and final cyclization are confirmed by M.Shimura and S.Tajima 15,16).

For the present purpose,,an important bath construction was designed by S.Tomita (17) which was registered as US and Japanese Patent(1980 and 1985) and further improved. The appearance of the bath in operation is shown in Fig.1. The anode works assembly is racked with all titanium frame. The counter cathodes are of graphite plates which are located below the electrolyte level in order to enhance cooling efficiency(cooled electrolyte circulation is not disturbed). One series of anode works are located between the two series of cathodes only. Works are not hanged but tightly fixed to the anode racks. No anode rocking is adopted. Instead,the anode works are subjected to anolyte jet stream(1.5 m/s). which is overflown to the outer jackets where the electrolyte is cooled by heat-exchanger and pumped up again into the anodes as jet stream. Thus the cooling-throw is uniform and the efficiency becomes excellent to avoid overheating from the desired temperature and to permit film thickening., In this way,anodizing can be performed at 2-6 A/dm^2 and at 5-30 C. in spite of great amount of heat evolved. Fig.2 and 3 show the rackings and finished products.

Measurement of Breakdown Voltage(Typical Examples)

The measurement is based on Probe tests as described before. Stainless steel rod (6 mm diameter) was pressed on the anodized specimen under the load of 100 g. By impressing DC or AC voltage,the breakdown voltage, is judged from the initiation of 40 mA flow . The apparatus used was the dielectric strength measuring apparatus made by the Toyo Seiko Co. and the maximum value is 5000 V

Table 2. Breakdown Voltage of Anodic Films on 5052(Al-Mg), mill-cut (V) DC

Sample	0 unsealed	1 boiling water 30 min	2 boiling water and paraffin	3 steam-sealed 5 kg/cm^2
	1400	3000	3100	1500
1	1400	2800	3000	1400
	1600	3000	2500	1600
(20 μ)	1800	3000	3100	2200
	1300	2900	3100	2400
ave	1500	2940	2960	1820
	3900	> 5000	4500	4600
2	4300	4700	4400	> 5000
	5000	4800	4500	> 5000
(50 μ)	4400	4200	4300	> 5000
	4400	> 5000	4500	> 5000
ave	4400	–	4440	–
	> 5000	> 5000	> 5000	> 5000
3	> 5000	> 5000	> 5000	> 5000
	> 5000	> 5000	> 5000	> 5000
(100 μ)	> 5000	> 5000	> 5000	> 5000
	> 5000	> 5000	> 5000	> 5000
ave	> 5000	> 5000	> 5000	> 5000
	> 5000	> 5000	> 5000	> 5000
4	> 5000	> 5000	> 5000	3200
	> 5000	> 5000	> 5000	4200
(150 μ)	> 5000	> 5000	> 5000	3900
	> 5000	> 5000	> 5000	> 5000
ave	> 5000	> 5000	> 5000	–

Table 3. Breakdown Voltage of Anodic Films on 5052(Al-Mg),mill-cut(V)AC

Sample	0 unsealed	1 boiling water 30 min	2 boiling water and paraffin	3 steam-sealed 5kg/cm^2
	900	2450	2150	1800
1	850	2500	2650	1050
	450	2450	1950	1450
(20 μ)	850	1450	2550	1450
	650	2050	2550	1500
ave	740	2180	2370	1450
	1500	3800	3450	3100
2	1450	3800	3450	3300
	1500	3600	3800	2900
(50 μ)	1550	3550	3650	2600
	1400	3850	3850	2700
ave	1480	3720	3640	2920
	1950	4100	3700	3400
3	2050	4300	3800	3350
	2250	4300	4100	3800
(100 μ)	2300	4200	3850	3450
	2300	4500	3300	4000
ave	2170	4280	3750	3600
	2950	4100	2850	3350
4	3300	4600	3500	2900
	3450	4750	4150	3700
(150 μ)	3500	4450	4600	3300
	3550	4350	4000	2500
ave	3350	4450	3820	3100

Table 4. Breakdown Voltage of Anodic Films on 5052(Al-Mg) as-rolled (V) DC

Sample	0 unsealed	1 boiling water 30 min	2 boiling water and paraffin	3 steame-sealed 5 kg/cm^2
1	1000	2000	2800	2350
(20 μ)	1200	1850	2500	1700
	1050	2700	1900	2600
ave	1080	2180	2400	2220
2	1300[1]	4700	>5000	3100[2]
(50 μ)	3000	4700	>5000	>5000
	2800	4350	>5000	4300[2]
ave	2900	4580	>5000	–
3	4900	>5000	>5000	4500
(100 μ)	>5000	>5000	>5000	4500
	>5000	>5000	>5000	4300
ave	–	>5000	>5000	4430
4	>5000	3800	3900[4]	3350
(150 μ)	>5000	4800	>5000	2800[3]
	4250[3]	5000	4100[4]	3150
ave	–	4530	–	3100

Note 1) material defects ?
2) cracked parts
3) fault
4) white spot

which is regretably low in the present experiment. By considering the effect of surface condition before anodizing, 5052(Al-Mg) plates were mill-cut or used as-rolled and finally alkaline-degreased. The reason for taking up 5052 is that it gives best and reproducible results,together with 3N or 4N Al.
The detailed data are shown in Table 5,6,7.
From the Tables,it is understood that mill-cut surfaces(DC) give best and stable results,clearing up 5000 V already at 100 microns(50 V up per micron).
It is already known that DC gives higher values than AC.
In any case , unsealed and steamed-sealed (6 kg/cm^2) gave lower and fluctuated values. Meanwhile, it is generally believed in Japan that the steam-sealed surface gives stable and higher values. The reasons in our case are not yet well clarified.A.Miyata(2) states that steam-sealing is best fitted for oxalic films.
During the research,we examined the limit of available thickness and obtained ca. 500 micron . The surface is deep reddish brown and still lustrous,but a few long streaks were noted instead of micro-cracks. Fig.4 shows 206-208, 303-306 and 494-497 micron (left to right) thick disks.

Tests for other Al-alloys

Here we show the brief summaries of Hardness, abrasion resistance,corrosion resistance(CASS R.N.) etc for typical Al, wrought and cast alloys as compared with the conventional sulfuric hard coatings.

(A) Wrought alloys ca. 50 micron thick
1. Excellent hardness Hv + 450 especially for pure Al and 5052. against 350 doe sulfuric acid coatings.
2. Abrasion resistance(ISO-1,400 g load,1500 cycles), excellent except 2024 and 7075
3. Corrosion resistance is all excellent. CASS R.n. 9.5-9.8 against 7-9.8 (Nickel acetate sealing)
4. Dielectric strength is also superior, ca. 2000 V/50 micron
5. Specific resistance is excellent especially for Al and 5083,10.0-123x10^{10} ohm cm.

(B) Cast alloys, ca.50 micron.
1. Hardness is superior in sulfuric acid coating except AC4A and AC7A.
2. Abrasion resistance is superior in the present process for AC,4A,7A and ADC. For others the conventional process is better.
3. Corrosion resistance is nearly the same.
4. Dielectric strength is not good in both processes.
5. Specific resistance is only superior by AC7A only and sulfuric acid coatings are usually superior.

SEM and Thermal Analysis

Fig.5 shows the 426 micron thick Al disk formed at 2.5 A/dm^2, 20 ± 1 C and its fractured surface and a SEM analysis sample on the right.
Fig.6 shows the fractured surface taken by scanning electronmicro scope(SEM, x10,000. Parallel pore structure is quite distinct. Cellsize ca 2000,pore dia,ca800 Å.
Fig.7 shows the SEM picture at Al and Oxide boundary cut by microtome x3000. Scratch on basis Al by microtome is distince but the pore just above is a little ambiguous.

Further,we have examined the same film(426 micron) with DTA and TG analysis. The experiments were made from 50 to 600 C(25 C/min). At 300 C, 0.9 wt. % water was lost and at 500 C, further 0.9 wt.%(organic substance).Thus totao 1.8wt% has been lost,which is surprisingly a small amount. It explains that the film, 425 micron thick is very compact, smooth and lustrous and hard--semi-barrier type.

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Fig. Captions

Fig.1 A newly designed anodizing tank at work. All the anode works and cathodes are located below the electrolyte level. Apparent eddy motion of the electrolyte is due to cooled jet stream. Details in the text(Tomita Electrochemical Research Laboratories)

Fig.2 Racking and the finished air-cylinders(Tomita Electrochemical Research Laboratories)

Fig.3 Racking of demonstration works. and the finished gifts(205 micron thick, reddish brown and lustrous(Tomita Denka Research Laboratories)

Fig.4 From left to right, 206-208, 303-306 and494-497 micron thick disks. These films are smooth and lustrous and reddish brown.

Fig.5 Disk,426 micron,,fractured and the specimenfor SEM examination near the right side

Fig.6 Fractured section of the sample,Fig.5. 10000 x. Details in the text. Cell size ca. 2000 Å and pore diameter ca.800 Å

Fig.7 The boundary of basis Al and the oxide(microtomed, 3000 x. Details in the text.

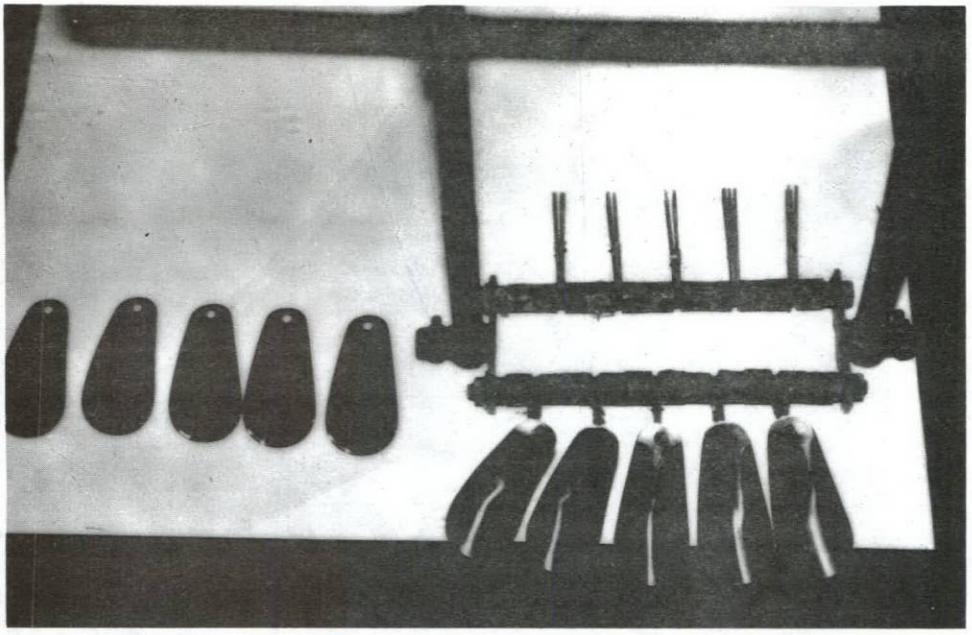

Fig.1

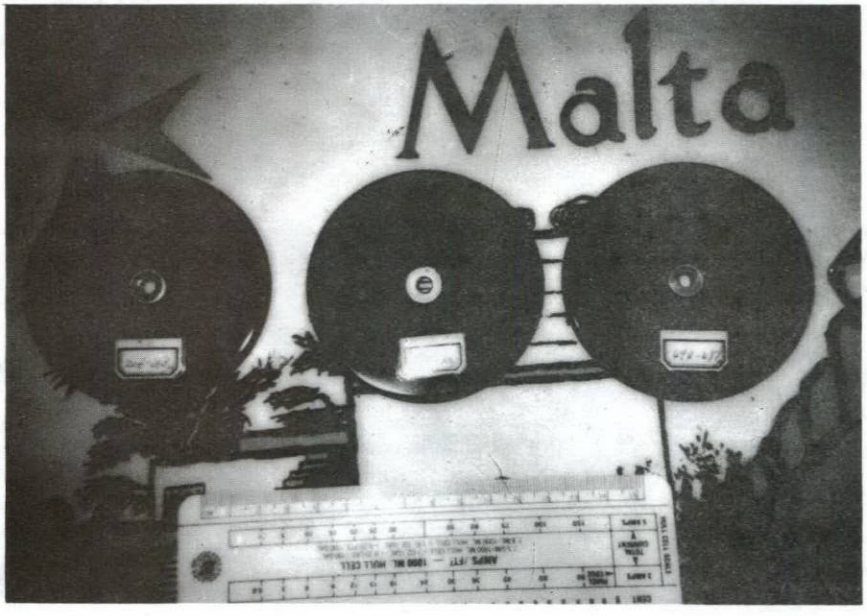

Fig 2

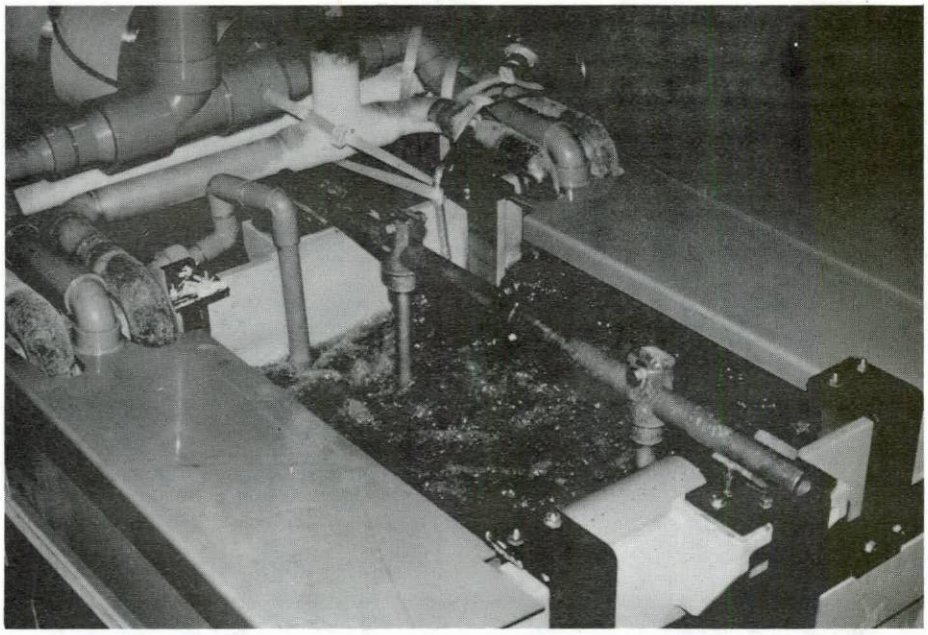

Fig.3

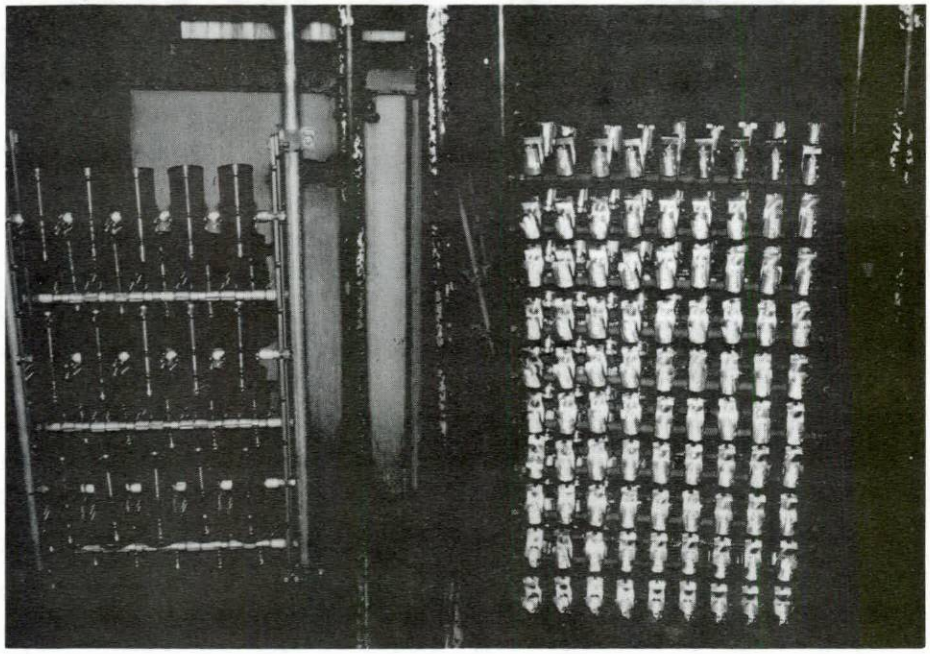

Fig.4



Fig.5

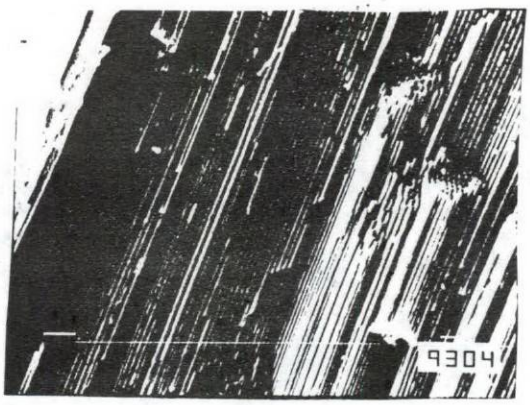

Fig.6

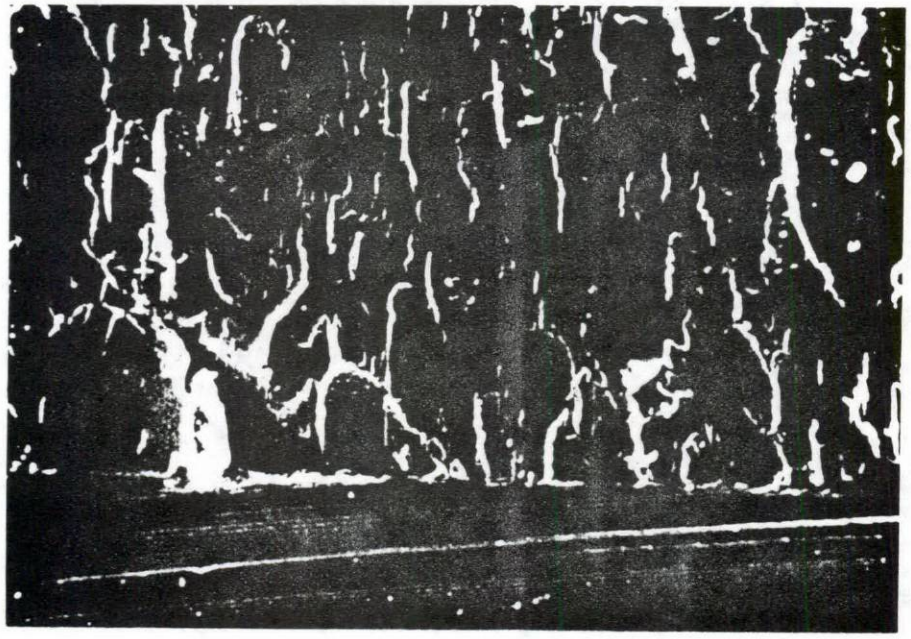

Fig.7

A-6

Light Metals Finishing
Session A

An Electrochemical Method to Control The Anodizing Process

S. Yousri
Pratt & Whitney Canada Inc.
1000 Marie Victorin
Lonqueuil, Quebec, J4G 1A1

AN ELECTROCHEMICAL METHOD TO CONTROL THE ANODIZING PROCESS

By
S. Yousri
Pratt & Whitney Canada Inc.
1000 Marie Victorin, Lonqueuil, Quebec, J4G 1A1

Abstract

An electrochemical method has been developed to rapidly evaluate the quality of anodized aluminum coupons. (1) The test has been optimized for quality control applications via a sample test fixture which allows standard sample coupons to be conveniently interchanged.

Introduction

The aluminum anodizer has to make decisions on a daily basis regarding the performance of his operations.

For example one part processed 10 days ago is showing corrosion in the Salt Spray (ASTM B-117)

Do I change the sealant tank?

Do I run a complete analysis of the anodizing tank?

Do I change or verify the cleaning process or the rinsing process?

Do I change everything and start fresh?

The answer could be one of the above or a combination thereof. Once action is taken you wait again for the salt spray test to be completed. You still face the distinct possibility that sooner or later the problem will return and you have to start all over again. At Pratt & Whitney Canada the use of the Electrochemical test method has removed all the doubts from the anodizing process control, with the following results:

- No salt spray failure of a part processed in 3 years
- The chromic acid anodizing tank was not changed in 3 years
- Sealant tank performance is monitored on a daily basis and the sealant solution cleaned or changed to maintain maximum performance.

Theory

The electrochemical techniques for corrosion rate measurements employ a potentiostatic circuit to simultaneously apply a potential to the specimen in solution while measuring the current that flows due to the electrochemical reaction induced by the applied potential. It has been shown (2,3) that if the applied potential is systematically scanned in a region close to the specimen's open-circuit potential (Ecorr), a plot of applied potential versus the Log current can be used to calculate the corrosion rate. This type of plot is called the Tafel plot.

Figure 1 shows an idealized Tafel plot. It can be seen in this figure, that for a simple metal-solution system, linear regions of the scan can be extrapolated back to the open-circuit potential to yield a quantity called the corrosion current (Icorr). Icorr is the current which will flow to support a corrosion reaction under naturally occurring conditions, i.e., at the open-circuit potential.

The physical interpretation of the plot is as follows: At the open-circuit potential a net current of zero is flowing at the electrode, because both oxidation and reduction reactions are simultaneously occurring at equal rates. As the potentiostat is used to remove the specimen potential from Ecorr, one or the other electrochemical reaction is accelerated. If the applied potential is positive of Ecorr, then the oxidation reaction will be enhanced and a net positive (anodic) current will be observed. If the applied potential is negative of Ecorr, then the reduction reaction will be enhanced and a net negative (cathodic) current will be observed.

Icorr is directly related to the corrosion rate by the equation:

$$\text{Corr. Rate} = \frac{0.13 \times \text{Icorr} \times \text{E.W.}}{d}$$

Where: E.W. = equivalent weight of the oxidized element in grams

Icorr = corrosion current density in microamps per square centimeter

d = specimen density in grams per cubic centimeter

The acquisition and analysis of Tafel plots can be automated via microprocessor-controlled or PC-based instrumentation.

Experimental

The electrochemical instrumentation consisted of an EG&G Princeton Applied Research Model 350-1 Corrosion Measurement System. This system was used to automate the acquisition of Tafel plots, identify linear trends in the plots, and calculate the corrosion rate estimates.

The specialized electrochemical cell shown in Figure 2 was used in place of the standard corrosion measurement cell which is normally supplied with the system. This cell consisted of a hollow Teflon cylinder (A) with a 5.00 cm outside diameter and 11.5 cm height. The walls of this cylinder were 1.5 cm thick at the top and widened to 6.0 cm at the bottom to facilitate clamping to the base (B). The base was a solid Teflon cylinder with a 7.5 cm diameter and 2.5 cm height.

The cell was assembled with the test coupon (C) inserted between the hollow cylinder and the solid base. A rubber o-ring was used along with a clamp to create a water-tight seal. In this way, the test coupon surface acually served as the bottom of the cell.
The test coupons were the same standard AMS 4037 test panels (3 inch x 10 inch) that are used in the salt spray testing. To facilitate electrical contact, one corner of the anodized panel was ground to expose bare metal.

The Teflon lid (D) for the cell had three holes bored into it to allow the platinum wire counter electrode (E), saturated calomel reference electrode (F), and an air agitation device (G) to be introduced into the test solution.

The resulting test cell, allowed a solution volume of 200 milliliters to be be used with a moderate air-stirring rate. This volume of solution was found to be sufficient to negate the effects of metal dissolution which occurred during the course of a typical test.

Prior to testing, each specimen panel was solvent degreased, rinsed with deionized water, and activated at a potential of +1.0 Volts vs. SCE for 30 seconds. Following this pre-conditioning potential, the open-circuit potential was monitored and the scan was initiated once the system had equilibrated (as evidenced by a stable open-circuit potential). This generally required between 20 seconds and 5 minutes.

The instrumentation automatically recorded Ecorr and executed the applied potential scan from Ecorr +400 mV to Ecorr -400 mV. A scan rate of 0.5 mV per second was used, which resulted in a scan time of 26 minutes.

Results

Figures 3a and 3b show actual instrument outputs for the tests of two anodized specimens. Figure 3a shows the Tafel plot report for a specimen with a relatively good anodic coating. Note the reported corrosion rate (designated MPY in the figure) of 0.013 milli-inches-per-year. It should be noted that the implied precision of the reported value is a function of how precisely the constants (equivalent weight and density) were input to the instrument by the operator. The real precision of this value is probably only good to the second decimal place. The high corrosion rate of 0.68 MPY is calculated in Figure 3b for a specimen with a poor anodic coating.

Four years of studies comparing different panels processed under different conditions and testing duplicates in the salt spray cabinets helped us establish the following process control parameters.

1. Panels showing corrosion rates under 0.1 MPY will not fail the salt spray.

2. When panels display a corrosion rate of over 0.1 MPY but under 0.5 MPY, the Laboratory warns Production that the anodizing process is deteriorating and corrective action is taken immediately.

   Panels processed under those conditions will pass the salt spray 9 times out of 10.

3. Panels with corrosion rates over 0.5 MPY: The Laboratory requests immediate corrective action. Parts are reprocessed if the corrosion rate is over 1 MPY. Between 0.5 and 1.0 MPY, the judgement is dependent on the parts application.

4. Optimized the sealant times: It was found that with very fresh deionized water the optimum seal time was 8 minutes. On the other hand a month old seal solution will require 15 minutes to seal properly.

5. Optimized the sealant temperature: Due to a failure in a steam heating coil, the temperature in the sealant tank dropped to 85°C (within our previous specs.). Panels tested that day showed corrosion rates higher than 0.5 MPY. The line was stopped until an auxiliary coil was added and the corrosion rate dropped to 0.01 when the temperature reached 95°C. The problem was corrected in a few hours. (95°C ± 5°C is our present spec).

Conclusions

Electrochemical techniques are quickly emerging as a tool for rapid control of any surface finishing process. We are presently working to extend our findings on the aluminum anodizing process to other finishes. We have tested the effects of different solutions on Titanium and Magnesium alloys and the results are encouraging.

The main advantage of the technique is that it answers a basic question: Since a coating or a finish is applied to prevent corrosion, how can we find out if it works without waiting several days.

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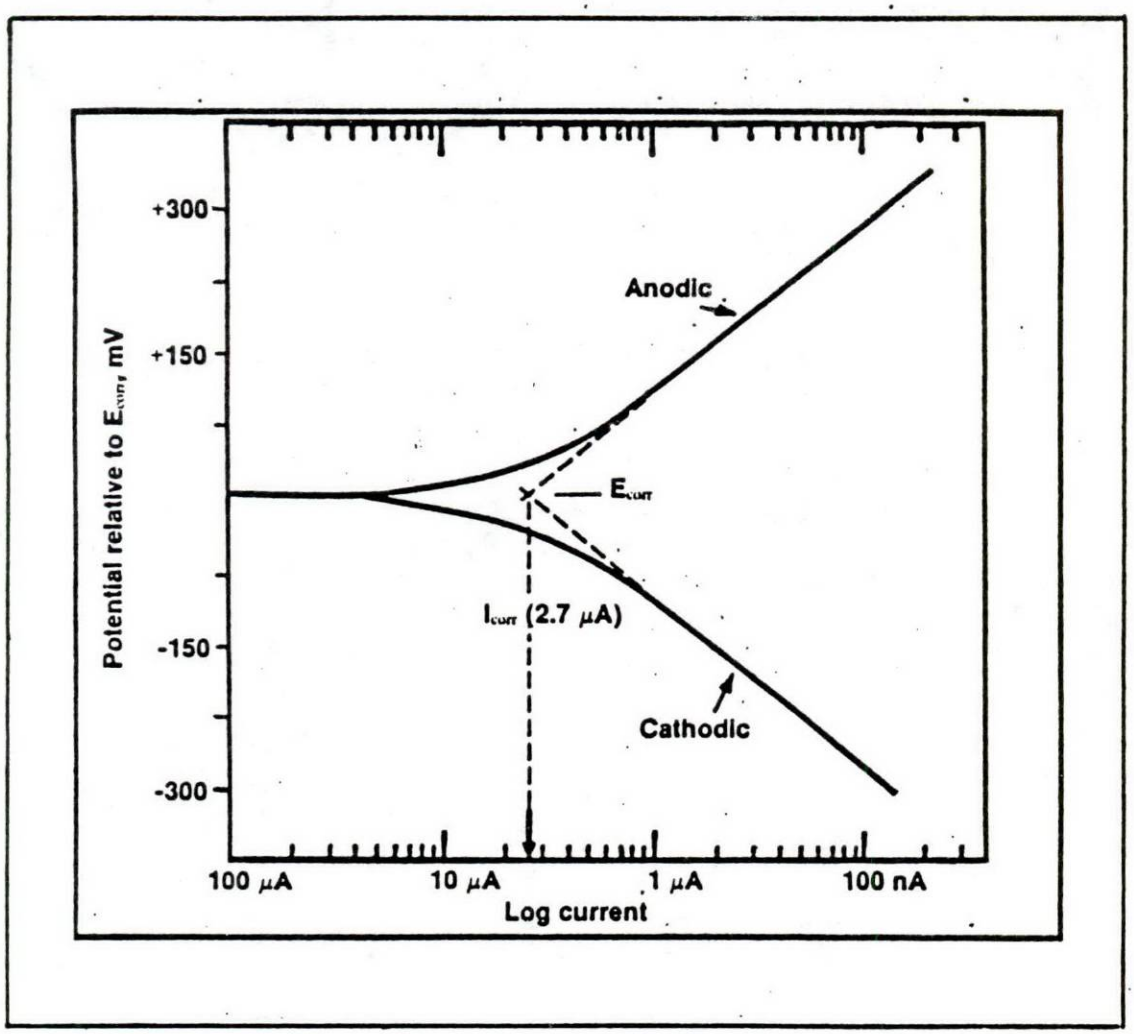

Fig. 1— Tafel plot for ideal electrochemical system

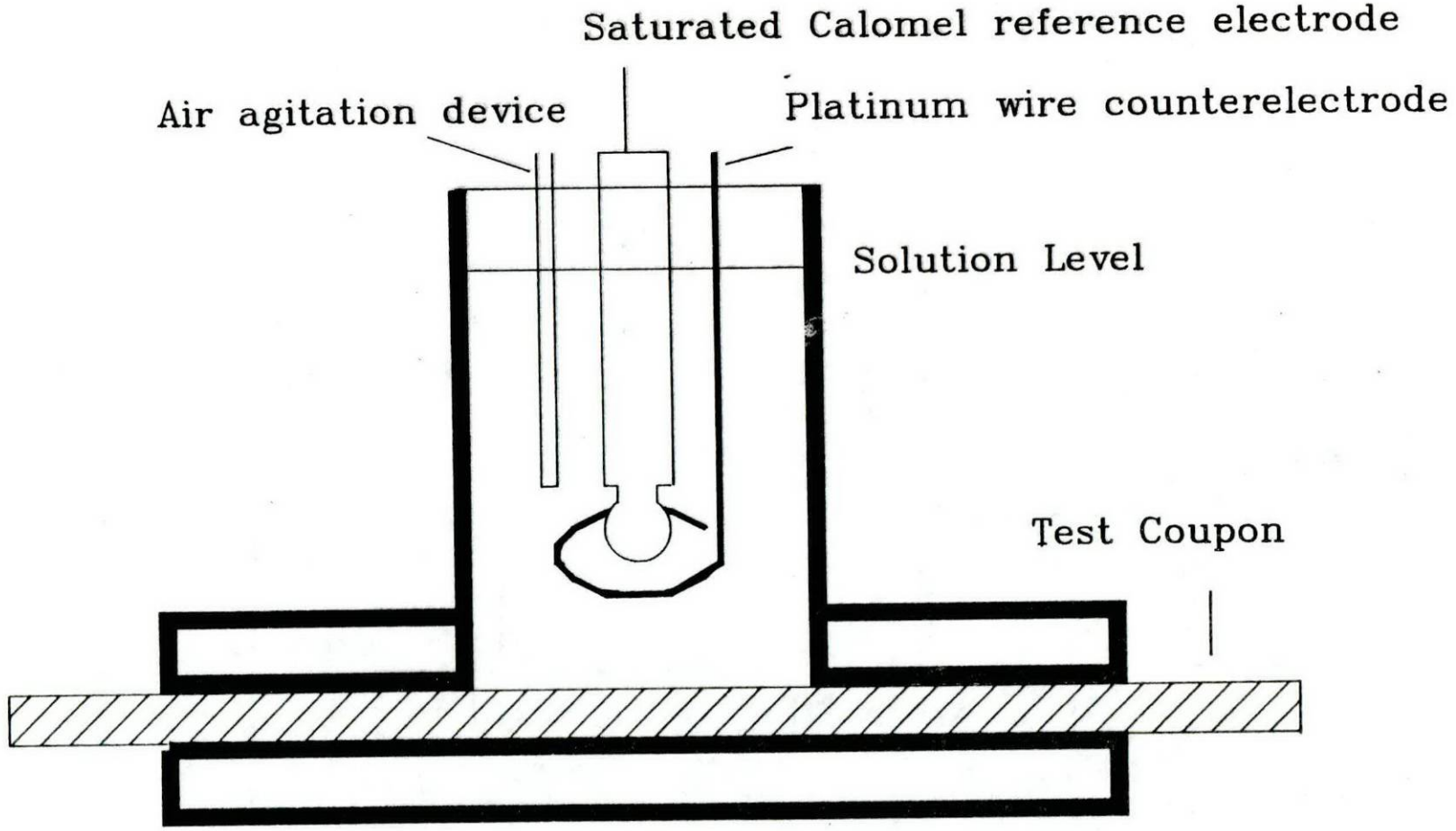

Fig. 2 – Cell for testing anodized coupons.

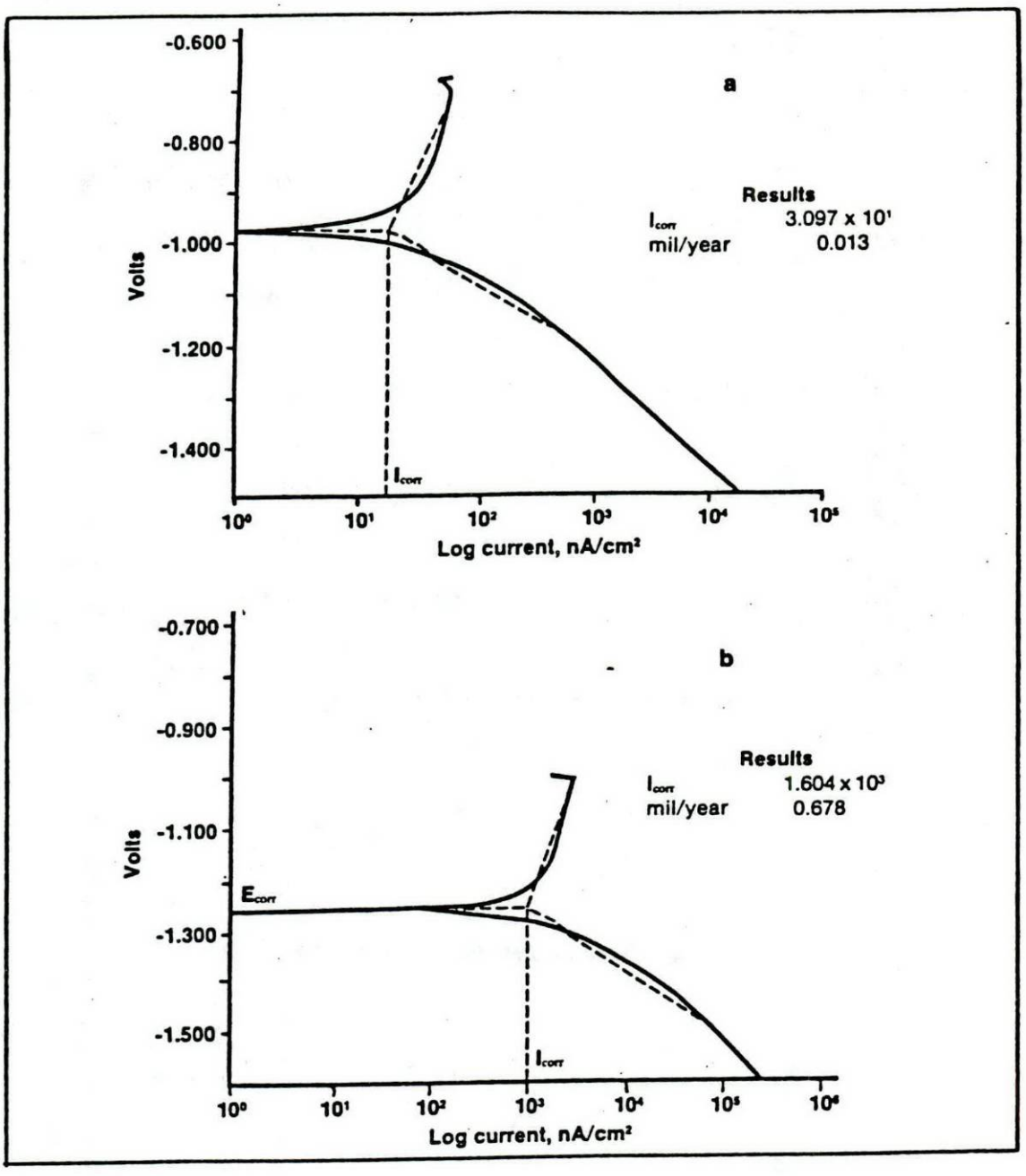

Fig. 3– System printouts for two typical tests (a) good and (b) poor coating

A-7

Light Metals Finishing
Session A

Designing an Automated Extrusion Anodizing Facility

Glenn C. Schoener
Walgren Company
Grand Rapids, MI

DESIGNING AN AUTOMATED EXTRUSION ANODIZING FACILITY

Glenn C. Schoener

Walgren Company
Grand Rapids, Michigan

Fully automated extrusion anodizing facilities represent the current state-of-the-art in anodizing technology. Five such facilities have been or are being built today. Several more are currently in the design stages. Automating an anodizing plant results in the realization of several significant benefits such as:

1. INCREASED PRODUCTIVITY
2. LOWER REJECT RATES
3. LOWER OPERATING COSTS
4. IMPROVED QUALITY

The installation of a fully automated extrusion anodizing facility requires the engineering and integration of seven major component sub-systems. These are:

1. TANK SYSTEM
2. HEATING SYSTEM
3. COOLING SYSTEM
4. POWER SUPPLIES
5. VENTILATION SYSTEM
6. MATERIAL HANDLING SYSTEM
7. COMPUTER CONTROL SYSTEM

Each of these component sub-systems must be engineered in terms of the available design options such that the sub-systems can be integrated into the total facility. The available design options for each sub-system must therefore be discussed in greater detail.

Tank System

The tanks employed in an extrusion anodizing facility can be constructed of five possible materials. These are:

1. MILD STEEL
2. STAINLESS STEEL
3. POLYPROPYLENE
4. FIBERGLASS
5. CONCRETE

Mild steel tanks are constructed of 1/4" thick material and can be built to almost any size, provided they are braced

properly. Tanks up to 115 feet long and 14 feet deep are currently being used in production facilities. Mild steel tanks are typically only used for alkaline solutions due to its lack of corrosion resistance. Mild steel tanks are fairly easy to repair and represent the lowest cost of installation.

Stainless steel tanks are usually constructed of 10-ga material and can also be built to almost any desired size. They exhibit excellent corrosion resistance to most of the chemical solutions employed in the anodizing process. Although stainless steel tanks can be easily repaired, they do require a significantly higher initial capital expenditure.

Polypropylene tanks are constructed of 1/4" to 1" thick material properly braced with an encapsulated steel structure. They can be built economically up to 10 feet long and 6 feet deep. They provide excellent corrosion resistance and good dielectric properties for use in electrified tanks. Polypropylene tanks have proven themselves suitable for most solutions encountered in an anodizing plant. Unfortunately, polypropylene is difficult to repair in the field.

Fiberglass tanks are usually fabricated of 1/4" to 1/2" thick material and can be constructed up to 10 feet long and 6 feet deep economically. They provide good corrosion protection to most solutions in an anodizing facility. They are easy to repair in the field but do exhibit a tendency to crack with age.

Concrete tanks are only economical for large tank systems in excess of 30 feet in length. Concrete tanks can reduce overall line length by utilizing 6" to 8" thick common walls between tanks. These systems must be lined inside and outside with a sprayed on coating of chopped fiberglass for corrosion and electrical resistance. Concrete tanks are difficult to repair and costly to maintain.

Corrosion resistant, non-conductive tank lining materials are required to electrically insulate anodizing or electrolytic coloring tanks that have been fabricated from conductive materials. Lining materials such as P.V.C., rubber and fiberglass are most commonly employed. Tank linings can be easily damaged and are very difficult to repair. It is therefore best to construct the tanks of suitable materials inside and outside and to utilize tank liners only where absolutely necessary.

Heating System

The second major sub-system that requires engineering expertise is the heating system employed to reach and maintain

the required processing temperatures. There are two main approaches to process heating.

1. IMMERSION BURNER TUBES
2. STEAM COILS

Gas fired, immersion burner tubes can be mounted in tanks from 6 feet to 40 feet long. The width or the depth of the process tanks must be increased as a result of the diameter of the tubes. Although burner tubes are less efficient than steam coils, they are less expensive to install and maintain than a steam coil-boiler system.

Steam coils can be used in any size tank down to two feet long. Coils are the most widely used heating system in anodizing process tanks today. Coils can be fabricated of the proper corrosion resistant material to withstand any solution found in anodizing lines. They are the easiest to remove, repair or replace.

Standard engineering calculations are used to determine the BTU heat input needed to reach and maintain the desired operating temperatures regardless of the type of heating system employed.

Cooling System

The third major sub-system requiring engineering is the cooling system. Cooling of the anodizing electrolyte is mandatory if acceptable quality anodic coatings are to be produced.

Small anodizing tanks less than four feet long employing no more than 1000 amps DC can be cooled by pumping a cooling solution directly through coils in the anodizing tank. The coils can be constructed of stainless steel, lead or teflon.

In most cases, larger anodizing tanks are cooled more efficiently with the use of an external heat exchanger. The anodizing electrolyte is pumped through one side of the exchanger and chilled water through the other side. The exchangers must be constructed of stainless steel and the electrolyte pumps must be Carpenter 20 stainless or F.R.P. (fiberglass reinforced plastic).

The primary component of the cooling system is the chiller. It is also the most expensive. The chiller must be sized to remove the total amount of heat generated by the application of electrical energy in the process tanks. The exact size of the chiller for any particular installation can be easily calculated. The total BTU/hr generated in the anodizing and elec-

trolytic coloring tanks can be found by multiplying the applied voltage by the amperage current flow and the factor 3.412. The BTU/hr heat generated divided by 12,000 equals the tons of refrigeration required by the chiller. If water cooled rectifiers are employed, the heat generated by the power supplies must also be added to the total chiller requirements.

Either water-cooled or air-cooled chillers can be utilized in the cooling system. Water-cooled units are more efficient than air-cooled units, especially on very hot summer days. Water-cooled units must be connected to a cooling tower located outside the building. Water is then pumped from the chiller condenser to the remote cooling tower. Air-cooled chillers located out of doors eliminate the cost of buying and maintaining a cooling tower and cooling tower pump.

The last major components of the cooling system are the external heat exchangers. The only practical choice for this type of heat exchanger is the plate type due to its very high heat exchange efficiency. The corrosive nature of the anodizing and electrolytic coloring solutions necessitate the use of 316 stainless steel. Other types of heat exchangers, such as the shell and tube, and other materials of construction, such as graphite, glass and teflon are also being employed. However, the 316 stainless steel plate heat exchanger is the most commonly recommended type due to it's relative cost, high efficiency and lack of required maintenance.

In addition to the chiller and external heat exchangers, the cooling system requires chilled water pumps, a cooling tower (only required if a water-cooled chiller is employed) and acid pumps to circulate the electrolytes. The solution flow rates required by each of these components are readily calculated from available engineering equations. Typical flow rates and materials of construction are shown below:

PUMP	FLOW RATE	MATERIAL
1. CHILLED WATER	2.4 GPM/TON	CAST IRON
2. COOLING TOWER	3.0 GPM/TON	CAST IRON
3. ELECTROLYTE	BTU/3000	CARP. 20

Power Supplies

The next major component sub-system to be considered in the design of a new extrusion anodizing facility is the power supply requirement. This would include both the DC rectifiers for the anodizing tanks and the AC power supply for the electrolytic coloring tank, if included in the facility. Care must

be taken to insure that the power supplies have been properly sized to provide the required output voltage and amperage based on the designed load size. Typical voltage and amperage requirements are shown below:

POWER SUPPLY	VOLTAGE	AMPERAGE
DC RECTIFIER	24 V	12 ASF
AC POWER	30 V	5 ASF (AVG.)

Multiplying the appropriate current densities, from the table above, by the maximum design load size in square feet of surface yields the current output which must be provided by the power supplies.

Most DC rectifiers in use today employ SCR's (silicon controlled rectifiers) for current output regulation and either SCR's or diodes for rectification of incoming AC to DC output.

AC power supplies utilize step-down transformers to convert high voltage/low amperage input to low voltage/high amperage output. Regulation of the applied output voltage can be controlled using either motor driven powerstats or SCR circuitry.

Both AC and DC power supplies are available in either air-cooled or water-cooled units. Water-cooled units are preferred because they are completely sealed thus protecting the internal components from humidity, dust and fumes.

The power supplies used in a fully automated anodizing facility must be more sophisticated than those normally used in the industry. They must be capable of receiving operating commands from and sending response signals to the automated control system.

Ventilation

Ventilation of the process tanks represents another major sub-system that requires engineering design for a new extrusion anodizing facility. The tanks that require ventilation are the soak cleaner, caustic etch, anodize and seal tanks. Chemical brite dip tanks, if installed, would also require ventilation equipment. In order to properly size the ventilation system, the amount of air to be vented per unit time per open tank surface area (CFM/SQ.FT.) must be known. Guidelines for CFM/SQ.FT. have been published in the Handbook of Industrial Ventilation.

There are two basic ventilation designs which may be utilized. They are referred to as "pull-pull" and "push-pull". Pull-pull systems require higher exhaust rates than push-pull systems and also require two exhaust hoods instead of one. Since considerably less air is exhausted with the push-pull ventilation system, it is less expensive to install and operate. The table below compares air exhaust rates typically required for each type system for the various process tanks.

TANK	PULL-PULL	PUSH-PULL
CLEANER	150 CFM/FT^2	75 CFM/FT^2
ETCH	200 CFM/FT^2	85 CFM/FT^2
BRITE-DIP	250 CFM/FT^2	95 CFM/FT^2
ANODIZE	250 CFM/FT^2	95 CFM/FT^2
SEAL	175 CFM/FT^2	80 CFM/FT^2

Ventilation hoods are of two different designs; either updraft or downdraft. The type best suited to the particular facility being designed is dependent upon the size of the process tanks and the design of the material handling system that will be employed.

The exhaust hoods can be constructed of mild steel, stainless steel, P.V.C. or F.R.P. The hood material must withstand the attack of the particular chemicals within the tank as well as the physical abuse from dropped parts and racks. Therefore, the main points to be considered when choosing a material of construction are the corrosion and mechanical damage resistance. Hoods should be designed with cross-sectional areas large enough to reduce excessive air velocity noise. Cross-sectional area based on 2,000 FPM air flow rate are usually adequate.

Both round and rectangular ventilation ductwork is used in the industry. Round is preferred since it is generally easier to install and requires no internal bracing. Ducts should be sized such that the velocity inside the duct does not exceed 2,500 FPM for maintaining low noise levels. Mild steel, stainless steel, FRP and PVC are all used for duct material. PVC is usually the preferred material due to its light weight, corrosion resistance and ease of installation.

In addition to the ventilation hoods and associated ductwork, anodizing ventilation systems must include a fume scrubber to remove chemical mists from the exhausted air. There are at least ten different scrubber designs available today. All of them are capable of adequately removing the very soluble fumes which are generated by the etch and anodize tanks.

Scrubbers are usually fabricated of PVC or fiberglass. The design of the scrubber most provide adequate cross-sectional area to allow the vapors to condense on the packing material. The proper packing thickness and density are critical to ensure adequate scrubber efficiency.

Tank ventilation systems on large extrusion anodizing facilities may exhaust several hundred thousand cubic feet of air per minute. The exhausted air must be replaced and this is usually accomplished using gas fired air make-up units. Typically, only 80% of the exhausted air is replaced so that a constant negative pressure is maintained in the building.

Material Handling System

The sixth major sub-system of an automated extrusion anodizing facility which requires engineering expertise is the material handling system. This is the most important sub-system of the facility since it directly effects the production output of the anodizing line as well as the overall quality of the parts produced. Since only automated facilities are being discussed, the choice of material handling system must be restricted to those systems which allow control of material movement through the use of a PLC (programmable logic controller). Therefore, only two types of material handling systems, shown below, need be discussed.

1. SIDE ARM HOIST
2. OVERHEAD HOIST

The side arm hoist system is a fully programmable material transport system which will process loads up to 500 pounds in weight and can work over tanks up to six feet long. It is the least expensive automatic material handling system to purchase and install. The side arm hoist system is easy to build and install due to the construction design. The side arm hoist provides a lot of cycle flexibility at minimal cost when operated over an anodizing line with numerous process cycles.

The overhead hoist systems offers the same flexibility in process cycles that the side arm hoist provides. Overhead hoist systems typically operate with loads from 1,000 to 12,000 pounds over tanks from 4 feet to 40 feet long. They can be equipped with variable speed drive motors to insure smooth starts and stops, thus eliminating rack sway. The overhead hoist system is the most widely used automatic material handling system in use in extrusion anodizing plants today.

Either of these material transport systems can be readily automated through the use of programmable logic controllers (PLC). The programmable controller can be programmed in "CATWALK LANGUAGE" such as; up, down, forward and reverse. The process cycle instructions can be entered into the programmable controller through an operator keyboard on the face of the control panel. The keyboard also permits easy program modification should alteration of the cycle sequence become necessary.

The hoist controllers can also be programmed to set the voltage or current output of the rectifiers and AC power supplies for each load entered into the system.

Computer Control System

The total automation of the extrusion anodizing facility can only be achieved by integrating all of the component sub-systems. This is achieved by utilizing industrial computers to oversee the operation of all of the component sub-systems. The computer can be programmed to contain all of the various load cycle date that would be necessary for random loading of different process cycles. The operator would only be required to key in the part number and quantity on each load. The computer would then select the proper load cycle recipe and calculate the proper current or voltage settings. This information would then be passed down to the programmable logic controller which would direct the operation of the hoist throughout the process sequence. The computer would control and record the current, voltage and temperature of appropriate process tanks for each load processed.

The chemical concentrations of the individual process baths can be determined and recorded by a computer controlled automatic chemical analyzer. This unit could be programmed to withdraw a sample of each process bath and perform the required analysis on a schedule basis. The chemical analyzer could be programmed to add the required amount of chemicals to the individual process baths when the concentrations are found to be below their set points. The chemical concentration data is recorded and can be displayed in either tabular or graphic formats.

Data communication between the PLC hoist controller, chemical analyzer and industrial computer would complete the automated control system. The inter-communication capabilities would facilitate the gathering and recording of important production information such as:

1. PART STATUS REPORTS

2. PROCESS LINE STATUS REPORTS
3. WORK SCHEDULES
4. PART PROCESSING SEQUENCES
5. PART HISTORY
6. CHEMICAL USAGE
7. MAINTENANCE SCHEDULES
8. CHEMICAL INVENTORIES
9. SPARE PARTS INVENTORIES
10. STATISTICAL PROCESS CONTROL DATA

All of this information could be displayed, stored, printed or passed along to a central factory computer.

In conclusion, there are many equipment options which must be considered when designing a new extrusion anodizing plant. All of them need be seriously reviewed in order to provide a new facility that is cost effective to operate and maintain. The use of programmable controllers and industrial computers to fully automate every aspect of the extrusion anodizing process are becoming more common in the industry. This is primarily a result of the significant production costs savings and increase in quality which result from the utilization of this technology.