# American Electroplaters' Society

# 67TH ANNUAL TECHNICAL CONFERENCE

**June 22 - 26, 1980 MECCA Milwaukee, WI**

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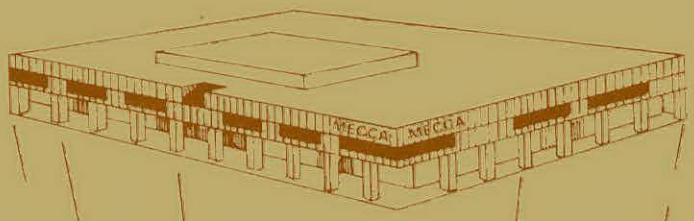


### LIGHT METALS FINISHING

**Session E**

AMERICAN ELECTROPLATERS' SOCIETY, INC.

67TH ANNUAL TECHNICAL CONFERENCE - MILWAUKEE, WI

LIGHT METALS FINISHING

SESSION E

E-1

# LIGHT METALS FINISHING SESSION E

## Hard-Anodizing of Aluminum by Low Voltage

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# HARD-ANODIZING OF ALUMINUM BY LOW VOLTAGE

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ABSTRACT

A new low voltage hard anodizing process employs DC voltage up to 20V with superimposed AC voltage, and provides up to 6-7 mil coatings with high abrasion resistance. The breadkown voltage of the coatings may reach 4-5 kV DC. The coatings are uniform, pit free and develop significantly less than usual edge-defect.

## INTRODUCTION

Anodizing of aluminum is a process of coating the metal with an oxide film which is formed through a combination of oxygen with aluminum. Anodizing processes differ in the sources of oxygen and in the means by which the oxygen is transported to the aluminum. Oxygen may be supplied from air, or plasma, or electrolyte, or some other source, with the help of diffusion, or heating or an electric field (for more details see [1,2,3]).

The anodizing process which is most extensively used in industry is the electro-chemical anodizing in an electrolyte. The process is carried out by having the current flow through the aluminum which is immersed in an oxygen containing electrolyte with the aluminum connected anodically. The properties of the anodic coating can change dramatically depending upon the composition of the electrolyte, its temperature, the waveform of the applied voltage, and the program under which the voltage is varied. Porous oxide films having sapphire hardness and with a thickness in the order of one or several mils (1 mil = 25.4μm) are produced by an electrochemical process which is called the "hard-anodizing process". The process was discovered in this country about three decades ago and is distinguished essentially a) by using an electrolyte, which contains a rather high concentration of a strong acid, (like sulphuric acid), b) by maintaining the electrolyte at a temperature which is well below room temperature (at 0°C, for instance), and c) by application of a gradually increasing voltage to keep the current from dropping below a reasonable level.

It became clear very early that it was not simple to create a "universal" hard-anodizing process which would be equally successful in providing hard-coating of any thickness of any aluminum alloy. A long effort to obtain this goal started and a number of different hard-anodizing processes were developed. These processes are known under different proprietary names such as the Martin Process, Sanford Process, Alumilite Process, etc. Each process has its own range of aluminum alloys and coating thickness at which the process is most efficient. We will discuss here the next step towards development of a "universal" hard-anodizing process. This step is primarily distinguished by implementation of a low DC voltage during the anodizing process.

## LOW-VOLTAGE HARD-ANODIZING PROCESS

It was recently discovered that with the aid of a special power supply, which superimposes AC voltage over DC voltage, it is possible to economically produce hard coatings on aluminum at a low anodizing voltage. This process we will further refer to as the "LV"-process versus high-voltage ("HV") processes ordinarily in use. The LV-process includes the raising of the DC voltage component to a maximum value, which is less than 20V (predominantly 18V) after which the voltage does not change substantially during the rest of the anodizing cycle (see Fig. 1).

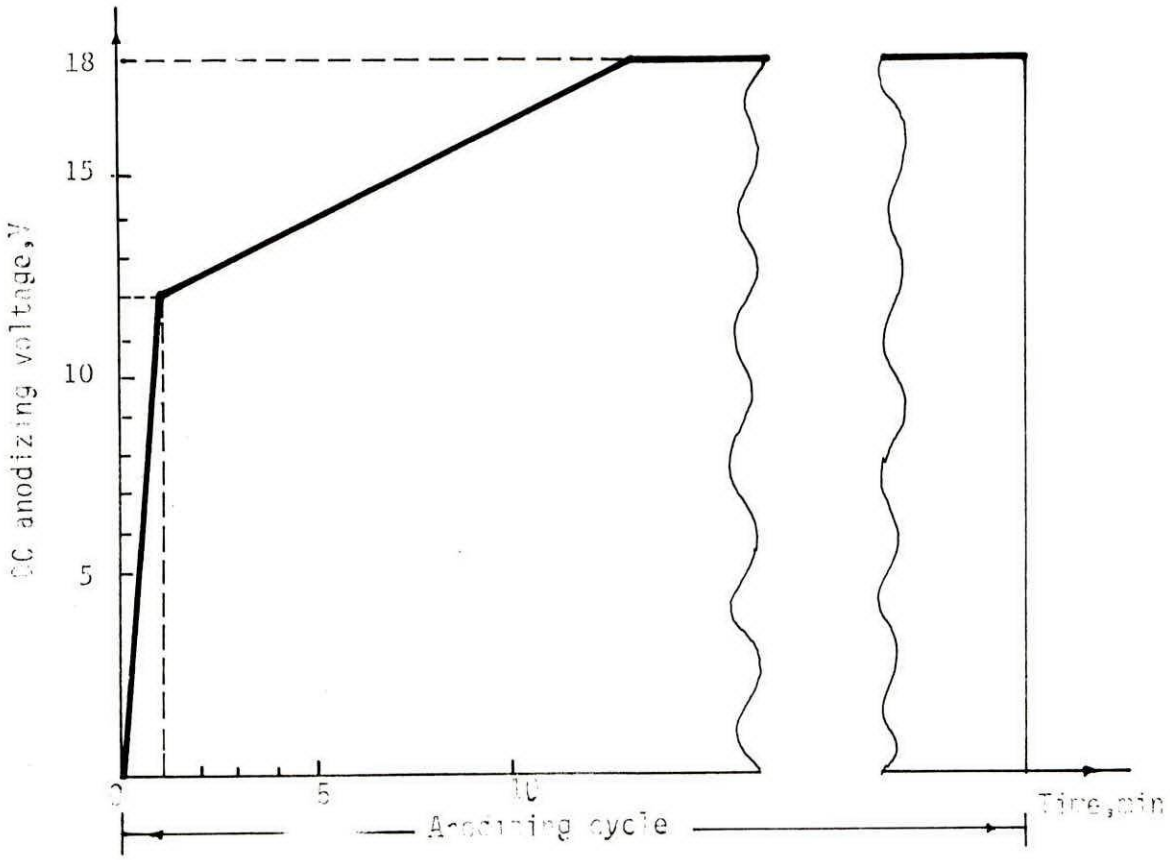



Fig. 1 Voltage-time relationship for the LV-process

The power supply may be with a single or three-phase input and it has a two-terminal output which provides DC voltage with a superimposed AC voltage (see Fig. 2). The AC component may be sinusoidal or non-sinusoidal and the ratio of the amplitude of a sinusoidal component to the DC component may vary. Preferably this ratio should be close to 100% (see Fig. 2c). Some properties of hard-coatings produces by the LV-process are illustrated on Fig. 3 and 4.

The 4 x 4 inch samples of aluminum alloys 2024, 6061, and 7075 were anodized in a water solution of sulphuric acid (200 g/l) with a weak acid additive according to [6] (1/3 of the sulphuric acid content). The temperature of the

electrolyte varied from 40°F to 50°F and is indicated in figure captions.

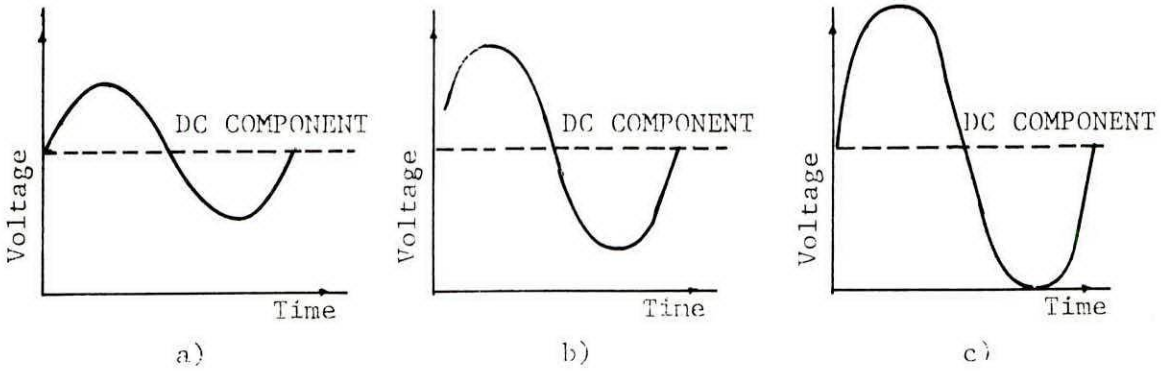



Fig. 2. Voltage waveforms provided by power source 5.
a) 50% AC component; b) 75% component; c) 100% component

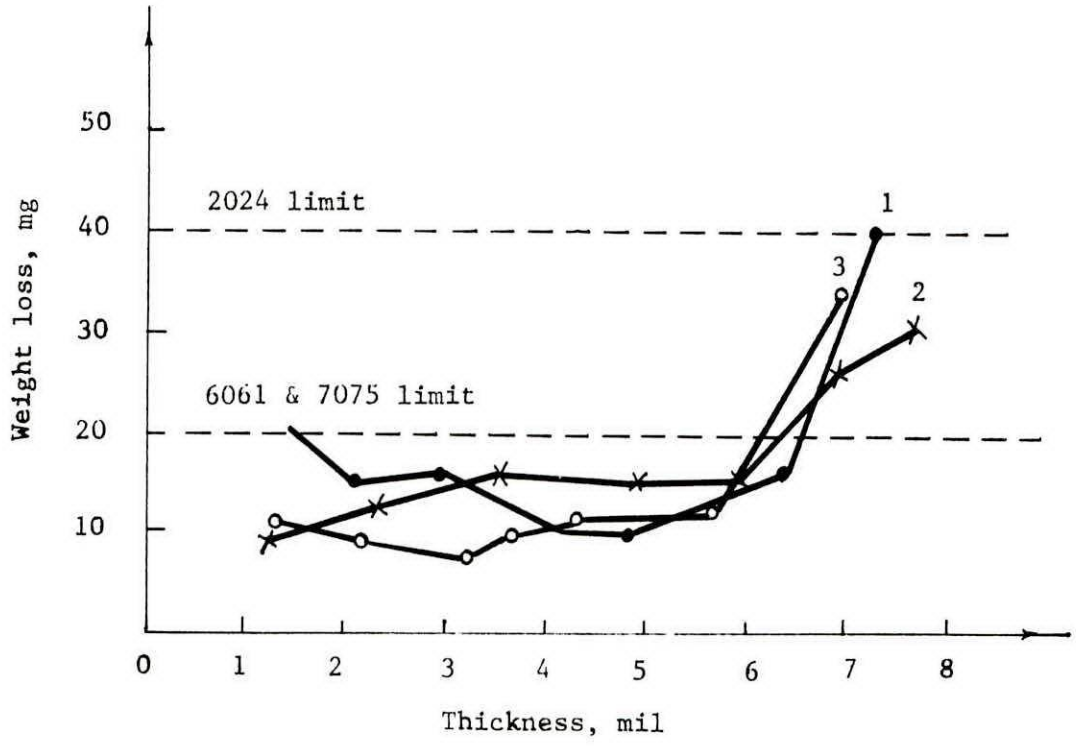



Fig. 3 Weight loss versus coating thickness for the LV-process. 1-2024 alloy, electrolyte temperature 40°F, 2-6061 alloy, 45°F, 3-7075 alloy, 40°F.

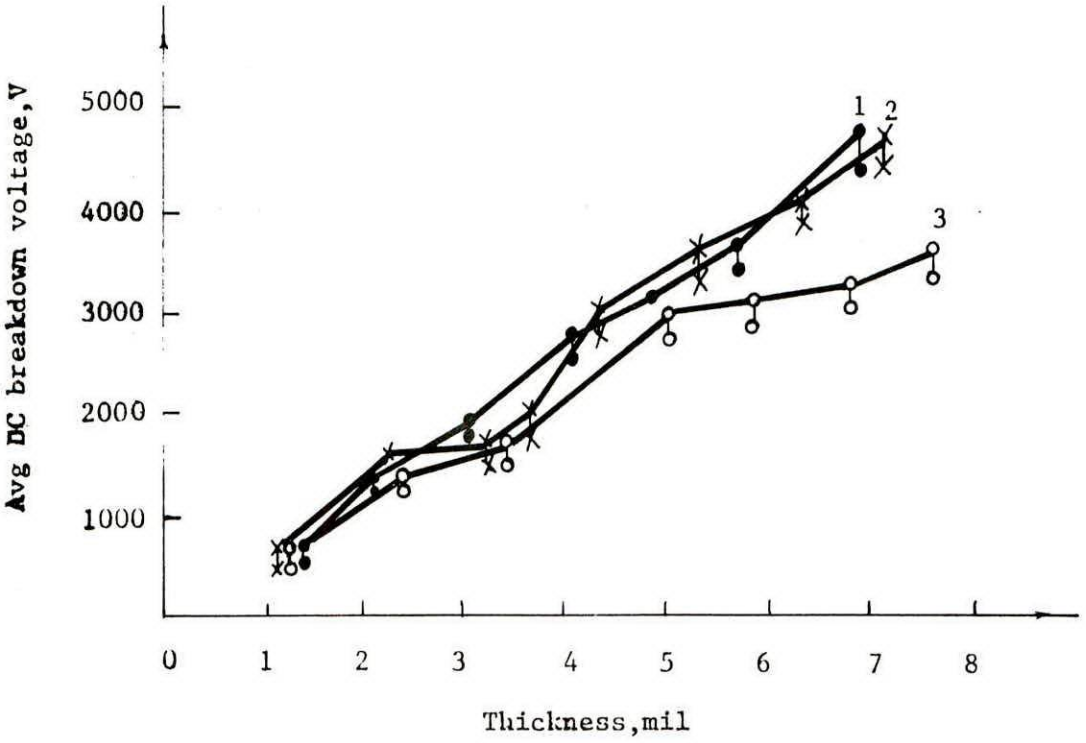



Fig. 4. DC breakdown voltage versus coating thickness for the LV-process. 1-2024 alloy, electrolyte temperature 40°F, 2-6061, 45°F, 3-7075, 40°F.

The LV-process was carried out at a voltage, the negative peak of which would be about the same magnitude as the DC component. The DC component was increased according to the pattern of Fig. 1. The Abrasion Resistance data presented on Fig. 3 were obtained with the help of a Taber Abraser according to method 6192 in Fed. Test Method Std. No. 141a. According to the test, the abrasion resistance is evaluated by the weight loss observed after 10,000 revolutions of the abrasive wheels under a load of 1 kg. A lesser weight loss means a higher abrasion resistance. The horrizontal broken lines represent the admissible level of abrasion resistance according to Military Specification MIL-A8625 C "Anodic coatings for aluminum and aluminum alloys". The possible fluctuations of the abrasion test results described in [7] are taken into consideration. The breakdown voltage data for different alloys are presented on Fig. 4 and were obtained at an average of 12 readings at 12 different spots on the anodized sample. The anodized aluminum was negative during the test. The positive electrode is made of copper with a hemispherical contact area having a 5mm radius. Besides the average data connected on the graph by a solid line, the magnitude of standard deviation is also indicated for each average data being located always below the corresponding average voltage.

The photograph on Fig. 5 illustrates the edges of the two anodized samples of 7075 alloy hard-coated by the LV-process (sample 1) and the HV-process (sample 2). The HV process was a Classic Sanford Process where a convention-

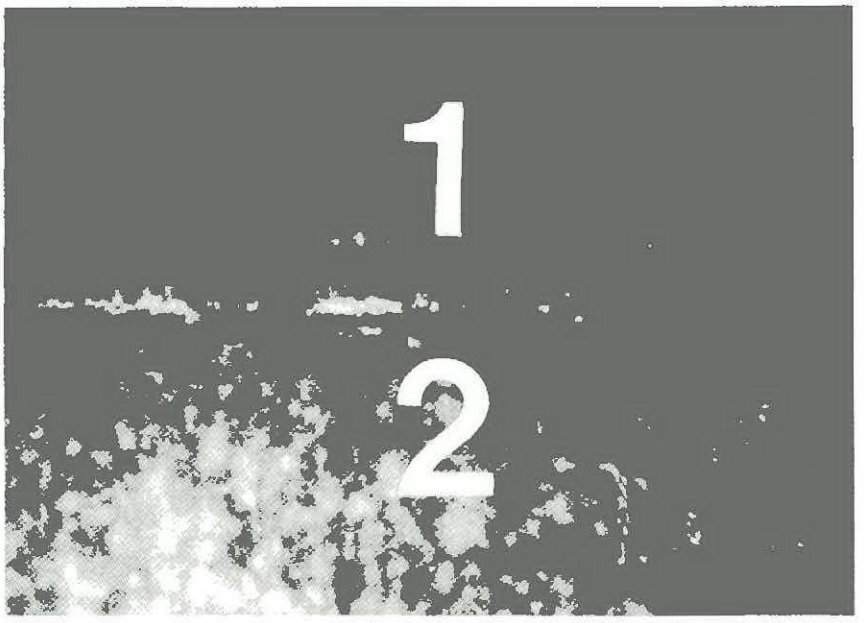
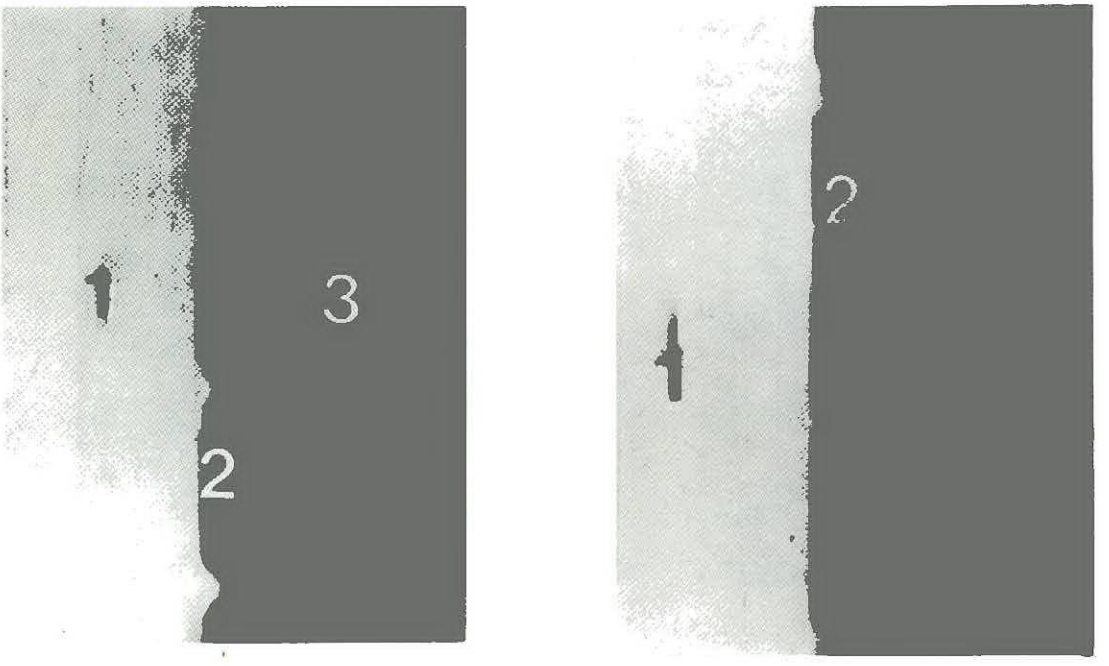



Fig. 5. Edges of two 7075 alloy samples with the same coating thickness. 1-anodized by the LV-process, 2-anodized by the HV-process.




a) b)

Fig. 6 Cross section of an oxide film formed by the HV-process at 29°F: a) 2024 alloy, 2.7 mil, b) 7075 alloy, 3.5 mil. 1 - aluminum, 2- oxide film, 3- plastic medium.

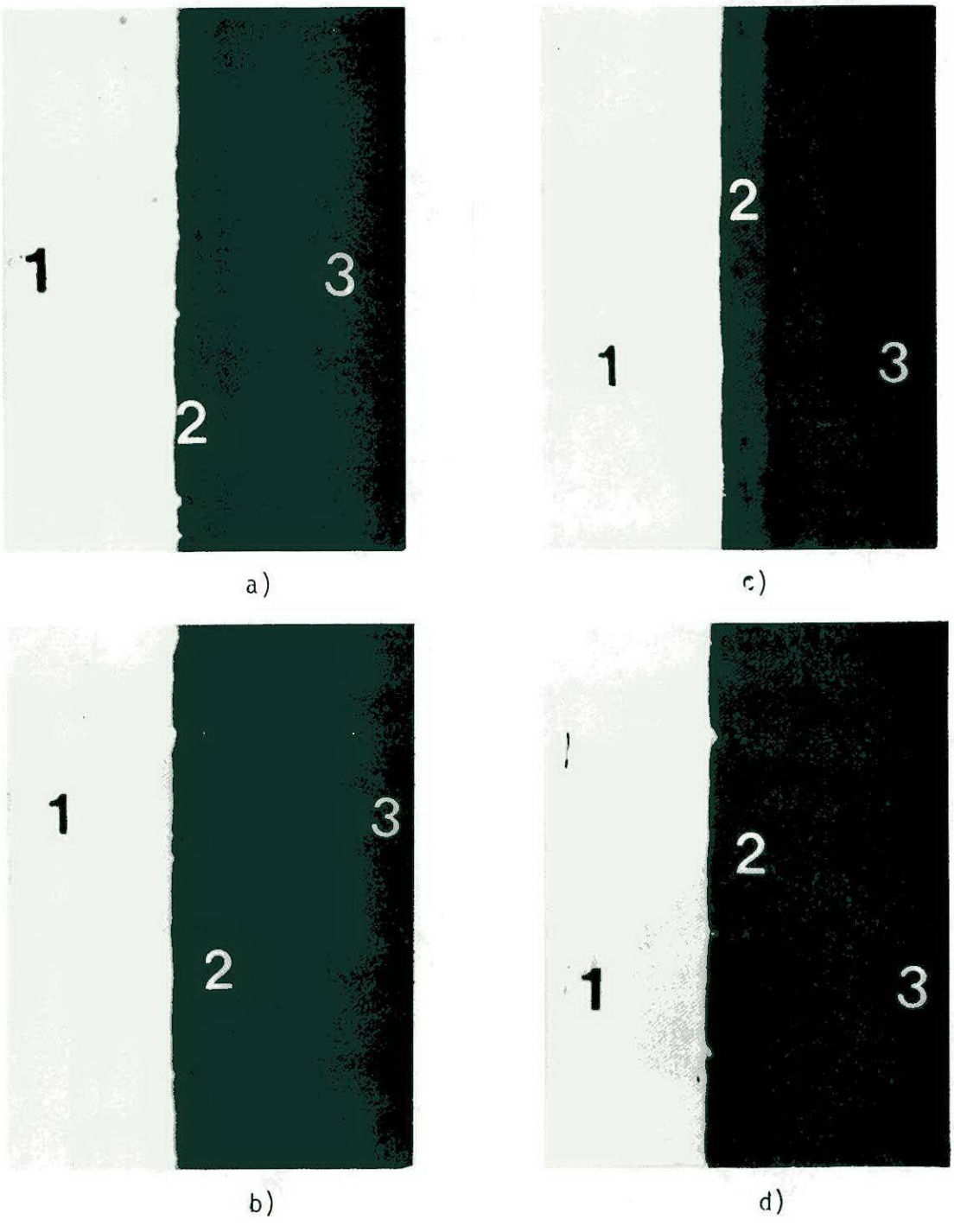



Fig. 7 Cross section of the oxide film formed by the LV-process: a) 2024 alloy, 2.6 mil thick, 40°F, b) 2024, 5.7 mil, 50°F, c) 7075, 3.1 mil, 40°F, d) 7075, 5.6 mil 40°F.

al electrolyte was used (320 g/l of sulphuric acid plus a weak acid additive according to [6]) at a temperature of 32°F. The DC voltage was raised to 18V during the first minute and then about 1V per 2 minutes. The thickness of the coatings on each of the samples was the same - 3 mils.

Photographs in Fig. 6 and 7 illustrate the uniformity of the LV-coatings compared to the HV-coatings (Fig. 6) produced by the Sanford Process described above. Regardless of being hard and meeting the Military Specifications as to Abrasion Resistance requirements, hard oxide films on heavily alloyed aluminum often have internal cavities called pits. A pit exposes itself whenever the oxide film is honed or ground to remove the outer surface.

In spite of conducting the process at a low anodizing voltage the current density during the LV-process is rather high going up to 70-80 A/ft$^2$ on alloy. That is why the time of anodizing is relatively short, which is illustrated by the dependance of the anodizing time upon coating thickness at Fig. 8.

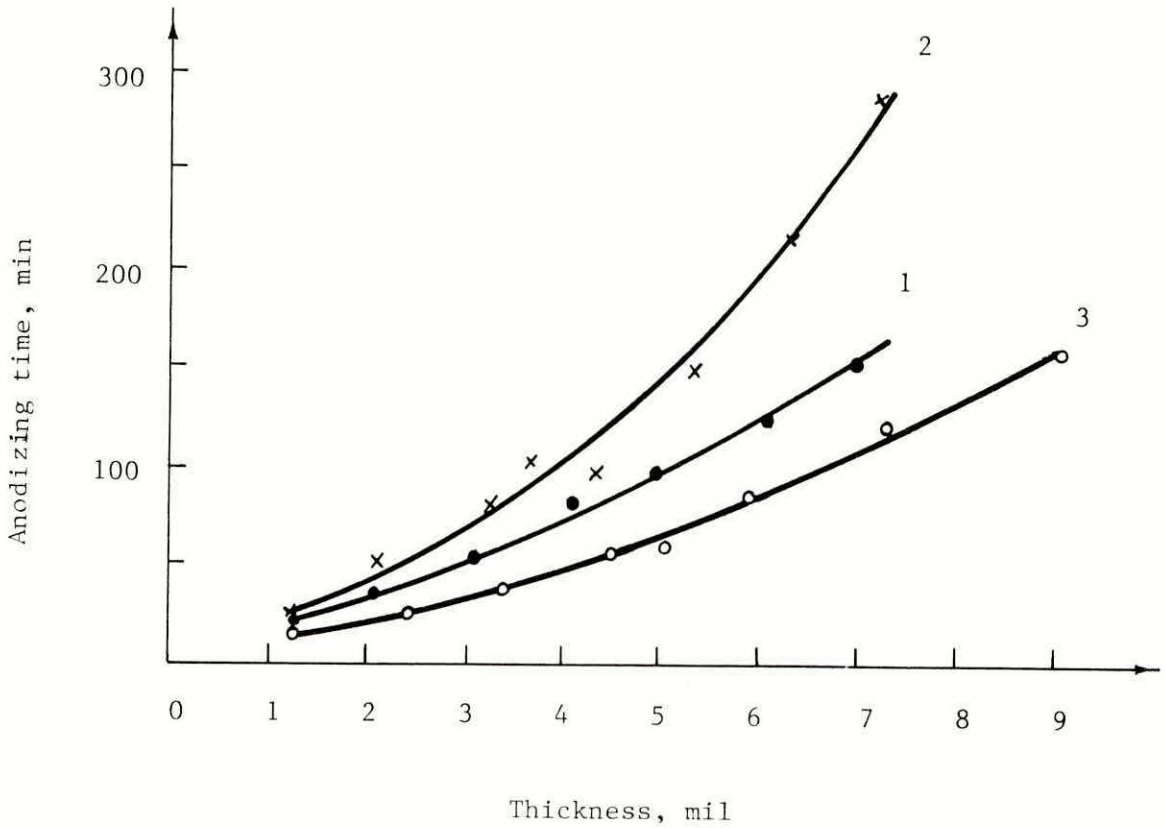



Fig. 8 Anodizing time versus coating thickness for the LV-process. Electrolyte temperature 45°F, 1-2024 alloy 2-6061, 3-7075

## DISCUSSION

The analysis of the abrasion resistance of LV-hard-coatings, as it follows from Fig. 3, shows that these coatings at thicknesses up to 6-6.5 mils remain very hard, meeting the Military Specification requirements with a good reserve. It is remarkable that the 2024 alloy, which in HV-processes yields an oxide film of considerably poorer quality than other alloys as to abrasion resistance, produces a hardcoat of about the same high quality as for other alloys when it is formed by the LV-process.

The data of Fig. 4 show approximately linear increase of the DC breakdown voltage versus thickness for 2024 and 6061 alloy. For a thickness of 6-7 mils the breakdown voltage may exceed 4000V DC. The examination of the photograph on Fig. 5 shows that the sample 1 which was anodized by the LV-process has a clean edge as compared to the edge of the sample 2 anodized by the HV-process. The two samples are shown on the photograph separated by a dark gap. The oxide film at the edge of the sample 2 is formed in a strikingly different manner as compared to sample 1. The sample 2 has a very pronounced "edge-defect".

The analysis of Fig. 6 and 7 demonstrates the dramatic deminishing of the number of pits on 2024 and 7075 alloys when the LV-process is used. The LV-process provides comparatively pit-free coatings not only at 3 mils, but also at 6 mil thicknesses as well.

We believe that the remarkable properties of LV-coatings ensue primarily from the fact that the LV-oxide films are more uniform and ductile. Uniformity is sequential from the anodizing voltage being kept unchanged through a considerable portion of the anodizing cycle. As has been known[8], the distance between the pores in an oxide film is proportional to the applied voltage. This means that the higher the anodizing voltage, the fewer pores per unit of surface area will be formed. In the LV-process, the maximum $V_{max}$ is reached during a short period (run-in period) and then the voltage stays unvariable (dwell period). At Fig. 9 the run-in period is schematically represented only by two voltage steps, $V_1$ and $V_2$, before the maximum voltage $V_{max}$ is reached. At each step, the formed oxide has a porosity corresponding to the voltage of the step. So, when the maximum voltage was reached two different layers, 1 and 2, with different porosity had been formed. The major part of the coating, layer 3, is formed during the rest of the anodizing cycle (dwell period) when the voltage remained maximum. That is why the coating, except the very external layer, (See Fig. 9) has homogeneous porosity.

On the other hand, since the maximum DC voltage is much lower than in the case of a HV-process the oxide film is much more porous. As a consequence the oxide film is more ductile and less susceptible to cracking, ensuring a neat and clean edge at a thickness where HV-process will cause a considerable edge-defect. Higher porosity also causes savings of Coulomb electricity. According to Faraday's law, a definite amount of electricity Q (in Coulombs) is needed to produce a definite mass M of coating via an electro-chemical

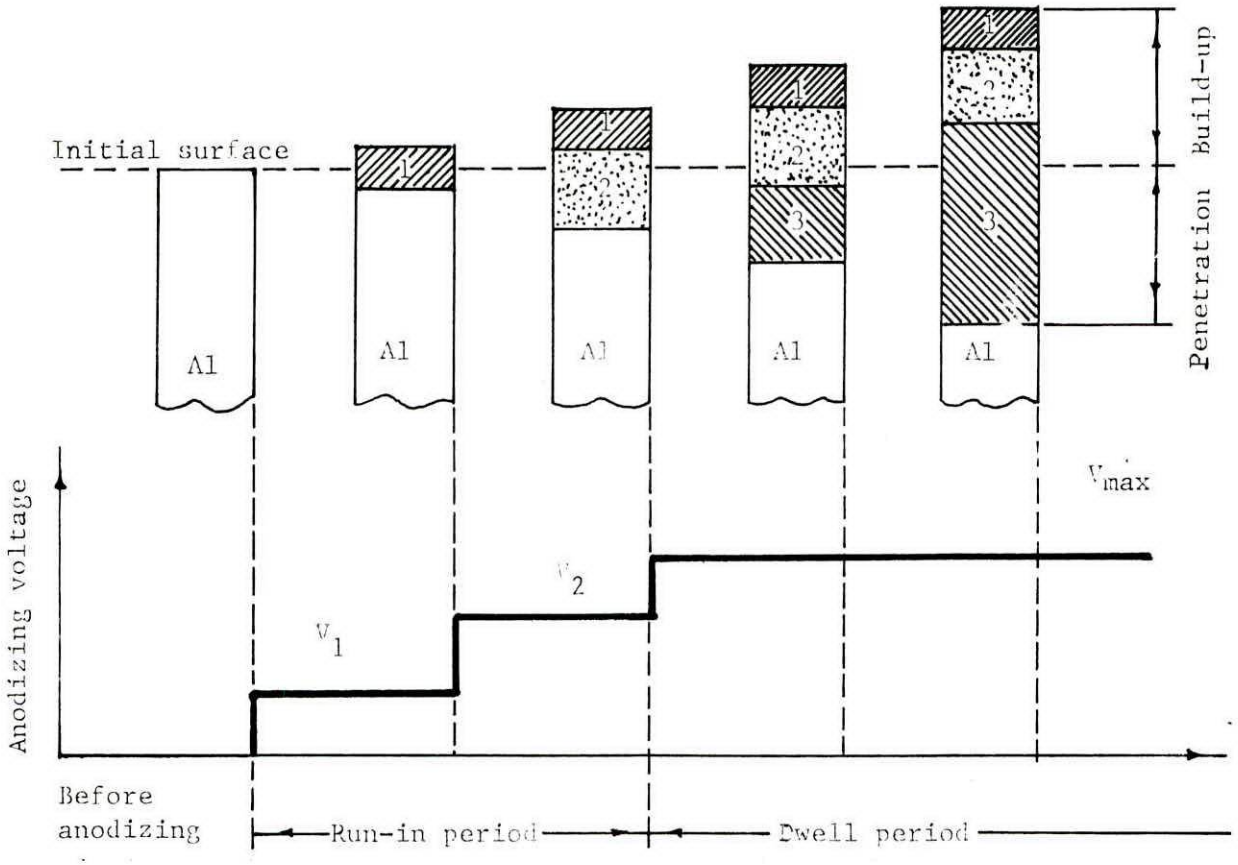



Fig. 9. Schematic diagram for oxide film growth during the LV-process. 1,2-oxide film formed during the run-in period, 3-oxide film formed during the dwell period.

process:

$$Q = K M \qquad (1)$$

where k is Faraday constant.

Mass is related to coating surface S, thickness d and density D by equation

$$M = d.SD \qquad (2)$$

Consequently from (1) and (2) we deduce

$$Q = k.Sd.D$$

From this equation if follows, that if density D of the oxide film diminishes, which happens when anodizing is conducted at a lower voltage, then the amount of electricity which is needed to produce a coating of the same thickness d on the same surface S also diminishes. The HV-process, like Sanford Process, needs 12 ampere-hours to cover 1 square foot (929 $cm^2$) with one mil (25.4 ) thickness. The LV-process needs only 10.6 A.h/$ft^2$/mil, which gives about 15% savings of electricity.

Examination of the anodizing time data, presented at Fig. 8, shows that the 7075 alloy needs the shortest period to form an oxide film of the same thickness as on other alloys. 2024 alloy needs about 30% more time, and 6061 alloy about 2.5 times more. It is remarkable that with the help of the LV-process 6 and even 7 mil-thick-films may be anodized on 6061 alloy temper T6 after a reasonable period of time (200-250 min - see Fig. 8) and these coatings are still hard (see Fig. 3). It is ordinarily difficult to obtain more than 3-3.5 mils on this alloy if a HV-process is used.

## CONCLUSIONS

Low voltage hard anodizing process, (the LV-process) permits the manufacture of oxide films which are superior to the coatings anodized by the HV-process. The new coatings produced by the LV-process are more uniform, have higher abrasion resistance, less pronounced edge-defect, higher breakdown voltage, and are more porous and ductile. The new process is simple to operate and it saves energy.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge Roger Huebsch and Donald Gosch for the constant encouragement and support which helped to develop the new process. They are also indebted to M. Bessendorf and J. English for their assistance in the Laboratory and shop research. The authors are very thankful to Mrs. Mary Perry for the help in preparing this paper.

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# LIGHT METALS FINISHING SESSION E

## Continuous Coil Anodizing—A Technical Update

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# CONTINUOUS COIL ANODIZING - A TECHNICAL UP-DATE

Howard A. Fromson

The current annual consumption of pre-anodized coil in the United States is estimated at more than 100,000,000 pounds. During its early market development preanodized coil was used primarily as a substitute for batch-anodized aluminum in transportation (truck siding, trailer roof panels, etc.), consumer durables (appliance panels, welded furniture tubing) building components (lighting reflectors, ceiling panels, kitchen tiles). Its relative flexibility permitted post-anodizing fabrication such as bending and punching without any significant damage to the anodic coating, particularly in applications for interior use.

The costs were substantially less than batch anodizing, in some cases 1/4 the cost, and where exposed edges or slight crazing could be tolerated, many millions of dollars were saved.

These existing markets for traditional pre-anodized products have continued to expand, but at a much slower rate. Organic coatings, high temperature resistant, corrosion resistant, and esthetically attractive, have provided strong competition.

But other markets, primarily technical in nature, have provided new opportunities for continuous coil anodizing.

The single largest non-decorative market for pre-anodized aluminum coil is in lithography. Approximately 400,000,000 square feet of anodized aluminum coil are consumed for lithographic purposes in the United States alone.

Millions of pounds of aluminum are also pre-anodized to form the separator on the double and triple glazed window and door sections so much in demand in these days of high-energy costs. Pre-anodized aluminum coil is even used in such sophisticated applications as the phosphorescent luminescent panels now becoming so popular in automotive and aeronautical instrument panels.

Most of these new technical applications for pre-anodized coil demand high-speed operations to minimize unit costs. The thickness or gauge of the coil in these new markets is generally under .020", and in some cases is as thin as .002"

The limiting parameter in continuous coil anodizing for technical use, particularly for light gauges has been the ability to introduce current into the web at high rates without burning the web. As most of you are aware, in continuous coil anodizing the web is used as its own conductor. The ultimate constraint is the current-carrying capacity of the web, which in turn is a function of its cross-sectional area.

Various methods have been proposed to increase productivity or the rate at which current can be introduced into the web without burning. They divide themselves into four techniques:

A. Baffled Entry, a process for limiting electrical current flow at the moment of critical entry into the electrolyte to guarantee formation of a completely sound barrier layer before high current anodizing begins.[1]

B. One Side Anodizing, a process to minimize the amount of total current required by limiting the anodizing process to one side of the web.[2]

C. Stepped Current Introduction, a process to maximize the amount of total current carrying capacity at higher voltages by a gradual step-wise increase in a multi-cathode, multi-rectifier tank, the increase in cathode area being controlled with respect to the current per unit cross section, so as to prevent premature return of current to the rectifier.[3]

D. Turbulent Pressurized Cooling, a process to increase the current carrying capacity of the web/conductor by high turbulent flow of a continuously recirculating electrolyte around the web within the confines of an enclosed elongated vessel containing both the positive and negative electrodes.[4]

In the early 1970's, our company, Ano-coil Corporation of Rockville, Connecticut began to experiment in new ways of introducing current into continuous anodizing lines, which eventually resulted in a series of patents. We chose to remain with our basic contact cell technology: our goal was to increase our productivity without substantially altering our physical and electrolytic plant. Ten years of experience of operating our lines had taught us how critical very minor changes in cathode configuration, pump velocities, temperature of electrolyte, as well as simple line tension could be when introducing current into continuous webs. We elected, therefore, to stay with our basic line concept of highly visible webs and easily accessible rolls in open-faced tanks.

The process was based on the unique valve characteristics of anodized oxides, similar to that of semi-conductors. When aluminum is made the anode in a standard polyvalent acid such as sulfuric acid, the barrier oxide is formed at somewhere around 12v. With the same electrolyte, and the same amperage used to originally anodize the surface, but reversing the polarity on the already anodized aluminum surface to make it the cathode, the voltage dropped from 12 to 2 volts. In other words, the voltage required to form the anodic oxide is approximately 12 volts, but the voltage required to carry the current through the oxide cathodically is only 2 volts.[5]

With this insight, we designed an anodizing cell where the current was introduced into the web through an already existent oxide film. Let me explain!

A typical coil anodizing line would use a contact drum or a liquid contact cell. The liquid contact cell permits the introduction of somewhat larger currents into the moving web, but the cross section of the web is still

the limiting factor. In order to understand the theory of our process, let me first describe how the conventional liquid contact works. Figure 1 shows a schematic diagram of a coil line where the web enters the liquid contact cell A. Current is fed from the positive side of the rectifier to lead

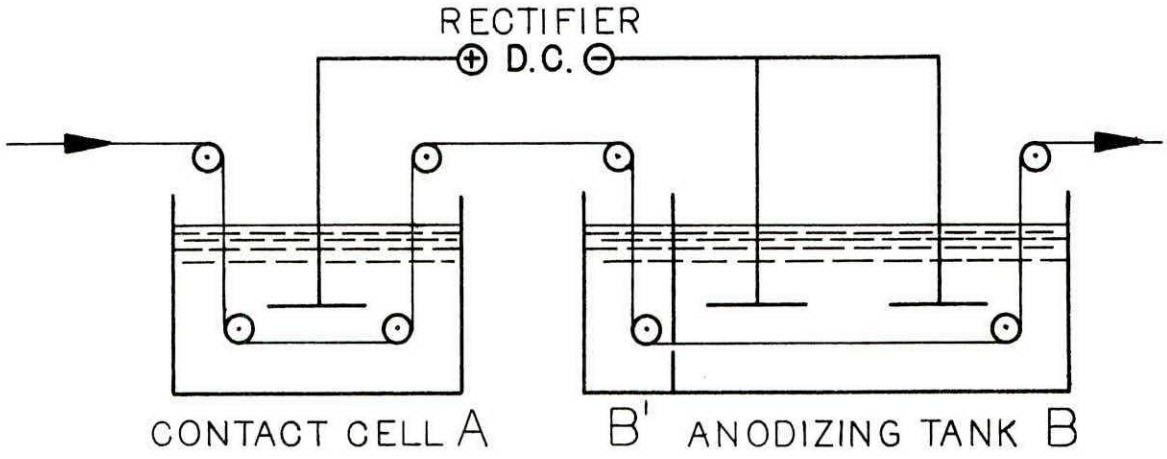


FIG. 1

anodes, and flows through the electrolyte to the web which is negative relative to the anode. The negative side of the rectifier is connected to lead cathodes in the anodizing tank B. The current travels through the web, which enters the baffle area $B^1$ as it passes through the anodizing tank. In this tank, the web becomes the anode, and an anodic coating is formed on both surfaces of the web. The web then passes through rinses, a dye bath if required, and a seal bath.

Our process adds another anodizing tank located upstream from the liquid contact cell as shown in Figure 2. Furthermore, we add one more rectifier. We now have anodizing tank A, followed by liquid contact cell B, followed by anodizing tank C. (We call this the ABC process). The positive side of Rectifier 1 is connected to one of the lead anodes in the liquid contact cell and the negative side is connected to lead cathodes in tank A, the first anodizing cell. The positive side of Rectifier 2 is connected to the second lead anode in the same liquid contact cell, and the negative side is connected to the lead cathodes in the second anodizing tank B. The current from Rectifier 1 now forms a loop through the web in Tank A and back to the Rectifier. The moving web, which now has an anodic coating, passes through liquid contact cell B. The current from Rectifier 2 passes through the oxide coating to the web into tank C where the anodizing continues as the current completes the loop back to Rectifier 2.

Having made it possible to introduce current into an aluminum web

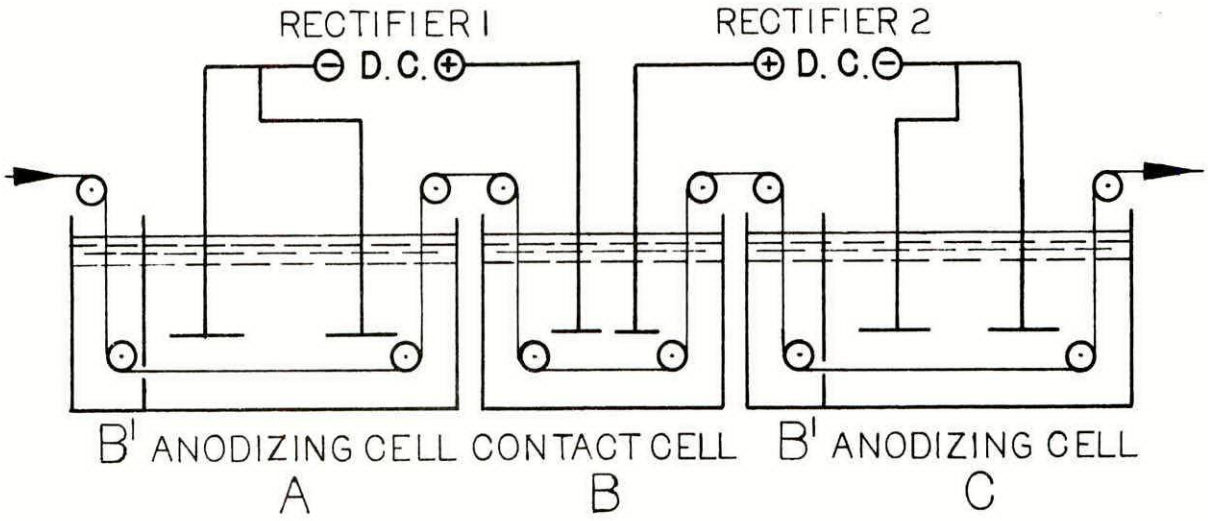


FIG. 2

through the oxide itself, at a cost of only 2 volts of resistance, it now became possible to design a series of cells, such that substantially all the current is pumped into the web at a multiplicity of points, each cell functioning with its own anodizing circuit, so current can be introduced into the web through a multiplicity of cross-sections.

Having determined that current can be introduced intc an aluminum web through the oxide at a cost of only 2 volts, a completely new design concept is now possible. Since the ABC process eliminates the need to carry the total anodizing current through one cross-sectional area of the web, it is possible to double or even quadruple the amount of energy in the web by simply introducing additional current at one or more sections of the web. viz. Figure 3

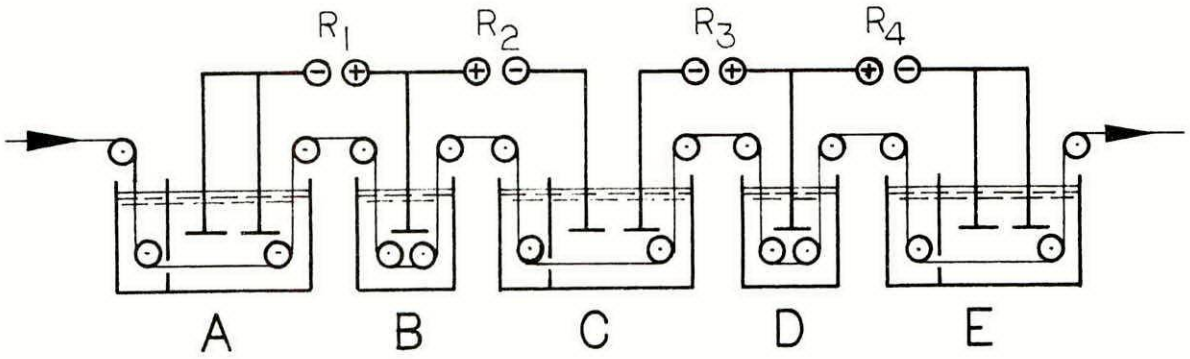


FIG 3

It will be apparent also that it is possible and desirable to use different voltages at succeeding locations as the anodic oxide becomes thicker.

Since the electrolyte dissolves a portion of the newly formed anodic coating, close control of the temperatures in all tanks, particularly the liquid contact cell, is critical. A correction must be made for the slight loss of anodic oxide which occurs, but this has been found to be constant for any given set of conditions.

We at Ano-coil have been using the ABC process for more than six years. During this period we have anodized webs as thin as .002 x 48" and we have increased the productive capacity of our equipment by more than 100% without additional lines. We presently have licensees who, without the ABC process would not have been able to produce an anodic film at a competitive price.

The unique features of our process make it possible to utilize the anodized web for many other subsequent treatments. With ABC it is now possible to simultaneously anodize, and often times with the same current, electro-plate, electro-paint, and/or electrolytically dye a continuous web or wire of aluminum at high speeds.[6] We have successfully deposited nickel, copper, and chrome in and on anodized substrates by utilizing the negatively charged web in the contact cell with suitable electrolytes as the plating substrate. And if there were sufficiently large markets ABC lends itself to the continuous production of coiled sheet or wire self-dyed by the Kalcolor ™ or Duranodic™ processes of Kaiser Aluminum and Alcoa.

To sum up, the Ano-coil ABC process results in the following advantages for coil anodizing:

A. A more than 100% increase in productivity.

B. A substantial slash in capital cost per unit capacity.

C. The opportunity to continuously anodize in electrolytes that require stepped increases in voltage.

D. The possibility to continuously electro-deposit metallic and organic coatings and inorganic dyes in and on porous anodic oxides.

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E-3

# LIGHT METALS FINISHING SESSION E

## The Coloration of Anodized Aluminum Architectural Components by the Overdyeing of Integral Color or Two-Stage Electrolytically Colored Oxide Films

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# The Coloration of Anodized Aluminum Architectural Components by the "Overdyeing" of Integral Color or Two-Stage Electrolytically Colored Oxide Films.

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## Abstract

The range of colors available from the currently used architectural anodizing processes leaves much to be desired for the architect who wishes to make full use of color as a design element. The overdyeing of either integral color or two-stage electrolytically colored anodic oxides with selected organic dyes enables the architect to offer new shades which were previously unavailable. The suggested processing conditions and control procedures to assure consistantly high quality are discussed in detail. The results of laboratory tests and preliminary exterior exposures are also presented.

In the presentation today, we will describe new methods for producing a wide range of colors heretofore unattainable. These colors are produced by combining current available technology; that is to say we will 'over-dye' either an integrally colored or a 2-stage electrolytically colored oxide film with selected organic dyes to obtain a colored film having the characteristics of both methods for coloration.

We will discuss the basic integral color process, the basic two stage electrolytic coloring process and the combined process, with emphasis on the controls required in the dyeing steps, since these procedures may not be familiar to you.

We will also present some data concerning the lightfastness of the combined process, the amount of dye actually in the coating, and the location of the various colorants within the oxide film.

During the past twenty years the continued improvements in old methods and new developments in processing technology for the production of colored architectural components, have been responsible for the increasing use of color as well as form as a part of the structural component.

At present there are basically two methods for producing colored aluminum architectural components: (Slide 1)

COLORED ORGANIC COATINGS --- PAINTS

ANODIC COATINGS ------

INTEGRAL COLOR
TWO-STAGE ELECTROLYTIC
ADSORBTIVE DYEING

Slide 1

METHODS FOR COLORING ARCHITECTURAL COMPONENTS

COLORED ORGANIC COATINGS — PAINTS

ANODIC COATINGS— —

- INTEGRAL COLOR
- TWO-STAGE ELECTROLYTIC
- ADSORBTIVE DYEING

Using paints it is possible to obtain an almost unlimited range of colors, including pastels and even white. In spite of this obvious advantage, the method is not without drawbacks - the possible loss of adhesion of the coating, scratching or abrasion of the film, and most importantly, the hiding of the metallic characteristics of the aluminum substrate.

With those methods based on anodizing, we are able to preserve the metallic appearance of the substrate, due to the relative transparency of the oxide film.

Let us now discuss the ways of producing architecturally "useful" colored oxide films.

The next slide shows the basic integral color process. (Slide 2)

INTEGRAL COLOR PROCESS

| | |
|---|---|
| Basic Electrolyte | "SULFO" acid with low sulfuric acid content |
| Current Density | 2.5-3.7 amps/sq.dm<br>24-36 ASF |
| Voltage | 65-80 final voltage |
| Temperature | 21-30°C (70-78°F) |
| Colors | Limited range - BRONZE<br>GREY<br>BLACK |

In the next slide we show the basic two-stage electrolytic process. (Slide 3)

TWO - STAGE ELECTROLYTIC COLOR PROCESS

Conventional Sulfuric Anodize -- Followed by
Electrolytic Color Deposition
AC Treatment in electrolyte containing
NICKEL, COBALT, COPPER or TIN salts

Two Separate Processes

Oxide thickness determined by function, NOT COLOR
Easier color control - NOT alloy or temper dependent
Lower voltage & current needed - AC rather than DC
Color independent of thickness

The two-stage processes seem to be gradually replacing the integral color processes, in spite of requiring additional tanks and equipment. They do not need the high DC voltages or refrigeration needed in the integral color process. Also in the two-stage electrolytic process the color is not dependent on the

Slide 2

## INTEGRAL COLOR PROCESS

| | |
|---|---|
| Basic Electrolyte | "SULFO" acid with low sulfuric acid content |
| Current Density | 2.5-3.7 Amps/sq.dm (24-36 ASF) |
| Voltage | 65-80 V — Final |
| Temperature | 21-30 °C (70-78 °F) |
| Colors | Limited range — BRONZE<br>GREY<br>BLACK |

## TWO — STAGE ELECTROLYTIC COLORING PROCESS

Conventional Sulfuric Anodize — — Followed by

Electrolytic Color Deposition
AC Treatment in electrolyte containing NICKEL, COBALT, COPPER or TIN salts

- Two Separate Processes

Oxide thickness determined by function, NOT COLOR
Easier color control-NOT alloy or temper dependent,
Lower voltage & current needed — AC rather than DC
Color independent of thickness
Limited color range

oxide film thickness, the alloy, temper or some of the other variables as in the integral color processes.

With regard to the over dyeing of these colored oxides, any of the colors which can be produced are suitable, but the bronze shades offer the most interesting range of new colors.

It is not possible to do the dyeing step before the electrolytic coloring, since in some cases the presence of the dye will interfere with the deposition of the inorganic colorant. Also, the treatment of the dyed film in a highly acidic media, such as that required in electrolytic coloring even without the current, generally causes bleeding out of the dye, resulting in non-uniform color and inherent lightfastness problems.

It should also be pointed out that the RINSING between the various processing steps MUST be of the highest quality, preferably a cascade, counter-current station with a total dwell time of about 10 minutes followed by a standing distilled or DI water rinse of 2-3 minutes duration. This will ensure that there will be minimal drag-in of either the electrolytic coloring bath or the sulfuric acid into the dyebath.

For the dyeing step, we find that the same high standards which are required for the dyeing of clear architectural work must be adhered to. These are shown in the next slide. (Slide 4)

DYEING CONDITIONS

| | content g/l* | pH + 0.5 | Shade |
|---|---|---|---|
| Yellow 3GL | 3.0 | 5.5 | Lemon Yellow |
| Red B3LW | 5.0 | 5.5 | Garnet Red |
| Blue G | 5.0 | 5.5 | Dark Blue (navy) |
| Turquoise PLW | 12.0 | 5.0 | Turquoise |
| Black GL Paste | 30.0 | 5.0 | Black (Graphite) |
| Deep Black MLW | 10.0 | 4.5 | Jet Black (Telephone) |
| Gold 4N | 10.0 | 4.5 | Gold Shades** |

*"Effective Dye Content ---- 75-80% of nominal
Dye Time 20-30 Minutes except Golds
Dye Temperature 60°C ± 5 (140°F. ± 9 except Golds)

**Gold --- Bath Temperature 50°C. (120°F.)

| Immersion Time | |
|---|---|
| 2 minutes | Champagne |
| 4 minutes | Pale Gold |
| 6 minutes | Medium Gold |
| 10 minutes | Dark Gold |

Slide 4

## DYEING CONDITIONS

| | Nominal Content g/l* | pH ±0.5 | Shade |
|---|---|---|---|
| Yellow 3GL | 3 | 5.5 | Lemon Yellow |
| Red B3LW | 5 | 5.5 | Garnet Red |
| Blue G | 5 | 5.5 | Dark Blue (Navy) |
| Turquoise PLW | 12 | 5.0 | Turquoise |
| Black GL Paste | 30 | 5.0 | Black-Graphite |
| Deep Black MLW | 10 | 4.5 | Jet Black |
| Gold 4N | 10 | 4.5 | Gold Shades** |

*"Effective" Dye Content — 75 - 80% of NOMINAL

Dye Time 20 - 30 Mins — Except Gold
Dye Temperature 60°C + 5 (140°F + 9) — Except Gold

| | | | |
|---|---|---|---|
| GOLD | Bath Temp. | 49°C — | 120°F |
| | Immersion Time | 2 Mins. | Champagne |
| | | 4 Mins. | Pale |
| | | 6 Mins. | Medium |
| | | 10 Mins. | Dark |

The controls needed are shown in the next slide. (Slide 5)

DYEING CONTROLS

| | |
|---|---|
| Constantly Monitor | Temperature of Dyebath<br>Immersion Time |
| Each Shift or Daily | pH of the dye solution |
| Daily | Dye Concentration |
| Weekly | "Effective" Dye Concen=<br>tration |

As for the Sealing operation, we suggest the conditions which are shown in the next slide. (Slide 6)

SEALING CONDITIONS

| | |
|---|---|
| Nickel Acetate | 3-5 g/l Nickel |
| pH | 5.5-6.0 |
| Temperature | 97°C (207°F) Minimum |
| Time | 45 Minutes |

In the control of the dyeing operation, the techniques required for measuring the dye content (both nominal and effective) are NOT widely practiced. I will briefly outline them for you. For the nominal, we optically compare (using a spectrophotometer or colorimeter) the absorbtion, at a fixed wavelength in the visible region, of a freshly prepared solution of the proper dye content with the absorbtion, at the same wavelength, of a sample of the tank solution. Naturally both solutions must be at the same dilution, pH, etc. By calculation we can arrive at the ratio of the strength of the working tank.

In order to determine the "effective" strength of the dye tank, and by "effective" dye content, I mean that portion of the total dye content present which is actually effective in the coloration of the oxide. To measure this "effectiveness", we must do the following: Using two pieces of anodized aluminum of the same convenient size, (area known) we dye one in a fresh solution of the proper dye content (100% activity) and the other in the working solution. We then strip the coating and dyestuff using inhibited sodium hydroxide, (to prevent destruction of the dye), and measure the absorbance of these two solutions. From this we can calculate the "effective" dye content.

Knowing the effective dye content, we can make additions to the tank to bring it up to the correct dye strength. It has been

## CONTROLS FOR DYEING

| | |
|---|---|
| Constantly — | Temperature |
| | Immersion Time |
| Each Shift — or Daily | Dye Bath pH |
| Daily — | Dye Concentration |
| Weekly — | "Effective" Dye Content — Gold |

## SEALING CONDITIONS

| | |
|---|---|
| Nickel Acetate | 3 - 5 g/l Nickel |
| pH | 5.5 - 6.0 |
| Temperature | 97° C (207° F) Minimum |
| Time | 45 Minutes |

found in practice that, when the effective strength falls to 75-80% of the nominal content, it is NOT practical to reinforce the bath because the level of contamination is too high. The things that decrease the effective content are mainly sulfate and aluminum ions, both of which combine with the dye molecule and render it ineffective in coloring the oxide film. Good rinsing, therefore, is essential to keep sulfates and aluminum out of the dyebath.

Having discussed the individual processing steps in some detail, we shall now present some test data which was obtained from specimens prepared as follows. (Slide 7)

SAMPLE PREPARATION

| | |
|---|---|
| Degrease and Matte Etch | |
| Anodize to 25 Micron (1.0 Mil) | 16% Sulfuric Acid<br>60 minutes<br>14-15 Volts DC<br>1.3 amps/Sq. dm.<br>(12 ASF)<br>21°C (70°F) |
| Electrolytically Color | AC Treatment in either<br>1. Nickel Bath<br>2. Tin Bath |
| Dye | GOLD 4N<br>YELLOW 3GL<br>RED B3LW<br>BLUE G<br>TURQUOISE PLW |
| Seal | Nickel Acetate Based |

The next slide shows admittance data for a number of samples prepared in a nickel bath. (Slide 8)

Slide 7

## SAMPLE PREPARATION

| | |
|---|---|
| Degrease and Matte Etch | |
| Anodize to 25 Micron (1.0 Mil) | 16% Sulfuric Acid<br>60 minutes<br>14-15 Volts DC<br>1.3 amps/Sq. dm. (12 ASF)<br>21 °C (70 °F) |
| Electrolytically Color | AC Treatment in either<br>1. Nickel Bath<br>2. Tin Bath |
| Dye | Gold 4N<br>Yellow 3GL<br>Red B3LW<br>Blue G<br>Turquoise PLW |
| Seal | Nickel Acetate Based |

Slide 8

## ADMITTANCE VALUES
Micro Siemens

| | ELECTROLYTIC BRONZE NICKEL SALT | | | |
|---|---|---|---|---|
| | CLEAR | LIGHT | MEDIUM | DARK |
| CLEAR | 12 | 12 | 12 | 13 |
| Red B3LW | 12 | 12 | 12 | 12 |
| Yellow 3GL | 13 | 13 | 13 | 13 |
| Turquoise PLW | 14 | 14 | 14 | 14 |
| Blue G | 50 | 50 | 50 | 50 |

ADMITTANCE - MICRO SIEMENS

| | ELECTROLYTIC BRONZE NICKEL SALT | | | |
|---|---|---|---|---|
| | CLEAR | LIGHT | MEDIUM | DARK |
| CLEAR | 12 | 12 | 12 | 13 |
| RED B3LW | 12 | 12 | 12 | 12 |
| YELLOW 3GL | 13 | 13 | 13 | 13 |
| TURQUOISE PLW | 14 | 14 | 14 | 14 |
| BLUE G | 50 | 50 | 50 | 50 |

The admittance data is as anticipated and is similar to the values found on clear dyed films. The high values found for the blue were also found in our earlier work.

The results of both standard salt spray and the Kasternich tests are the same as those of either the electrolytic or dyeing process alone. Thus the corrosion resistance of the combined process is anticipated to be the same as that of either process alone.

In the accelerated corrosion tests, no differences were noted between dyed and undyed specimens prepared as we have discussed. Acid dissolution tests show no effects of degradation of the oxide film by either the dye or the dyeing operation with the exception of Sanodal Blue G, which seems to cause a loss in corrosion resistance as measured by this test. This does not show up in either CASS or the Salt Spray results, however.

The admittance values for electrolytic films colored in tin salts (not shown) are all higher, due no doubt to the low pH of the tin bath attacking the unsealed oxide.

The results of weight-loss tests are all in the range of 2-8 $mg/dm^2$ - well within the permissible limits.

The loss of colorant intensity after 3200 hours of Fade-O-Meter exposure is shown in the next slide. (Slide 9)

Slide 9

## LOSS OF COLOR INTENSITY

Fade-O-Meter 3200 Hours

| | ELECTROLYTIC BRONZE | | | |
|---|---|---|---|---|
| | CLEAR | LIGHT | MEDIUM | DARK |
| CLEAR | 0 | 0 | 0 | 0 |
| Gold 4N | 5 | 5 | 5 | 5 |
| Red B3LW | 0 | 0 | 0 | 0 |
| Yellow 3GL | 0 | 0 | 0 | 0 |
| Turquoise PLW | 10 | 10 | 10 | 10 |
| Blue G | 0 | 0 | 0 | 0 |

LOSS OF COLOR INTENSITY 3200 Hours FADE-O-METER

| | ELECTROLYTIC BRONZE | | | |
|---|---|---|---|---|
| | CLEAR | LIGHT | MEDIUM | DARK |
| CLEAR | 0 | 0 | 0 | 0 |
| GOLD 4N | 5 | 5 | 5 | 5 |
| RED B3LW | 0 | 0 | 0 | 0 |
| YELLOW 3GL | 0 | 0 | 0 | 0 |
| TURQUOISE PLW | 10 | 10 | 10 | 10 |
| BLUE G | 0 | 0 | 0 | 0 |

The behavior exhibited by the gold and turquoise are the same as was seen in previous work, and we also see that the presence of the electrolytically deposited colorant has no adverse effect on the light fastness of the organic dye. The exposure corresponds to about 5 years of natural weathering. The preliminary results of long term exterior exposures confirm the laboratory findings - these tests are continuing.

It is possible to measure the quantity of organic dye in an anodic coating by dissolving the oxide and then measuring the amount of colorant using spectrophotometric methods. The extinction values shown are dimensionsless and are a measure of the amount of dye present in the film. (Slide 10)

EXTINCTION VALUES

| | ELECTROLYTIC BRONZE | | |
|---|---|---|---|
| | CLEAR | MEDIUM | DARK |
| RED B3LW | 0.66 | 0.58 | 0.64 |
| YELLOW 3GL | 0.43 | 0.36 | 0.36 |
| TURQUOISE PLW | 0.84 | 0.83 | 0.84 |
| BLUE G | 0.70 | 0.78 | 0.78 |

From this data we see that the amount of organic dye absorbed is not materially affected by the presence of the inorganic colorant.

By means of X-ray fluorescence, one can also determine the amount of the colorant in the oxide film. The impulse counts

Slide 10

## EXTINCTION VALUES

| | | ELECTROLYTIC BRONZE | |
|---|---|---|---|
| | CLEAR | MEDIUM | DARK |
| Red B3LW | 0.66 | 0.58 | 0.64 |
| Yellow 3GL | 0.43 | 0.36 | 0.64 |
| Turquoise PLW | 0.84 | 0.83 | 0.84 |
| Blue G | 0.70 | 0.78 | 0.78 |

found using Tin in the case of the electrolytic colored film, and Copper for the dyes (since they are copper complexes) are shown. (Slide 11)

X-RAY FLUORESCENCE
TIN - COUNTS IN 100's PER SECOND

| | ELECTROLYTIC BRONZE | | | |
|---|---|---|---|---|
| | CLEAR | LIGHT | MEDIUM | DARK |
| CLEAR | 0 | 20 | 26 | 34 |
| RED B3LW | 0 | 21 | 26 | 34 |
| TURQUOISE PLW | 0 | 19 | 26 | 34 |

From this data we see that as the color of the electrolytic bronze becomes darker, the amount of tin present in the film increases. We also note that overdyeing does not change the amount of tin present.

In the next slide data for the organic dye is shown. (Slide 12)

X-RAY FLUORESCENCE
COPPER - COUNTS IN 100's PER SECOND

| | ELECTROLYTIC BRONZE | | | |
|---|---|---|---|---|
| | CLEAR | LIGHT | MEDIUM | DARK |
| RED B3LW | 17 | 17 | 19 | 19 |
| TURQUOISE PLW | 10 | 10 | 12 | 10 |

From this data we see that the amount of organic dye absorbed is independent of the electrolytic pre-coloring and, in fact, is the same as we would find on clear oxides.

This data shows that the two methods of coloring do not interfere with each other, and hence we would expect that the properties of each will not be adversely affected by the other.

The distribution or location of the colorants within the anodic oxide was investigated using an Electron microprobe. In the slides which follow, we show plots of the elements characteristics for each of the various treatments. Tin for the electrolytic coloring, Copper for the Red and Turquoise dyes, Chromium for the Black and Nickel for sealing.

Slide 11

X-RAY FLOURESENCE

TIN

COUNTS IN 100's PER SECOND

| | ELECTROLYTIC BRONZE | | | |
|---|---|---|---|---|
| | CLEAR | LIGHT | MEDIUM | DARK |
| CLEAR | 0 | 20 | 26 | 34 |
| Red B3LW | 0 | 21 | 26 | 34 |
| Turquoise PLW | 0 | 19 | 26 | 34 |

Slide 12

## X-RAY FLOURESENCE

## COPPER

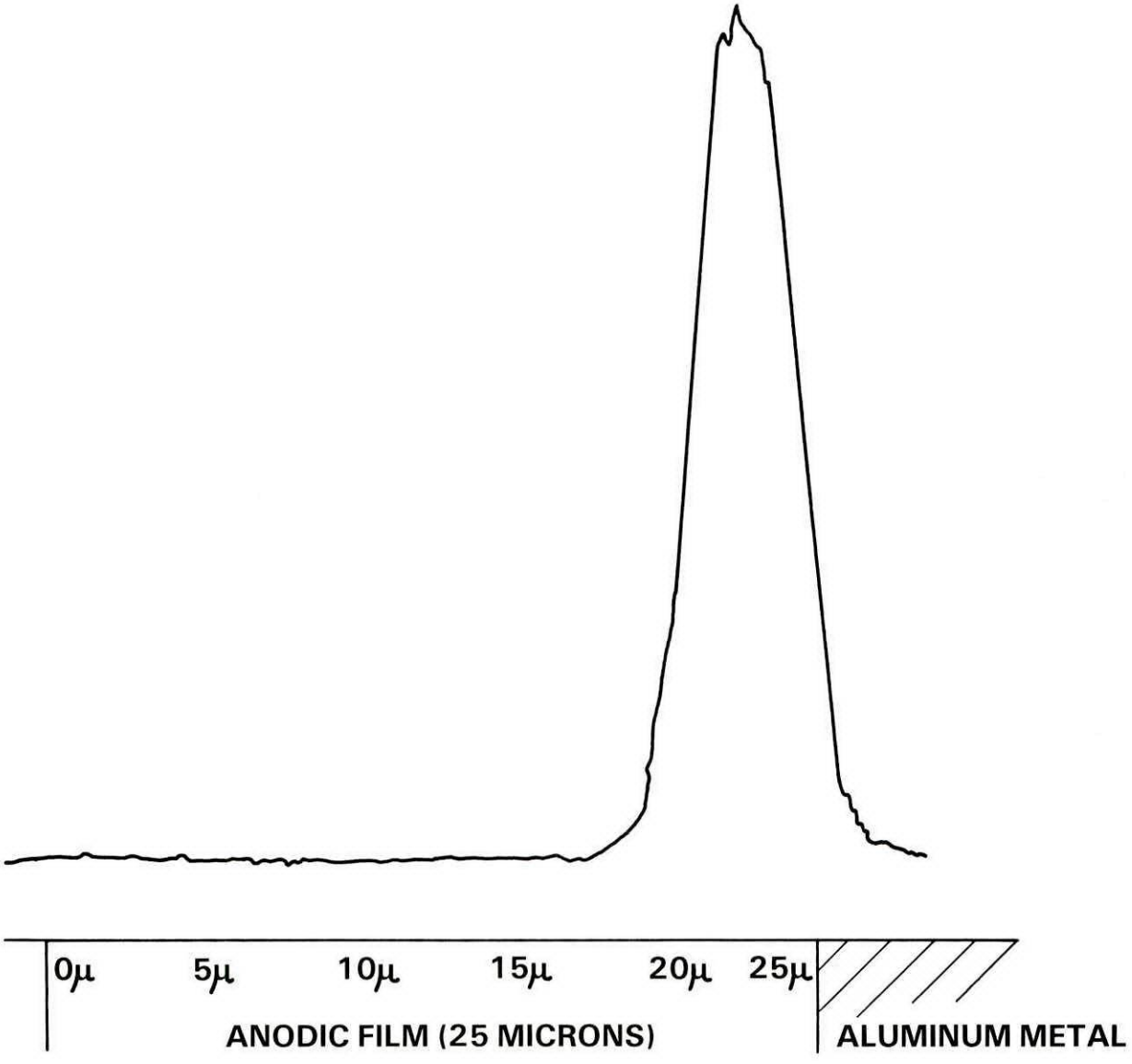
## COUNTS IN 100's PER SECOND

| | ELECTROLYTIC BRONZE | | | |
|---|---|---|---|---|
| | CLEAR | LIGHT | MEDIUM | DARK |
| Red B3LW | 17 | 17 | 19 | 19 |
| Turquoise PLW | 10 | 10 | 12 | 10 |

The first slide shows a medium bronze tin film. (Slide 13)

Slide 13

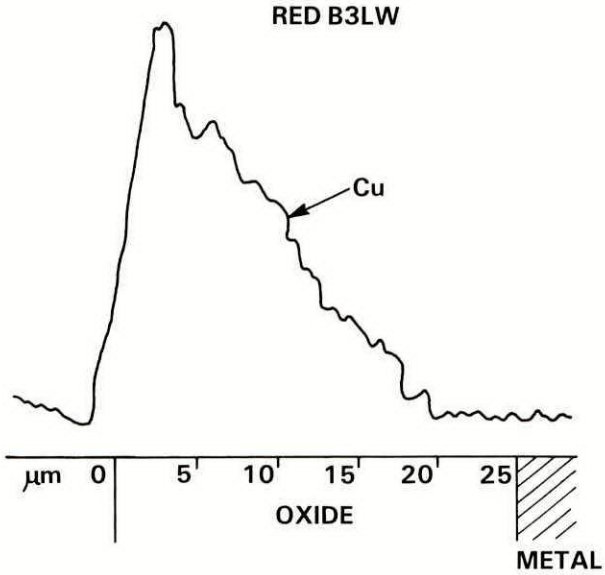
**ELECTRON MICRO-PROBE**
**TIN TRACE**
**MEDIUM BRONZE — TIN BATH**



In the next slides data for the organic dyes are shown. (Slides 14, 15, 16)

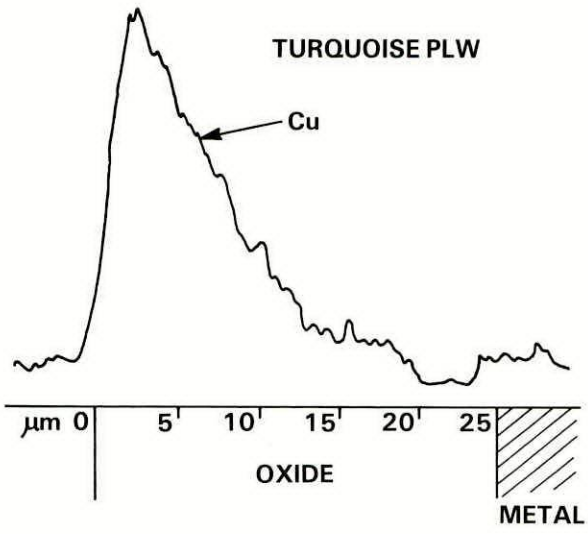
Slide 14

**ELECTRO MICRO-PROBE**
**DYED CLEAR FILM**
**COPPER TRACE**



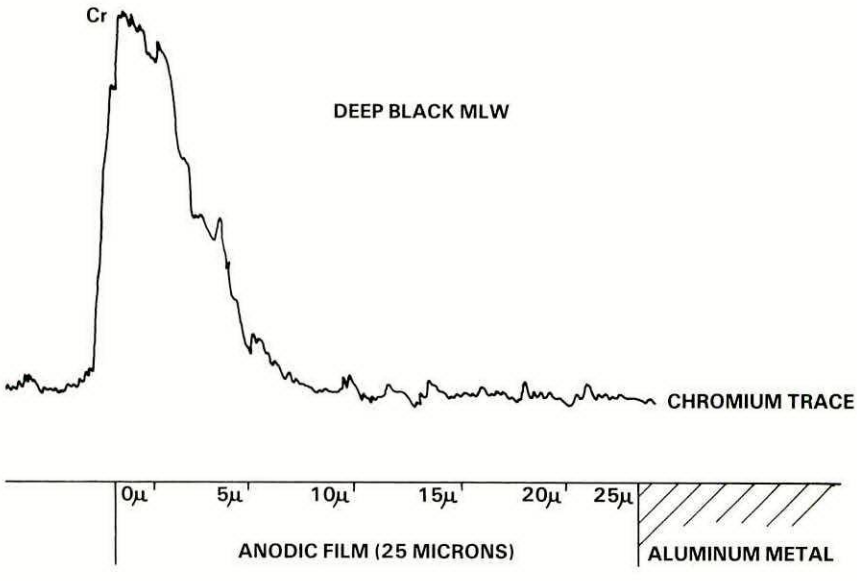

Slide 15

**ELECTRON MICRO-PROBE**
**DYED CLEAR FILM**
**COPPER TRACE**




Slide 16

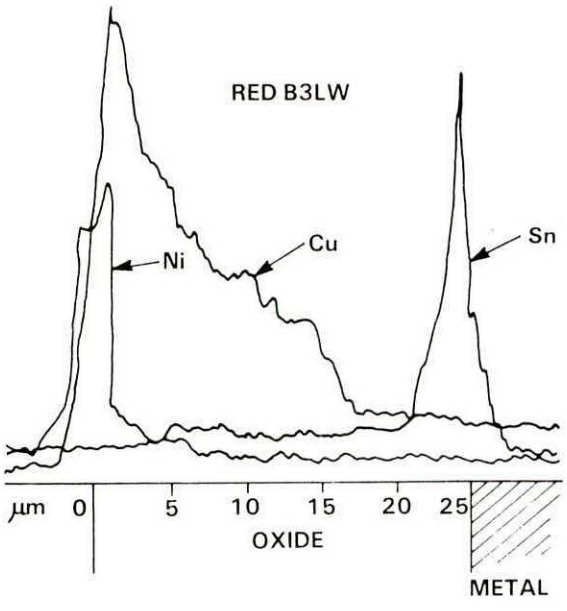
**ELECTRO MICRO-PROBE**
**DYED CLEAR FILM**
**CHROMIUM TRACE**



The next slides show a medium bronze electrolytic film, over dyed with either the Red and the Turquoise dye then nickel acetate sealed. We see the location of the 2 colorants is the same as in the individual process alone. (Slides 17, 18)

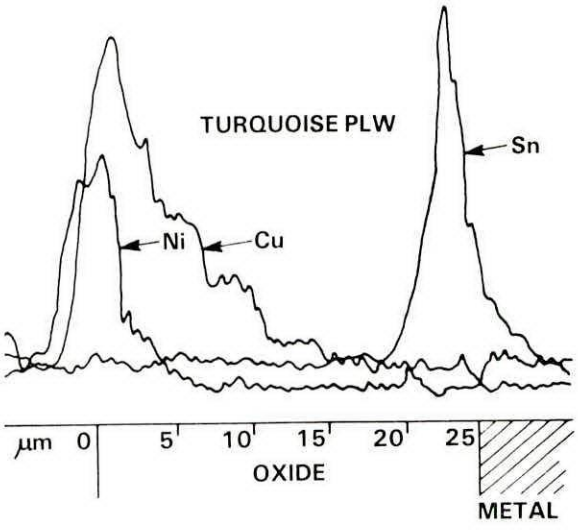
Slide 17

**ELECTRON MICRO-PROBE**
**ELECTROLYTIC BRONZE (TIN)**
**DYED (COPPER)**
**NICKEL SEAL (NICKEL)**
**METAL TRACES**




Slide 18

**ELECTRON MICRO-PROBE**
**ELECTROLYTIC BRONZE (TIN)**
**DYED (COPPER)**
**NICKEL SEAL (NICKEL)**
**METAL TRACES**




In all cases, we see that the electrolytically applied colorant is found deep within the oxide near the metal-oxide interface - roughly 23 microns. The dye is predominantly in the first 10 microns from the air-oxide interface and that the nickel from the sealant penetrates only 2 or 3 microns.

This data indicates that the lightfastness of the over dyed electrolyte films will be of the same order as that of a similarly dyed clear film of the same thickness, which previously have been shown to be suitable for the potential use.

In the presentation today we have discussed some methods for the production of an interesting new range of colors suitable for use in architectural applications. This entails the 'overdyeing' of either an integral color or a two-stage electrolytically colored anodic oxide film.

We have discussed, in some detail, the processing controls that are necessary and also presented data concerning the sealing quality, lightfastness and corrosion resistance of these films.

We have also presented some data dealing with the location and distribution of the various colorant materials within the anodic coating.

List of Slides

1. Methods for Coloring Architectural Components
2. Integral Color Process
3. Two-Stage Electrolytic Coloring Process
4. Dyeing Conditions
5. Controls for Dyeing
6. Sealing Conditions
7. Sample Preparation
8. Admittance Values
9. Loss of Color Intensity 3200 Hours Fade-O-Meter
10. Extinction Values
11. X-Ray Fluorescence Tin Content Electrolytic Bronze
12. X-Ray Fluorescence Copper Content Dyed Films
13. Electron Micro-probe Tin Trace Electrolytic Bronze
14. Electron Micro-probe Copper Trace Red B3LW Dyed Film
15. Electron Micro-probe Copper Trace Turquoise PLW Dyed Film
16. Electron Micro-probe Chromium Trace Black MLW Dyed Film
17. Electron Micro-probe Metal Traces RED-Electro Bronze-Nickel Seal
18. Electron Micro-probe Metal Traces BLUE-Electro Bronze-Nickel Seal
19. Color Fan

E-4

# LIGHT METALS FINISHING SESSION E

## Self-Regulating High-Temperature Anodizing Process with Full Utilization of Alkaline and Anodizing Wastes

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# SELF-REGULATING HIGH TEMPERATURE ANODIZING PROCESS WITH FULL UTILIZATION OF ALKALINE AND ANODIZING WASTES

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## ABSTRACT

The anodizing electrolyte consists of sulfuric acid-ammonium sulfate which permits operation up to 30-40°C and as anodizing proceeds, alum is continuously precipitated, keeping Al content in the electrolyte at optimum concentration. Caustic etching solution with gluconic acid is recovered by adding $Na_2SiO_3$ to spent solution, precipitating zeolite, and alkali and gluconic acid are recovered for re-use. Both precipitates and that from rinse water are utilized for adsorbent, molecular sieve, substitute for tri-polyphosphate etc. and raw materials for artificial gems, watch glass etc. The process is successfully operated at a big architectural plant both for as-anodized and for further electro-colored, windows, curtain walls etc.

## Introduction

Some years ago, at the laboratory of the University, the research was made to develop an anodizing process by which the properties of the produced films are comparable or superior to those of normal sulfuric acid anodizing process, at operation temperatures up to 40°C. The process should be used, of course, at normal temperature (18-22°C) and also for so-called "hard anodizing". The idea was independently conceived by one of the authors (S.Tajima) in order to train young freshmen for aluminum surface finishing by a contract with a certain company. We found that the sulfuric acid bath containing mainly alkali sulfate was to this purpose by which alum is continuously precipitated, keeping $Al^{3+}$ content at optimum[1,2]. Later, one of the authors (Y.Umehara) in collaboration with a certain pharmaceutical company, developed a process of recovering alkali etching solution including gluconic acid , a chelating agent and by this existence, Al sludges are usually difficult to be removed during alkaline pretreatment of aluminum and aluminum alloys (mainly 6063). These two processes were combined by Y.Umehara and brought into practical use at the Tokorozawa plant of the Showa Koki Co., Tokyo, one of the leading architectural aluminum producers in Japan. Thus, the self-regulating, high temperature continuous anodizing process with full utilization of caustic and anodizing wastes for adsorbent, molecular sieve etc. on the one hand and for producing $\alpha$-alumina (artificial gems), color-intensifier of vegetable pickles are successfully operated together with collected waste solution treatment and

ever-improved up to now. The anodic films produced by this process is comparable with or even superior to normal sulfuric acid anodizing films and they can also be subjected to succeeding electro-coloring operation. The paper describes the principles underlying the processes and outlines the practical processes being operated at the Showa Koki Co., Tokorozawa factory, Japan.

## Principles of Self-Regulating High Temperature Anodizing

The normal surfuric acid anodizing is performed at about 20°C and above this temperature, the film dissolution loss is larger and also the quality deteriorates. In order to avoid temperature rise, it is usual to cool by refrigerators. As a means of securing the same film forming efficiency and quality at higher temperature, an idea of adding common anion-containing soluble salts to suppress the film dissolution occurred to the author and it was found that ammonium sulfate and/or potassium sulfate addition was particularly effective and profitable.[1)]
By this process, electrolysis below 40°C is possible and some of the merits are as follows;
1) Refrigeration is not always required. Natural cooling or cooling by air or water or only occasional use of refrigerator is enough according to the climate conditions.
2) The anodized film obtained at or above 20°C is usually harder and of excellent qualities.
3) Rapid anodizing is possible. For rapid anodizing, high current densities than normal 1-1.5 A/dm$^2$ must be used, which naturally lead to the elevation of the bath temperature, which in turn, lowers the film forming efficiency and degenerate the quality of the film. Therefore, the possibility of rapid anodizing means roughly high temperature anodizing.
4) Further, the important merit of this process is that $Al^{3+}$ ion which is formed by anodic dissolution (i.e. which does not contribute to the film formation) gradually precipitates as alum of lower solubility, thus the concentration of $Al^{3+}$ ion in the solution is automatically maintained at about 0.5% in the above-mentioned temperature range, which is considered to be an optimum $Al^{3+}$ concentration for surfuric acid anodizing. Thus by only recovering the by-product (alum), the continuous operation without waste became possible. When the process was developed, the author called it as SRHT process (Self-regulating, high temperature process).
5) The films thus formed can be further electro-colored by presently popular two step electro-coloring processes by which Sn, Ni, etc. are electrodeposited in the pores by AC or DC in respective salt solutions. At the Showa Koki Co., this electro-coloring process is practiced. The hitherto known electro-coloring processes by V.Caboni (Italy, 1936),[3)] G.Elssner (Germany 1940), Asada (Japan 1966), Eurocolor 800 (Pechney) etc., specify electro-coloring on normal sulfuric, or chromic, or oxalic acid films, while the present films, can also be subjected to electro-coloring process.

To express the film forming efficiency, Mason[5] of ALCOA defined in early 1940s', the term "coating ratio" which is still used very often.

$$\text{Coating ratio (C.R.)} = \frac{\text{weight of formed oxide}}{\text{weight loss of substrate Al}}$$

Although the theoretical value is $Al_2O_3/2Al=1.89$, in normal sulfuric acid anodizing, C.R. is said to be about 1.35-1.40. The data obtained in one of the authors' (S.Tajima) laboratory are shown in Fig.1, which indicates that the efficiency lowers steeply with the temperature rise.

According to Tajima & Shimura,[6,7] the statistical calculation of the thickness of anodic films in 15vol% $H_2SO_4$ at $1A/dm^2$ for 99.99% Al is as follows:

$$d\ (m\mu)=0.347t-10^{0.025T-2.078}t^{1.34}$$

for example, the time t needed for d=0 at T=48°C is 16.5 min, and for T=48°C, the film grows at first but after passing through maximum thickness, d=0 in 16.5 min, where only thin barrier film remains.

In contrast, when ammonium or potassium sulfate is added to sulfuric acid electrolyte, the C.R.-Bath voltage relations are shown at 35°C in Fig.2.

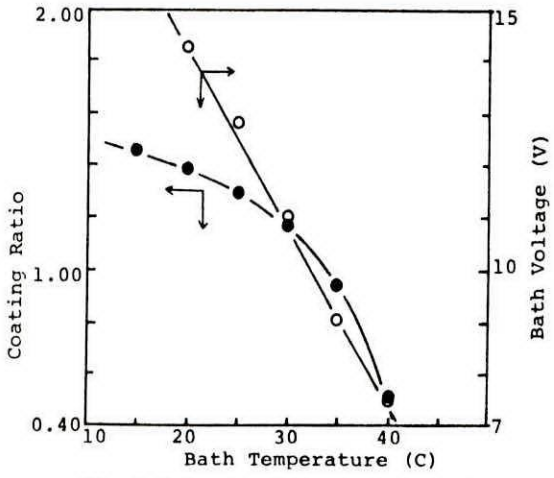


Fig.1 Relation between Temperature, C.R. and Bath Voltage. (15wt.%$H_2SO_4$, $1A/dm^2$)

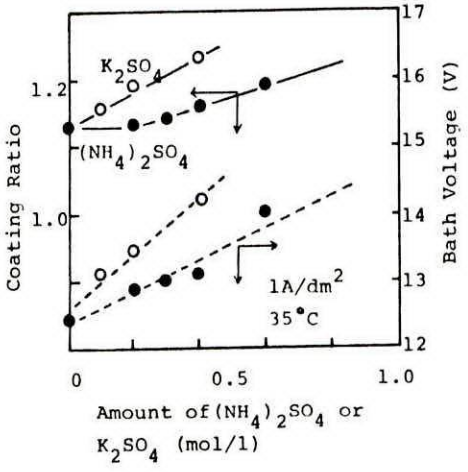


Fig.2 Relation between $(NH_4)_2SO_4$, $K_2SO_4$ addition, C.R. and Bath Voltage.

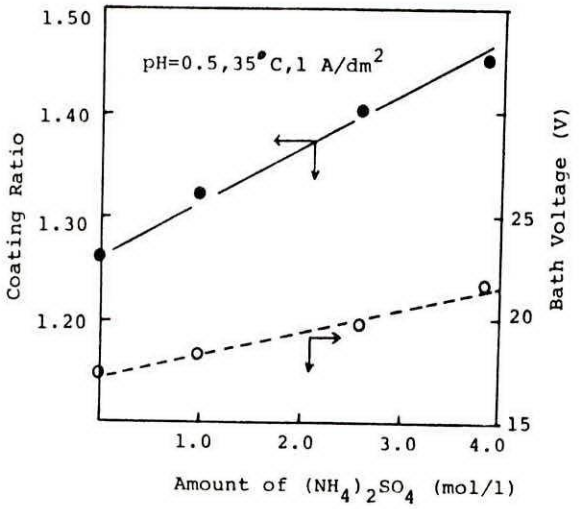


Fig.3 Relation between $(NH_4)_2SO_4$ addition, C.R. and Bath Voltage (pH=const.)

About 0.4-0.6 mol addition of salts to sulfuric acid is comparable to straight 15vol% sulfuric acid at 20°C.
Fig.3 shows the relation between C.R. and bath voltage at 35°C when ammonium sulfate is added to sulfuric acid, by keeping pH of the solution at 0.5. By addition of 4.0 mol of ammonium sulfate, the C.R. surprisingly attains 1.45. When 0.4 mol/l of $K_2SO_4$, $(NH_4)_2SO_4$ or $Na_2SO_4$ is added to 1 mol $H_2SO_4$ (about 10wt%), the coating ratio is in the order $K_2SO_4$(1.21), $Na_2SO_4$ (1.16) and $(NH_4)_2SO_4$ (1.16). From these data, it is clear that sulfuric acid-soluble alkaline sulfate bath is fitted for high temperature anodizing, as well as at normal or lower temperatures.
For reference,the authors will show the solubilities of aluminum sulfate and alum in Table 1, as a basis for self-regulating, continuous operative anodizing bath with gradual precipitation of alum.

Table 1
Solubilities of aluminum sulfate and alums in water at 0, 20 and 40°C.

| | molecular wt/temp | 0°C | 20°C | 40°C |
|---|---|---|---|---|
| $Al_2(SO_4)_3.18\ H_2O$ | 666.45 | 60.7 | 70.7 | 89.2 |
| $AlK(SO_4)_2.12H_2O$ | 474.40 | 5.43 | 11.0 | 25.0 |
| $AlNH_4(SO_4)_2\cdot 12H_2O$ | 453.34 | 4.97 | 12.6 | 23.61 |
| $AlNa(SO_4)_2.12H_2O$ | 458.30 | 70.7 | 75.1 | 83.6 |

It is clear that the solutions of ammonium and potassium alum in water is particularly smaller. The $Al^{3+}$ ion concentration in these saturated alum solution is calculated as 7.5 & 14 g/l at 20 & 40° C, This $Al^{3+}$ concentration is optimal for anodizing in sulfuric acid. In normal sulfuric acid anodizing, it is usual that the electrolyte must be discarded when $Al^{3+}$ content in the solution becomes 12-20 g/l, while in these alum anodizing electrolyte, $Al^{3+}$ ion concentration is automatically controlled by gradual precipitation of alum which can be recovered and used as by-product. Thus the $H_2SO_4$-alkaline sulfate electrolyte is automatically controlled and continuously used only by occasional addition of ammonium sulfate, or ammonia and sulfuric acid.
The film available by this process at 35°C is comparable or superior to normal sulfuric acid films in appearance, thickness, abrasion resistance, Vickers' hardness, dye adsorption and in corrosion resistance.
Further, the additions of aliphatic carboxylic acid such as oxalic, malonic. lactic or formic acid to the bath gives superior films to the normal sulfuric acid films without losing self-regulating characteristics.[2]

Principles of recirculation of caustic etching solution and utilization of its waste[7]

The Showa Koki Co., where one of the authors (Y.Umehara) is active as chief engineer, with cooperation of a certain pharmaceutical company, developed a process of recirculating caustic etching solution which includes 0.5% or more of gluconic acid to make possible uniform etching of the architectural aluminum panels without any flow marks which may happen during withdrawal of the panels from the etching solution, and gives products a refined beauty.(Photo 1) Further the addition of gluconic acid which is rather popular, prevents aluminate deposition at the bottom of the tank, the insides of piping and transfer pumps.

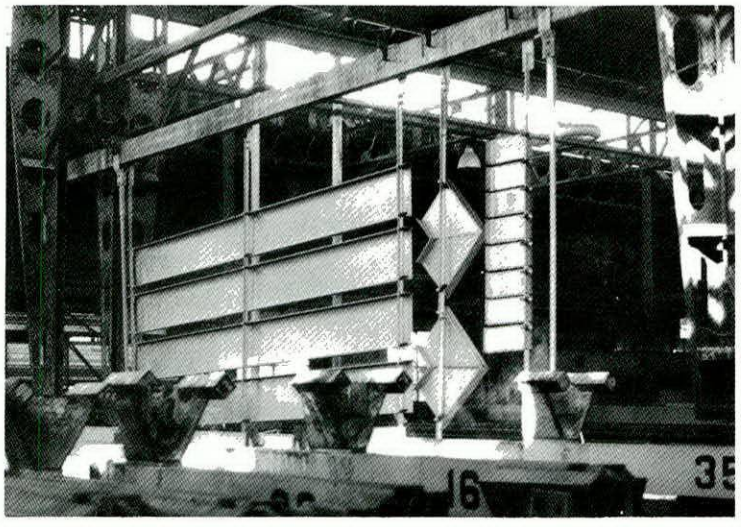

Photo 1
Withdrawal of panels from alkali etching tank
(Showa Koki Co., Tokorozawa Factory, Japan)

This merit is, at the same time, a demerit since 0.1% or more of gluconic acid addition makes difficult the "crystallization of aluminum hydroxide", which is a basis of the so called "Bayer" waste recovery process.
To overcome the demerit of the use of gluconic acid, one of the authors (Y.Umehara) developed a process of regenerating alkali and gluconic acid from waste alkali. $Na_2SiO_3$ reacts just as calculated within a few hours, at rather high temperature. Sodium alumino silicate, the so-called "synthetic zeolite" precipitates in large crystals and is readily filtered off and separated.

$$6 \cdot NaAl(OH)_4 + 2 \cdot Na_2O(SiO_2)_3^{*} \rightarrow 3 \cdot Na_2O : Al_2O_3(SiO)_2)_2 + 4NaOH_2O$$

One typical practical example is shown in Table 2.

Table 2
Alkali Recovery Process
Waste Caustic Soda

| Volume | NaOH | Na-gluconate | Al in g/l |
|---|---|---|---|
| 20 $m^3$ | 130 g/l | 8.5 g/l | 45.0 |

*JIS spec. NO. 3

## Recovered Caustic Soda

| Recovered Volume | Free NaOH | Yield | Na-gluconate | Yield | Zeolite |
|---|---|---|---|---|---|
| 20 $m^3$ | 84.4 g/l | 53.84% | 6.8 g/l | 80.0% | 6 tons |

By good conditioning of the reaction, the products can be separated, one as synthetic zeolite and the other as pure sodium hydroxide. The recovered caustic soda contains virtually no Al, which makes the control of the etchant components easier. Thus, both caustic soda and sodium gluconate are recovered in ca. 80% yields without discarding even a single drop* of the waste alkali solution and the zeolite produced is 6.0 tons.
It is possible to maintain the amount of Al dissolved in the etchant at a minimum (2% or less) during the run. Accordingly, the drag-out loss of Al from the etching solution is minimized and the amount of hydroxide formed during adjustment of the pH of waste water is reduced to less than half of the popular value. The filtration of aluminum hydroxide becomes easier and the amount of suspended solids in waste water solution, a factor contributing to water pollution, can be made virtually nil.
The flow sheet of alkali recycling process is shown in Fig.4.

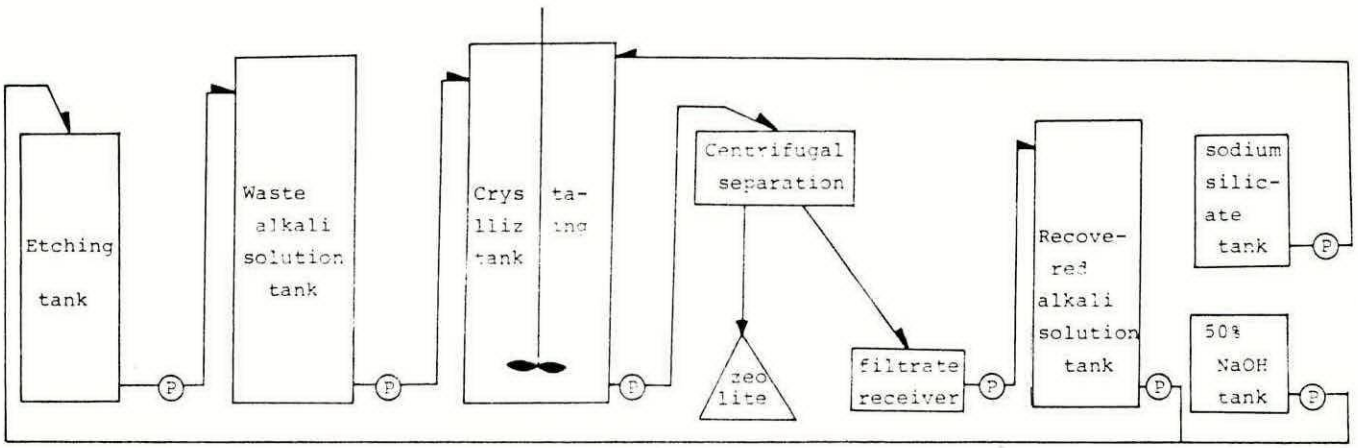


Fig.4

Properties of the by-product zeolite
1) The examination of by-product zeolite can be deemed as the same as that of zeolite 4A of US make from X-ray diffractograph.
2) The chemical composition is, for example, shown in Table 3.

Table 3
Composition of by-product zeolite

| $Al_2O_3$ | $Na_2O$ | $SiO_2$ | $Fe_2O_3$ | $H_2O$ | Cr | Cu | Mn | Ni | As |
|---|---|---|---|---|---|---|---|---|---|
| 24.0 | 15.9 | 32.5 | 0.0056 | rest | 7 | 4 | 4 | 8 | 0.1 |
| | | | | | (%) | | | | |

| Mg | Pb | Cd |
|---|---|---|
| 0.001 | 0.4 | 0.01 (ppm) |

* see next page.

*
This zeolite still includes caustic soda and is discharged from the centrifugal separator with recovery of 20% of caustic soda solution.

3) Ion exchange capacity 4.5 meqv/g
4) Gas absorption $H_2O$ (in Rh 30%) 24%; $SO_2$, $NO_x$ $NH_4^+$ gas 22-24%

5) Particle size distribution is shown in Table 4.

Table 4
Particle size diameter dispersion

| Specimen | 5 | 6 | 7 | 8 | 9 | 10 | 15 | 20 | 25 | 30mμ |
|---|---|---|---|---|---|---|---|---|---|---|
| Crude | <16 | 6.6 | 12 | 10 | 10 | 10 | 22 | 5.1 | 3.1 | 1.7 |
| Washed in water | <23 | 29 | 19 | 8.4 | 3.5 | 2.2 | 7.8 | 3.1 | 1.0 | 1.2 |

6) Morphology of zeolite is shown in Photo 2. (20 mm in the Photo corresponds to 5 mμ)

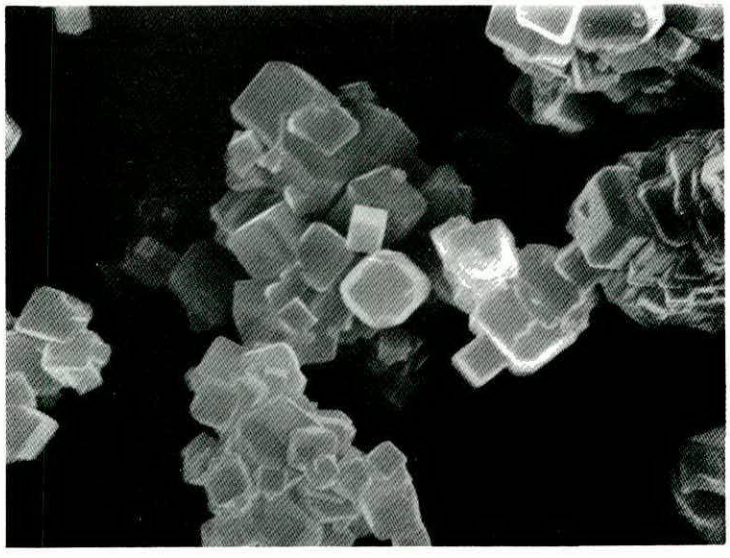

Photo 2
Morphology of zeolite

7) Economical consideration of recovery of caustic soda from waste etching solution
The balance data per one recovering operation of 20 $m^3$ caustic soda solution as of Nov.1979 is shown in Table 5 (where US$ 1.00 =Japanese ¥230)

8) New use of zeolite
In Japan, the total demand of zeolite 4A as molecular sieve, moisture remover, ion-exchanger etc. was not over 80 tons per year, while since 1968, a new use of builder instead of sodium tri-polyphosphate has been developed. It is expected that total

demand of zeolite 4A as builder will be over 50.000 tons per year and the half of anodizing plants in Japan, if the process is adopted, is expected to easily supply above demand at a reduced price.

Table 5
The balance data

| Expenditure | ¥ | $ |
|---|---|---|
| 1. Labor cost | 12.000 | 52.17 |
| 2. Fuel cost | 15.500 | 67.39 |
| 3. Electric power cost | 10.000 | 43.47 |
| 4. Sodium silicate | 185.000 | 804.34 |
| 5. Cost of materials consumed | 20.000 | 86.95 |
| 6. Repay of construction & equip. | 100.000 | 434.78 |
| Total | 342.500 | 1489.13 |
| **Income** | | |
| 1. Recovered NaOH as 7%, $20m^3$ | 91.000 | 39.56 |
| 2. Recovered Na-gluconate | 83.200 | 36.17 |
| 3. By-product zeolite (unit price of crude zeolite ¥35,000/ton) | 210.000 | 91.30 |
| Total | 382.000 | 166.08 |

Balance + ¥39.500 (US$ 171.73)/charge

Practice of self-regulating anodizing process using $H_2SO_4$-ammonium sulfate

By the order-made window and curtain wall manufacturers excepting USA, many of their products are now surface-treated with two-step electro-coloring process[3,4] which was originally developed by V.Caboni in Italy, 1936 and practically applied by Asada in Japan in 1965 or with similar process mainly in Japan and in Europe. However, they are subjected to a strict inspection of color matching, corrosion resistance, hardness and alkali-resistance to satisfy the requirement for higher class buildings. To keep high quality of color-anodized films, severe control of the electrolyte as well as caustic soda etching solution are needed. During anodizing, unnegligible amount of aluminum dissolves into the electrolyte resulting in the reduction of coating ratio as shown in Fig.1 and in the loss of Al. According to our experience, ca. 20g of Al is lost in the conventional 15% sulfuric acid anodizing when we intend to get 12 μm oxide film on 1 $m^2$. Thus we must control the $Al^{3+}$ concentration at optimum, say, between 5-10g/l to secure good quality of the film. Excess Al ion is needed to be removed by a simple operation.
For this purpose, one of the authors (Y.Umehara) has applied the self-regulating $H_2SO_4$-ammonium sulfate bath developed by Tajima (co-author) and by his co-workers referred to above.[1]

The practical details now being applied at the Showa Koki Co., Saitama Factory is as follows:
1) Electrolyte; 15wt.% sulfuric acid, 0.5% $NH_4$ ion, 1% Al ion. Under these conditions, ammonium alum and accordingly Al ion is automatically precipitated to keep the anodizing electrolyte at optimum conditions.
2) Recycle and recovery treatment from waste electrolyte to fresh electrolyte is shown in Fig.5.

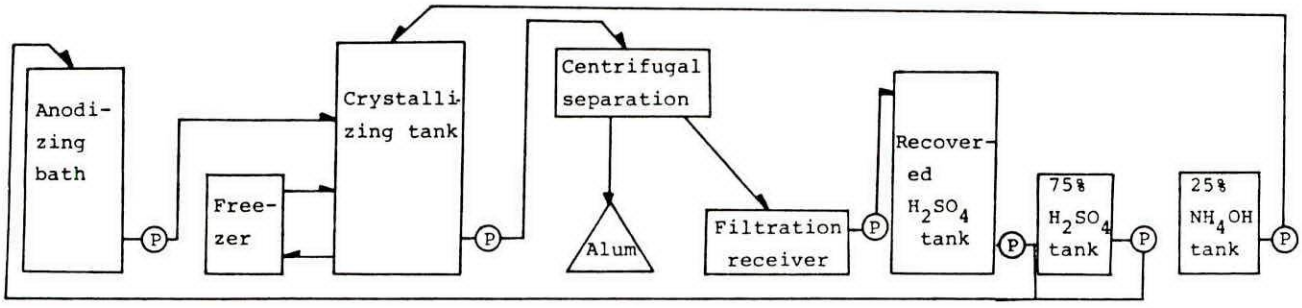


Fig.5

The electrolyte with excess Al ion content (over 1%), is pumped up to the crystallizing tank together with equivalent ammonium. Dissolved Al ions immediately combine with ammonium sulphate $(NH_4)_2SO_4$ to precipitate as fine crystals of ammonium alum, by rapid cooling of the solution by moderate freezer outside the anodizing bath (note:the process can be operated up to 40°C, but presently at Showa Koki, moderate cooling of the solution is done from the view point of efficiency and required quality of the film). The electrolyte containing alum is transferred to the centrifugal separator. Separated alum is scratched down and the filtrated sulfuric acid is fed back through the recovery acid tank to the anodizing tank. The compositions of waste electrolyte and the recovered one are shown in Table 6.

Table 6

Waste Electrolyte (average value from 5 lots)

| Volume | Total $H_2SO_4$ | Al ion | Added 25% $NH_4OH$ |
|---|---|---|---|
| $15.9m^3$ | 16.9% | 1% | 296 litre |

Recovered Electrolyte

| Recovered Vol. | Free $H_2SO_4$ | Al ion | By-produced alum | Yield |
|---|---|---|---|---|
| $15.2m^3$ | 13.4% | 0.54% | 1212Kg | 76.2% |

3) Properties of the film anodized with recovered electrolyte
Recovered electrolyte which contains a small amount of $Al^{3+}$ gives better result then non-$Al^{3+}$ containing bath. Moreover, the films obtained from this bath are better electro-colored. The comparison of the films obtained from our bath and from

normal sulfuric acid bath shows that the present film is superior, by 10 um thickness, particularly in corrosion resistance in NaOH and in abrasion resistance (according to the Japan Industrial Standard tests). The original patent of this process states that the electrolyte containing moderate ammonium ion in sulfuric acid can be used up to 40°C, but aluminum for order-made architectural products can better be anodized at room temperature to get harder and better alkali-resistant properties.

4) The purity of by-product ammonium alum

The by-produced crude alum still contains a small amount of recovered electrolyte. However, other impurities are very small as shown in Table 6.

Table 6

| Cr | Cu | Fe | Mg | Mn | Ni | As | Hg | Cd | |
|---|---|---|---|---|---|---|---|---|---|
| 1.5 | 0.7 | 36.3 | 9.8 | 0.9 | 0.4 | 9.0 | 0.3 | 0.6 | (ppm) |

5) The use of by-product alum

1. Addition agent to foods; It is effective to keep clear color of salted vegetables. Ammonium alum is used after calcination.
2. Raw material for artificial jewellies; We can make nearly 100% purity $\alpha$-alumina from pure alum subjected to 3 times recrystallization. The use of this artificial gems are extending not only to decorative accessories but also to watch glass and to lens for deep-see use, etc. at remarkably reduced cost, which are shown in Photo 3.

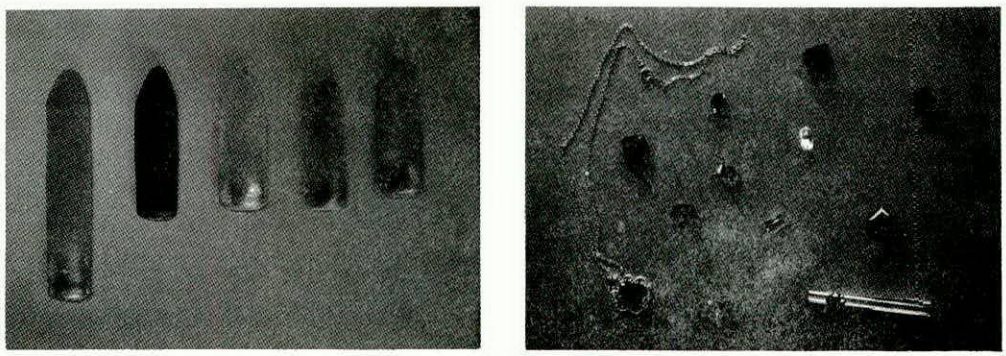

Photo 3. Roh materials($\alpha$-alumina) and artificial gems

6) Economic consideration of $H_2SO_4$-ammonium sulfate process

The balance data per one recovery operation of 16m$^3$ waste electrolyte is shown in Table 7.

Table 7

| 1. Expenditure | | ¥ | $ |
|---|---|---|---|
| Cost of 25% ammonium solution | ¥32/litre x 300 | =96.00 | 41.74 |
| Electric power | ¥20/KWH x 50 | =1.000 | 4.35 |
| Labor cost | 2/3man, ¥12000/day x 2/3 | =8.000 | 34.78 |
| Repayment for construction/batch | | 9.500 | 41.30 |
| Total | | 28.100 | 122.17 |

| 2. Income | ¥ | $ |
|---|---|---|
| Price of recovered sulfuric acid | 54.315 | 236.15 |
| By-product alum ¥20/Kg x 1212= | 24.240 | 105.39 |
| Total | 78.555 | 341.52 |
| Balance | +50.455 | 219.37 |

Pollution treatment of collected waste rinse water and evaluation of by-product aluminum oxide grains

In anodizing operation, a lot of waste rinse water that over-flows from each rinse tank is discharged after oil removal, etching, neutralizing and anodizing. The discharged waste water which contains more or less $Al^{3+}$ ion, alkali and/or acid must be neutralized to produce a large amount of aluminum hydroxide, so called suspending solid (SS). To comply with the national regulation of waste water pollution that is specified as SS below 90 ppm and pH 5.8 to 8.5, the following treatment is done as shown in Fig.6.

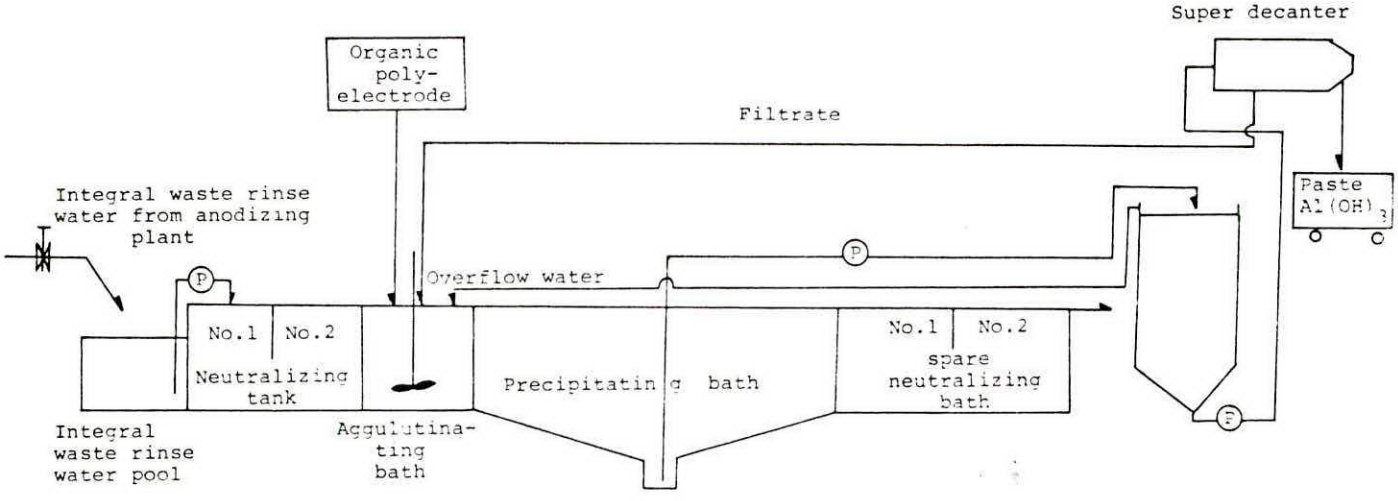


Fig.6

1) Collected waste rinse water treatment plant
Waste water is pumped up to the next bath to neutralize automatically with waste caustic soda solution, and the suspending aluminum hydroxide (SS) is agglutinated with organic poly-electrolyte in the next mixing tank and after aggulutination it is lead to precipitation bath where flocks (diameter 10mm) of aggulutinated SS precipitates on the bottom in the course of flowing down slowly (1 m/min) to the end of the bath and the cleaned water over-flows to the next bath where cleaning is confirmed. Precipitated SS flocks are separated with superdecanter to aluminum hydroxide paste and filtrate solution.

Hydroxide paste is dried and ignited in rotary furnace to become porous grain.

2) Explanation of rotary dryer and ignition furnace

Discharged paste from the super-decanter is put into the paste accumulator (ca. 1.5 $m^3$ capacity). The paste is pushed onto the rotary furnace and delivered down a little by little by 1 RPM with an inclination of 1/10. During the run, the charged paste is treated with direct high temperature flame that is shot from waste oil burner, and thus produced alumina is discharged from the end of the furnace, which is immediately blown into the cyclone through steel pipe.(Fig.7)

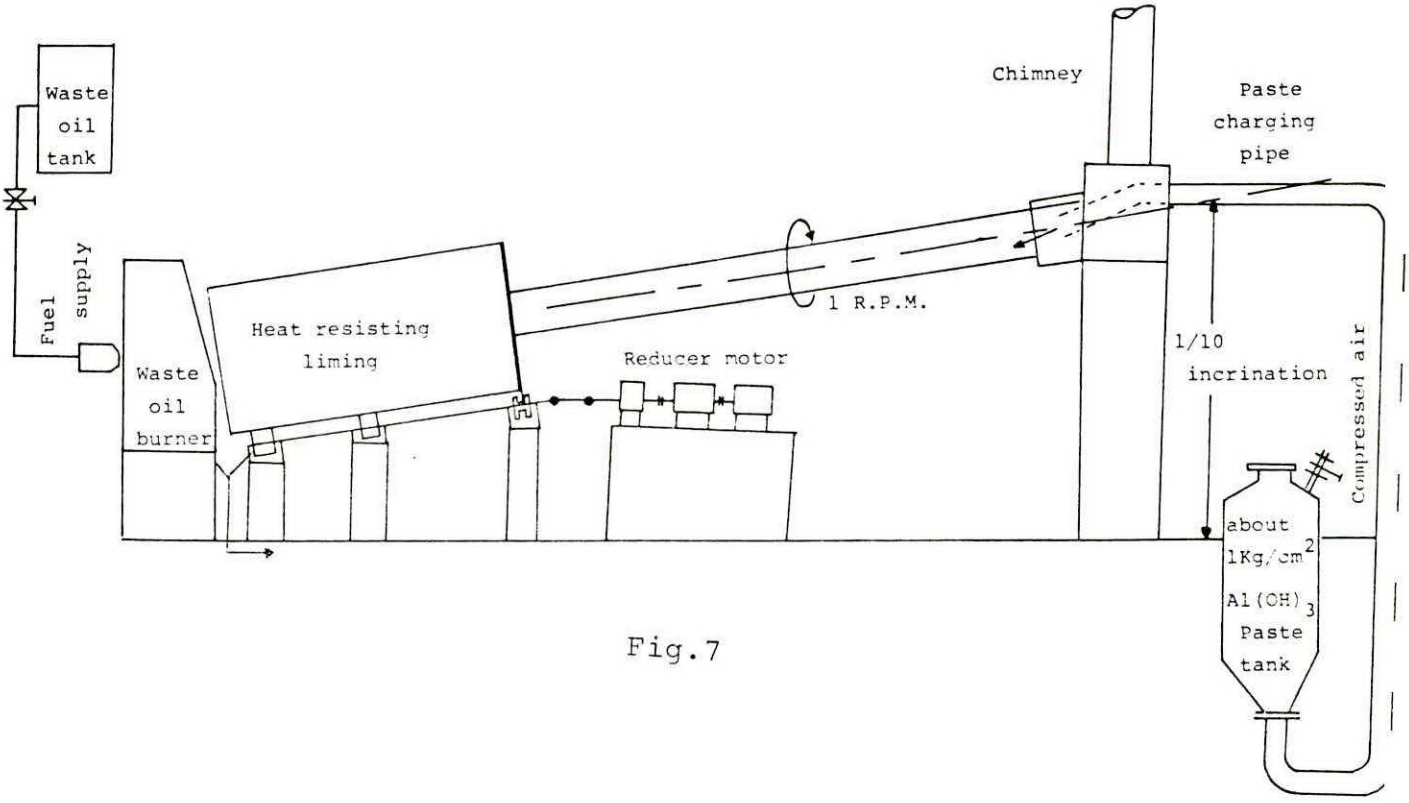


Fig.7

3) Chemical composition of ignited grains are shown in Table 7.

Table 7
Chemical composition of ignited grains (ppm)

| $Fe_2O_3$ | $SnO_2$ | $Pb_2O_3$ | $MnO_2$ | $Cr_2O_3$ | $As_2O_3$ | CdO | HgO | $Al_2O_3$ |
|---|---|---|---|---|---|---|---|---|
| 0.69 | 0.67 | 0.04 | 0.03 | 0.007 | 7.6 | 2.5 | 0.05 | rest |

4) The use of ignited grains

1. Oil removers; Scattered oil on the road due to, for example traffic accident, can be removed easily by covering with a small amount of this grains and by sweeping them off.
2. Filler for sand box of pets; As a filler of sand box for

removing various kinds of disagreable smell and their urin.

5) Economic Assessment of the operation of dry and ignition furnaces

From 2 tons of paste, 300Kg of ignited grains are produced with ca. 180 litre of waste oil and 1/3 working labor/day.

Table 8

| | ¥ | $ |
|---|---|---|
| 1. Expenditure | | |
| Cost of waste oil as fuel ¥35/l x 180 | =6300 | 27.39 |
| Cost of labor ¥12.000/day x 1/3 | =4000 | 17.39 |
| Repayment of construction/batch $\frac{¥3.000.000 \times 25\%}{12 \text{ months} \times 22 \text{ working days}}$ | =2840 | 12.35 |
| Total | 13.140 | 57.13 |
| 2. Income | | |
| Price of ignited grains ¥10/Kg x 300 | =3000 | 13.40 |
| The saving of money to be paid to the contract tender of aggulugated aluminum hydroxide ¥13.000/ton x 2 | =24.000 | 104.35 |
| Total | 27.000 | 117.39 |
| Balance | +13.860 | 60.26 |

ACKNOWLEDGMENT

Thanks are due to President K. Aoyama, Showa Koki Co. for permission of publication and to Dr. S. Matsuzawa for preparing the paper.

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$AL\ PO_4$

$AL\ (H_2PO_4)_3$

15 g/m² / hr al disolver

11
10ft²