United States Patent [15] **3,669,855**
Smith [45] **June 13, 1972**

[54] CONTROL OF INTEGRAL COLOR ANODIZING PROCESS

[72] Inventor: **Richard L. Smith**, Livermore, Calif.
[73] Assignee: **Kaiser Aluminum & Chemical Corporation**, Oakland, Calif.
[22] Filed: **Jan. 28, 1970**
[21] Appl. No.: **6,516**

[52] **U.S. Cl.** **204/58,** 204/228
[51] **Int. Cl.** **C23b 9/02,** B01k 3/00
[58] **Field of Search** 204/58, 228

[56] **References Cited**

UNITED STATES PATENTS

3,486,991	12/1969	Hatano et al.	204/58
3,384,561	5/1968	Michelson et al	204/58
3,328,274	6/1967	Bushey et al	204/58
3,280,013	10/1966	Economy	204/58
3,098,018	7/1963	Kissin et al	204/58
R25,566	4/1964	Deal et al	204/58

FOREIGN PATENTS OR APPLICATIONS

736,458	6/1966	Canada	204/58

OTHER PUBLICATIONS

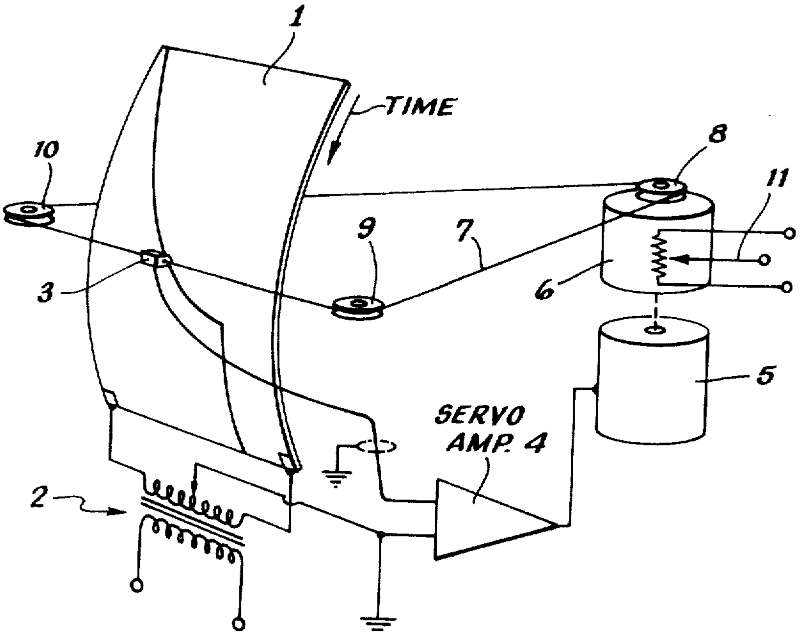
The Surface Treatment and Finishing of Aluminum by Wernick et al., 1964, pages 351-352.
Appearance Control of Architectural Anodized Finishes by Bushey & Kissin, Jan. 31, 1968, pages 7, 10.

Primary Examiner—John H. Mack
Assistant Examiner—R. L. Andrews
Attorney—James E. Toomey, Paul E. Calrow, Harold L. Jenkins and Edward J. Lynch

[57] ABSTRACT

A process for controlling an integral color anodizing process to minimize the effect of variations in electrolyte bath composition, temperature and the like upon the color of the anodic oxide coatings comprising developing a voltage-time relationship to obtain a desired color and controlling the anodizing process in accordance with the developed voltage-time relationship.

4 Claims, 4 Drawing Figures



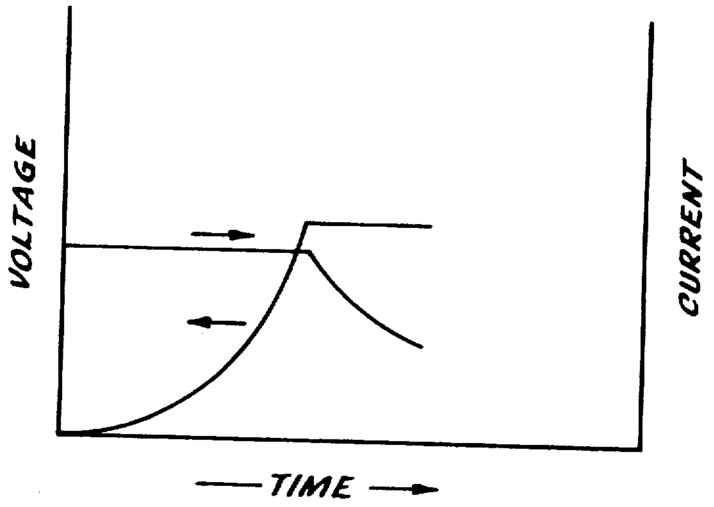


FIG. 1

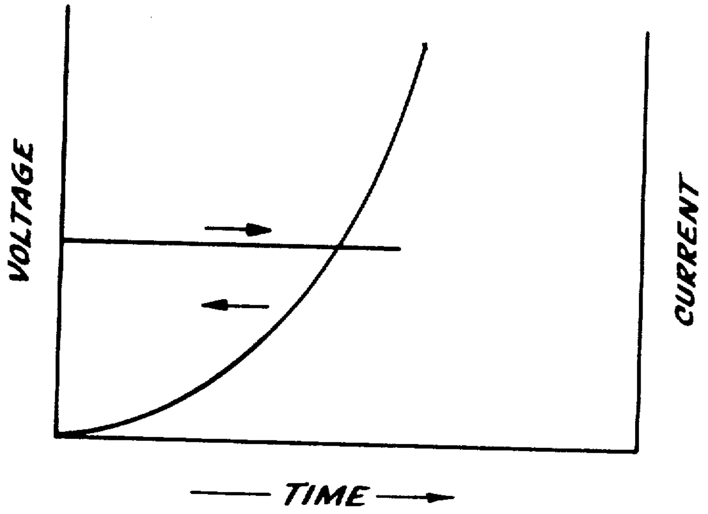


FIG. 2

RICHARD L. SMITH
INVENTOR

BY Frank M. Hansen
ATTORNEY

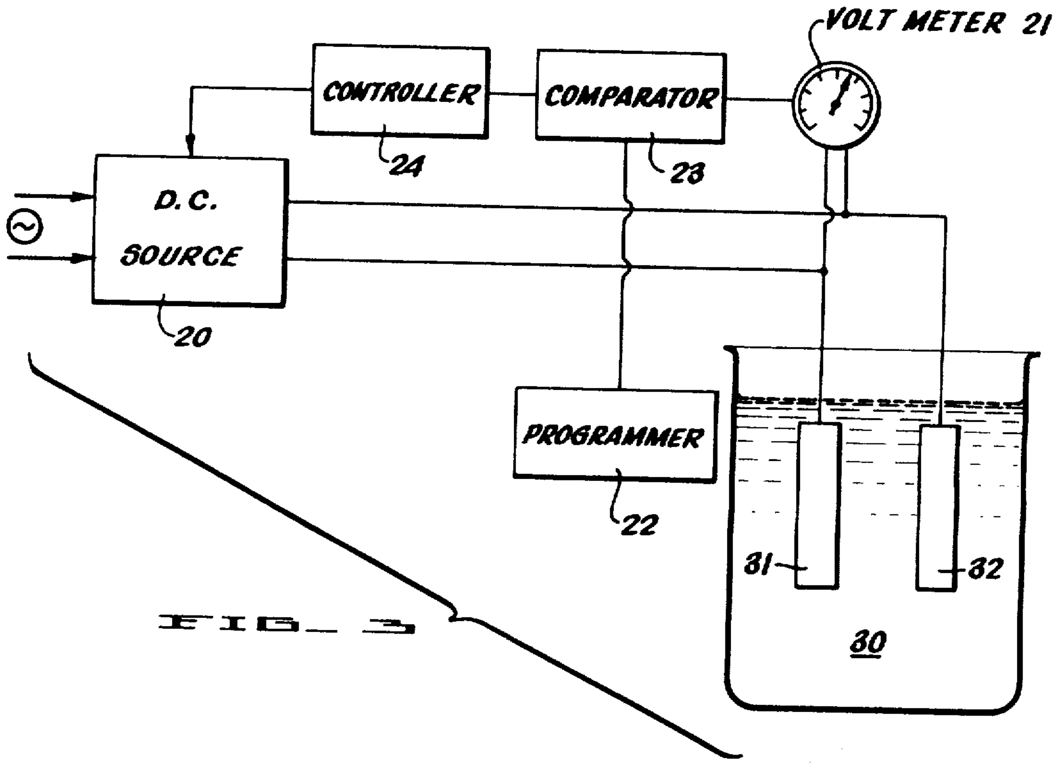


FIG_3

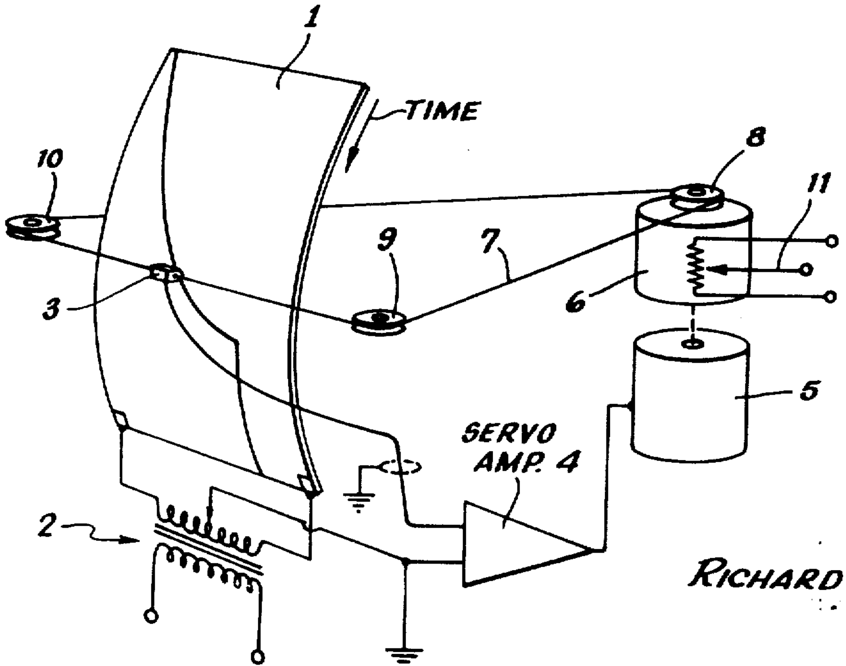


FIG_4

RICHARD L. SMITH
INVENTOR

BY Frank W. Hansen
ATTORNEY

CONTROL OF INTEGRAL COLOR ANODIZING PROCESS

BACKGROUND OF THE INVENTION

It is now well known to integrally color anodize aluminum and aluminum alloy products such as sheets, extrusions, castings and the like for architectural and other purposes where the integrally colored coatings provide a high aesthetic appeal. The basic process was first described by Deal et al. in Re. 25,566 assigned to the present assignee. The electrolyte described by Deal et al is an aqueous solution of sulfosalicylic acid with small amounts of sulfuric acid or metal sulfates included therewith. Subsequently, it has been found that many compounds, both organic and inorganic, can be utilized with small amounts of sulfuric acid and/or metal sulfates in aqueous solution to form integrally colored anodic oxide coating. Examples of these compounds include sulfophthalic acid, sulforesorcinol, ligno-sulfonic acid, oxalic acid, maleic acid, succinic and combinations thereof, and polyacid species such as dichromate, molybdate, tungstate and vanadate. All of these electrolytes are characterized by the production of anodic oxide coatings which have a resistance which increases during the anodizing process at a substantial rate and which the color density thereof is primarily voltage dependent. This resistance characteristic of the integrally colored anodic oxide coatings is to be distinguished from the resistance characteristics of clear or colorless anodizing in sulfuric acid electrolytes and the like which increases up to a certain value and remains substantially at this value or increases just slightly during the remainder of the anodizing process. The oxide coatings produced in chromic acid electrolytes do exhibit a rapidly increasing resistance during the formation thereof but the color density of these coatings, which is very low, is not primarily voltage dependent. Moreover, chromic acid anodizing is normally not used to anodize aluminum for architectural purposes because of the very limited color range obtainable.

In the process described by Deal et al, the aluminum workpiece is submerged in the electrolyte and subjected, as the anode, to electrolysis. Although many electrical programs can be employed, only two are presently being commercially used to any extent. The most efficient is a two-step process comprising subjecting the workpiece to a substantially constant current density until a particular voltage is reached and then maintaining this voltage at a substantially constant level until the desired total current quantity has passed through the workpiece. The elapsed time of the constant current density phase is commonly termed "time to peak" —that is, the time to reach peak voltage. The other method comprises maintaining the substantially constant current density until the desired total current quantity has passed through the workpiece.

A multitude of variables affect the color of the anodic oxide coating. These variables include workpiece composition and surface characteristics, bath composition, bath temperature, current density, peak voltage and total current quantity passed through the workpiece. In the past color control from batch to batch has been quite difficult due to the problems of controlling all the variables. This is particularly true over long periods of time due to the changes which occur within the controllable limits of bath composition. To minimize the color variance, the aluminum industry has placed stringent controls on the composition and thermal treatment of the aluminum workpiece. Similar controls have been placed on the initial and operating compositions of the electrolyte bath. In addition, most anodizing installations have cation exchange devices for the removal of dissolved aluminum and periodically analyze the bath to determine the need of adding other components — e.g., sulfuric acid and sulfosalicylic acid. Moreover, most anodizers attempt to control the temperature of the bath within ± 2° F by suitable refrigerating and heating means. However, due to the heat generation at the anode-electrolyte interface, temperature gradients exist within the bath. The anodizers agitate the bath either mechanically or with air to minimize these gradients; however, agitation does not ensure a constant temperature at the interface of the electrolyte and the surface of the workpiece—the critical place for color generation. Several anodizers have installed automatic control devices for maintaining the proper current density and peak voltage to eliminate human error in the operation of the anodizing program. Despite the above precautions, the control of color is still technically a difficult task and the reject rate remains quite high. Even with automatic control devices most, if not all, anodizers must visually inspect the workpiece to determine whether the color thereof matches the standard color sought. This is particularly noticeable over long periods of time due to the buildup of decomposition products in the bath. As the decomposition products build up in the bath, the color of the oxide coating will not match the standard color sought. Due to the cost of the electrolyte, frequent replacement would be economically prohibitive.

The purpose of this invention is to provide a process for controlling the anodizing process wherein the effect of variations of workpiece composition and surface characteristics, bath composition and temperature and the like on the ultimate color of the anodic oxide coating are minimized.

DESCRIPTION OF THE INVENTION

This invention relates to a process for controlling the integral color anodizing process wherein reproducibility of the color of the oxide coating from anodizing load to anodizing load is substantially improved. The invention is predicated upon the discovery of controlling the voltage across the electrolytic cell with respect to time in accordance with a preselected voltage-time relationship to obtain a particular color and thereby obtaining integrally colored anodic oxide coatings that will match from anodizing load to anodizing load despite variations in the workpiece composition and surface characteristics, the bath composition and temperature, and the like.

Moreover, the control process of the present invention eliminates the need for determining the surface area of the workpiece because the control program is based upon voltage which is not surface area dependent. The prior art color anodizing technique required surface area determinations because the control was based on current density (amps/ft^2 of workpiece surface). Furthermore, in the prior art it was believed that for reproducible colors the total current quantity should not vary from batch to batch, because the thickness of the oxide coating is dependent upon the total current quantity and the thickness of the coating affected the color.

The present invention was developed from the belief that the color generation of integral color anodizing processes is primarily dependent upon a dark band of anodic oxide immediately adjacent to the metallic substrate and below a relatively colorless oxide layer which is exposed to the atmosphere. A slight golden or brownish hue permeates the entire oxide coating, but this hue has very little effect on the colored appearance of the anodized workpiece. The colored appearance of the workpiece is a function of the color density and the thickness of the dark-band layer; however, the color density is primarily the color determinant. The dark-band formation occurs only after a threshold voltage is reached, the level of which varies depending upon the bath composition, temperature, etc. The color density, i.e., the lightness or darkness per unit thickness, of the dark band is primarily a function of voltage — the higher the voltage the higher the color density (i.e., the darker becomes the oxide layer). Moreover, although the total current quantity passed through the workpiece after the threshold voltage is reached determines the thickness of the dark-band layer, and thus to a certain extent the color of the workpiece, the effect of the total current quantity during that period is not as great as the effect of the voltage. Therefore, by controlling the voltage with respect to time, the color density is very reproducible and, although the current density and total current quantity will change from load to load, the change is insufficient magnitude to noticeably change the colored appearance of the anodized workpiece.

With the prior art programs of constant current density and constant voltage or constant current density alone, the color anodizing of complicated workpieces was extremely difficult due to the difficulty in determining surface area. A trial-and-error procedure was usually employed wherein the surface area of the workpiece was merely estimated and then standard programs were employed which were designed to produce the desired color. If the desired color for the workpiece was not obtained, the process was repeated on another workpiece and variables were changed such as peak voltage, current density, total anodizing time, and the like in an attempt to match the standard color sought. If complicated workpieces having different shapes and/or surface areas were to be anodized to the same desired color, the entire trial-and-error procedure would have to be repeated.

The control process of the present invention avoids this problem allowing aluminum workpieces of all shapes and sizes to be anodized by the same control program to give identical colored oxide coatings.

This control of the present invention is advantageously obtained by developing a voltage-time relationship for a given bath composition and temperature and particular workpiece composition to give an anodic oxide coating with the desired color; transferring said relationship as data to a data storage means; retrieving said voltage-time data in the form of a signal and controlling the voltage impressed across the electrolytic cell with respect to time by means responsive to said signal.

Reference is made to the accompanying drawing to illustrate various features of the invention.

FIG. 1 illustrates typical voltage-time and current density-time relationships characteristics of a prior art two-step, constant current density-constant voltage, integral color anodizing program.

FIG. 2 illustrates typical voltage-time, current density time relationships characteristics of a prior art single-step, constant current density, integral color anodizing program.

FIG. 3 is a schematic diagram of a control system for controlling the integral color anodizing in accordance with the present invention.

FIG. 4 is a diagramatic view of an advantageous device for storing and retrieving voltage-time data.

In accordance with the invention, a voltage-time relationship is developed for a particular aluminum alloy by anodizing an aluminum workpiece having the alloy composition, in accordance with known constant current density-constant voltage or constant current density programs for the particular alloy and bath composition to obtain the anodic oxide coating of the desired color and texture. During anodizing, the voltage with respect to time is noted, either continually by automatic means, or periodically by manually noting the voltage at particular intervals of time.

Having developed the voltage-time relationship, it is transferred or programmed into a data storage means. Although any suitable data storage means, including both digital and analog, may be employed, the function generating device shown in FIG. 4 has been found particularly convenient. It is manufactured and sold under the trademark Data-Trak by Research Incorporated. A similar device is described and claimed in U.S. Pat. No. 3,329,804 assigned to the same company.

In the device of FIG. 4, the voltage-time data is scribed on a Mylar card **1** coated with a conductive material. The scribing removes the conductive material from the card, dividing the card into two electrically isolated conductive planes. In operation the two isolated planes are separately charged by oppositely phased AC voltages, by circuitry **2** establishing an electrostatic voltage gradient across the scribed voltage-time curve. A probe **2** adjacent to, but spacially disposed from, the card scans the card at a particular time based speed. The prove picks up from the electrostatic field an error signal having a magnitude proportional to the probe's deviation from the center of the program line. A servo system comprising a servo amplifier **4** and a servo motor **5** responds to an error signal to correct the probe's deviation by rotating the shaft of an output potentiometer **6** which is mechanically connected to the probe by cable **7** and pulleys **8**, **9** and **10**. The rotational movement of the potentiometer shaft varies the position of the wiper **11** thus varying the output of the potentiometer which is directly related to the voltage-time curve scribed on the conductive surfaces as measured from a base coordinate. The output signal may then be conveniently employed as a reference signal for controlling the voltage impressed across the electrolytic cell because it is directly related to the voltage-time data stored on the card **1** measured from a base coordinate.

Referring particularly to FIG. **3**, a system is shown for controlling the voltage across the cell. The system comprises a direct current source **20**, a voltmeter **21**, programmer or function generator **22**, a comparator **23** and a control means **24** responsive to any error signal produced by the comparator **23** in conjunction with an electrolytic cell **30** with an anode **31** and cathode **32**. The DC source **20** normally comprises a rectifier and a suitable transforming device for converting alternating current to a relatively stable DC output. The voltmeter **21** senses the voltage across the anode and cathode of the anodizing cell. The comparator compares the measured cell voltage with the desired voltage represented by the signal from the programming or function generating means **22** and generates an error signal if the cell voltage does not correspond to the signal from programmer **22**. Should an error signal exist, the controller **24** will adjust the DC source to provide the programmed voltage across the cell.

In an alternative system similar to the one shown in FIG. 3, the voltmeter measures the voltage between the anode and an auxiliary electrode spaced a short distance from the anode. In this manner several anodizing tanks can be controlled by the same voltage-time program if the anode-electrode spacing is kept the same in each tank because the voltage drops in the bus bars, splines and the like are not included in the voltage-time program.

Other suitable control systems can be employed; for example, that shown in U.S. Pat. No. 3,121,054.

The following examples are given to more fully illustrate the advantages of the control process of the present invention.

A **5005** aluminum alloy sheet was cut up to provide specimens for the integral color anodizing tests. Three separate aqueous electrolytic baths were prepared having the compositions set forth in Table I.

TABLE I

Bath Composition—Grams/Liter

	Sulfosalicylic Acid	H_2SO_4	Al
Bath No. 1	64.6	5.8	1.7
Bath No. 2	61.9	5.6	1.9
Bath No. 3	67.3	6.0	1.5

EXAMPLE 1

To develop the required voltage-time relationship, a 5005 alloy specimen was subjected to anodizing in Bath No. 1 at a temperature of 25° C in accordance with a program known to give a light-amber color to this alloy. The program comprised subjecting the specimen to a constant current density of 30 amps/ft^2 until a voltage of 62 volts was obtained and then maintaining this voltage at a substantially constant level until a total current quantity of 10 amps-hours/ft^2 passed through the specimen and the anodic oxide coating was 0.88 mils thick. During the anodizing the cell voltage was noted at short periodic intervals. The voltage-time relationship obtained was scribed on a Data-Trak card.

EXAMPLE 2

Another 5005 specimen was subjected to anodization in Bath No. 2 at 20° C. The anodizing program was the voltage-time relationship previously developed and stored on the Data-Trak card in Example 1. The anodizing was controlled by placing the previously scribed card into a model 5300 Data-Trak programmer, the output potentiometer of which controlled the cell voltage. The color of the anodic oxide coating was a light amber which acceptably "matched" the first 5005 specimen anodized to obtain the voltage-time relationship. The oxide coating thickness was 0.70 mil.

EXAMPLE 3

A separate 5005 specimen was subjected to anodization in Bath No. 2 at a temperature of 25° C and controlled by the same Data-Trak card used in Example 1. The color of the anodic oxide coating "matched" both previously anodized samples. The oxide coating was 0.79 mil thick.

EXAMPLE 4

Another of the 5005 specimens was subjected to anodization in Bath No. 2 at a temperature of 30° C and controlled by the same Data-Trak card used in previous examples. The color of the anodic oxide coating "matched" the previously anodized samples. The oxide thickness was 0.84 mil.

EXAMPLE 5

The test described in Example 2 was repeated using Bath No. 3 and resulting color of the anodized specimen "matched" the other specimens. The oxide thickness was 0.78 mil.

EXAMPLE 6

The test described in Example 3 was repeated using Bath No. 3 and again the anodic oxide coating "matched" the other specimens. The oxide thickness was 0.82 mil.

EXAMPLE 7

The test described in Example 4 was repeated using Bath No. 3 and again the anodic oxide coating matched the others. The oxide thickness was 0.93 mil.

The instrumental color determinations of each of the above-mentioned specimens are set forth in Table II. The Green Reflectance values generally indicate the lightness and darkness of the specimen—the higher the value the lighter the color. An untrained eye usually cannot distinguish colors having a difference of Green Reflectance values of less than 2 reflectance units. For most architectural applications a variance of up to 3 units is acceptable.

The Green Reflectance values are obtained by measuring the reflectance of green light from the sample (a standard green filter is placed between the light source and the specimen), utilizing a standard tristimulus colorimeter. This system of color measurement is commonly termed the CIE system.

TABLE II

	Example No. 1	2	3	4	5	6	7
Green Reflectance, %	17	16.7	17.2	18.4	16.4	17.4	17.8

It is patent from the above examples and the data in Table II that wide variances in bath composition and temperature can be tolerated by employing the control process of the present invention with little or no perceptible differences in the color of the oxide coatings. Variations in workpiece composition and surface characteristics are similarly minimized. To appreciate the consistent results obtained with the present invention, it should be noted that, if the prior art techniques were employed, the temperature and composition variations shown in the above examples would produce differences in Green Reflectance values of from 5 to 15 units, i.e. the specimens would not match. The term "aluminum" as used herein includes pure aluminum and aluminum base alloys containing more than 50 percent aluminum.

What is claimed is:

1. In the process of integrally color anodizing an aluminum workpiece in an electrolytic cell, wherein the workpiece is subjected as an anode to anodization in an acidic aqueous electrolyte, which produces an anodic oxide surface characterized by a resistance which increases at a substantial rate during the formation thereof and by the color density thereof which is primarily voltage dependent, the improvement in the control of the color of the oxide coating comprising:

a. developing a voltage-time relationship to control the voltage during the time the workpiece is being anodized for a given bath composition and workpiece composition to give a desired color,

b. providing a voltage source to said cell,

c. generating a signal representing the desired voltage at a particular time in accordance with said voltage-time relationship,

d. sensing the voltage provided by said source,

e. generating a signal representing the sensed voltage,

f. comparing by an instrumentality the sensed voltage signal with the desired voltage signal, and

g. adjusting the voltage source by means responsive to said instrumentality to provide a voltage corresponding to the desired voltage.

2. The process of claim 1 wherein the voltage-time relationship is transferred into a data storage means by scribing a line representing said relationship on a plate having a conductive surface, thereby dividing said conductive surface into two electrically isolated conductive surfaces, the scribed plate is scanned at a time-based speed, and a signal is generated representing the voltage-time relationship as scribed on said plate.

3. The method of claim 1 wherein the electrolyte comprises an aqueous solution of 0.1 to 2.0 percent sulfuric acid and a compound selected from the group consisting between about 5 and 30 percent by weight of an organic acid selected from the group consisting of sulfosalicylic acid, sulfophthalic acid, lignosulfonic acid, sulforesorcinol, oxalic acid, maleic acid, succinic acid and combinations thereof; and between 0.03 to 0.50 gram-mol per liter of polyacid species selected from the group consisting of dichromates, molybdates, tungstates and vanadates.

4. The method of claim 1 wherein the voltage is controlled through a constantly increasing period until a desired peak voltage is reached and then through a substantially constant voltage at substantially said peak voltage.

* * * * *