**United States Patent** [19]
**Sugiyama et al.**

[11] **3,929,593**
[45] **Dec. 30, 1975**

# [54] METHOD OF FORMING COLORED OXIDE FILM ON ALUMINUM OR ALUMINUM ALLOY MATERIAL

[75] Inventors: **Noboru Sugiyama; Masahiro Takahashi; Hirosuke Kanamori; Ken Sato; Yoshio Hirayama,** all of Shizuoka; **Masahiro Mikamo,** Tokyo; **Toshiro Takahashi,** Shizuoka; **Toshihiro Nagano,** Shizuoka; **Kazuyoshi Kaneda,** Shizuoka; **Isao Hara,** Shizuoka, all of Japan

[73] Assignees: **Riken Light Metal Industries Company, Ltd.; Nippon Light Metal Co., Ltd.,** both of Japan

[22] Filed: **Sept. 18, 1974**

[21] Appl. No.: **507,216**

[30] **Foreign Application Priority Data**

Sept. 21, 1973 Japan .............................. 48-106656

[52] **U.S. Cl.** ........... **204/35 N;** 204/38 A; 204/58 A; 204/DIG. 8; 204/DIG. 9

[51] **Int. Cl.**$^2$.. **C25D 5/48;** C25D 11/22; C25D 5/18

[58] **Field of Search** .... 204/35 N, 38 A, 58, DIG. 8, 204/DIG. 9

[56] **References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 3,597,339 | 8/1971 | Newman et al. | 204/58 |
| 3,616,297 | 10/1971 | Cooke et al. | 204/35 N |
| 3,669,856 | 6/1972 | Gedde | 204/58 |
| 3,704,209 | 11/1972 | Patrie | 204/35 N |
| 3,704,210 | 11/1972 | Patrie | 204/35 N |
| 3,708,407 | 1/1973 | Newman et al. | 204/58 |
| 3,717,555 | 2/1973 | Chakravarti | 204/35 N |
| 3,769,180 | 10/1973 | Gedde | 204/35 N |

FOREIGN PATENTS OR APPLICATIONS

| | | | |
|---|---|---|---|
| 1,496,718 | 11/1971 | Germany | 204/58 |

*Primary Examiner*—John H. Mack
*Assistant Examiner*—Aaron Weinstuch
*Attorney, Agent, or Firm*—McNenny, Farrington, Pearne & Gordon

## [57] ABSTRACT

A method of forming a colored oxide film on an aluminum or aluminum alloy material by electrolyzing the aluminum or aluminum alloy material used as one or each of the electrodes in an electrolytic bath containing a metallic salt while applying a pulse voltage consisting of a plurality of unipotential pulses whose polarity is reversed at every predetermined conduction time. The aluminum or aluminum alloy material may also be one that has an oxide film previously formed thereon.

**14 Claims, 12 Drawing Figures**

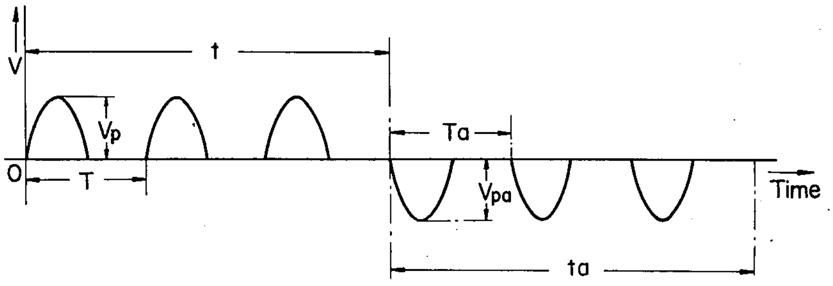


Fig. 1

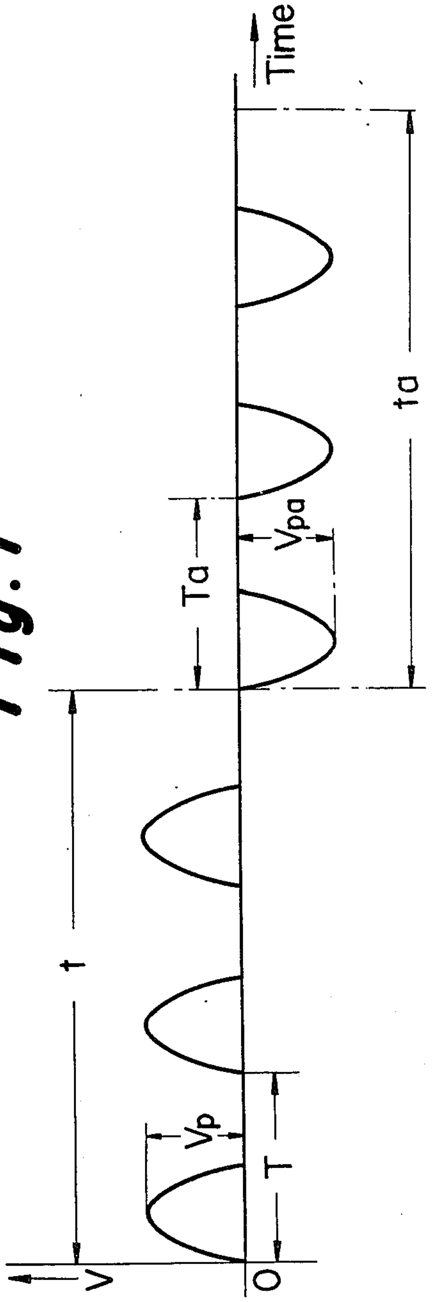


Fig. 2

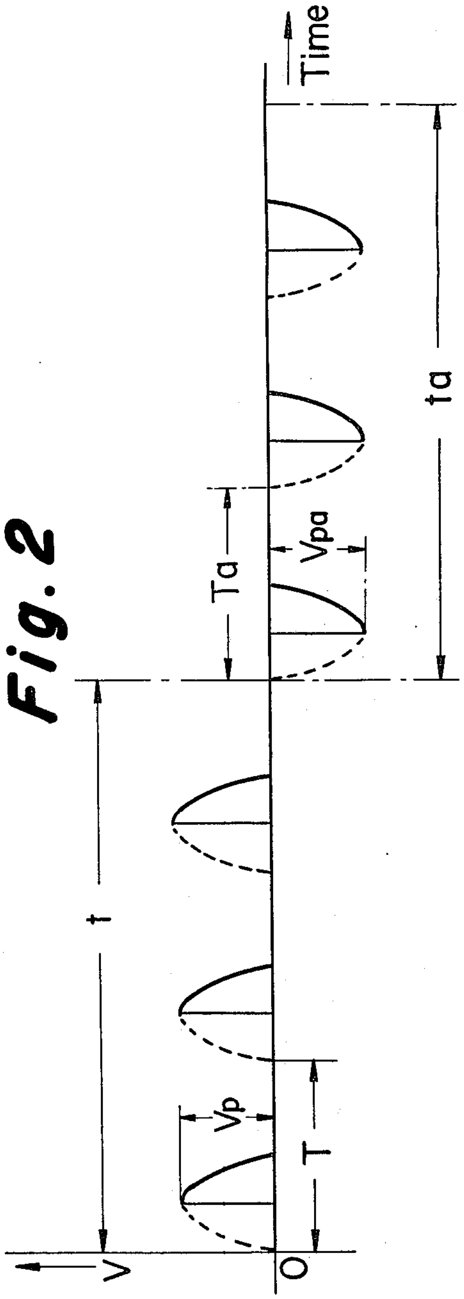


Fig. 3

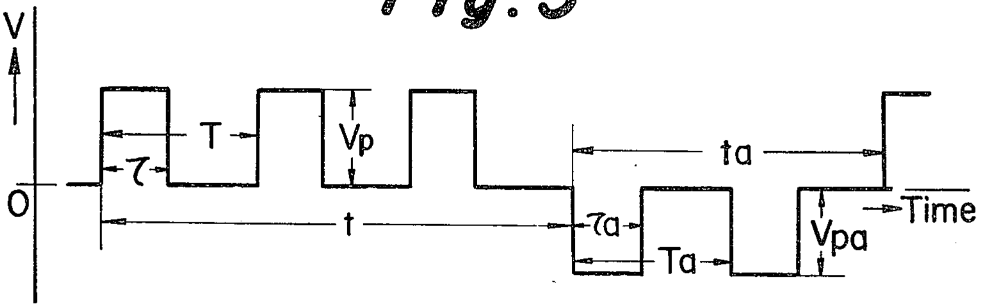


Fig. 4

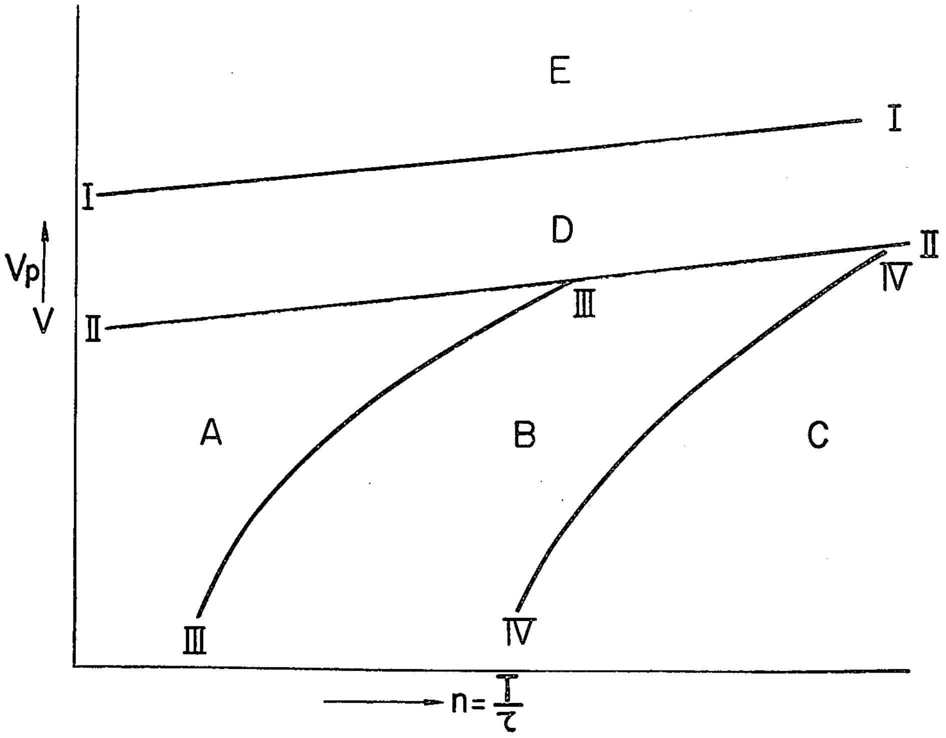


Fig. 5

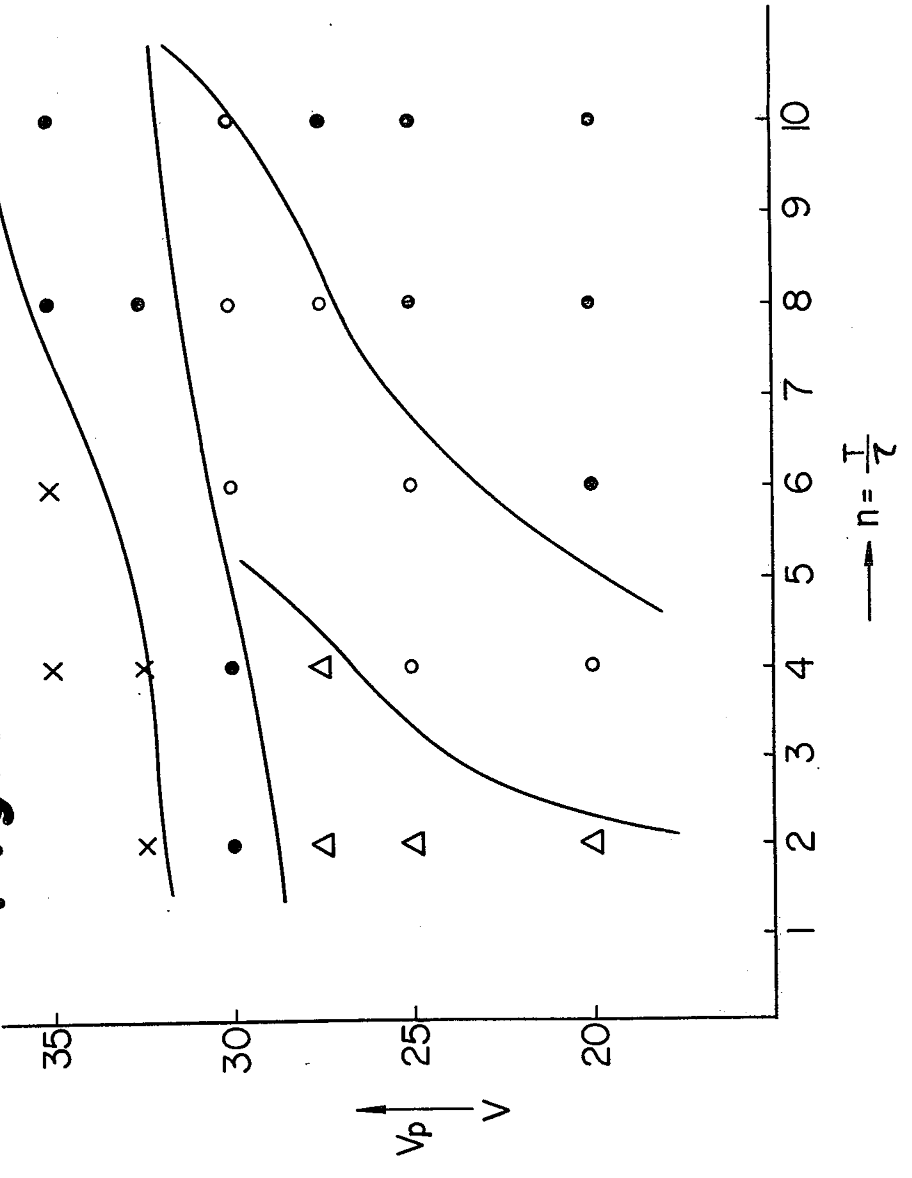


Fig. 6

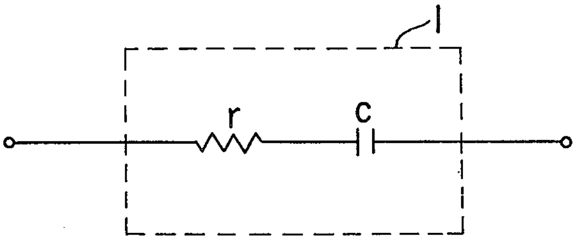


Fig. 7

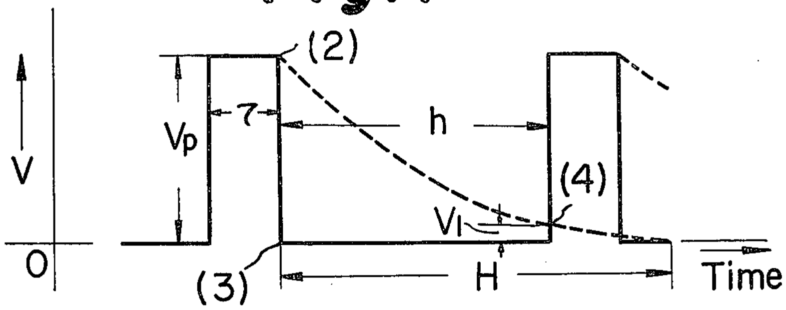


Fig. 8

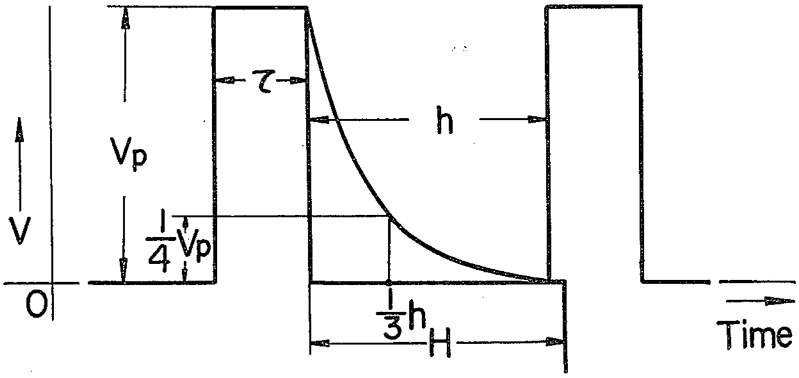


Fig. 9

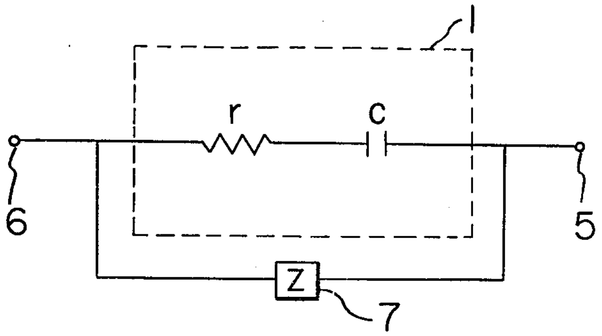


Fig. 10

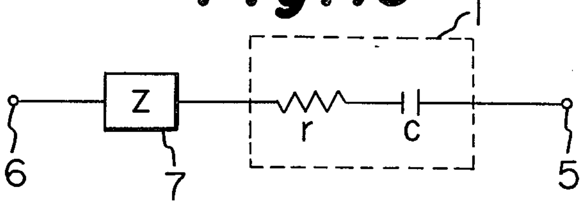


Fig. 11

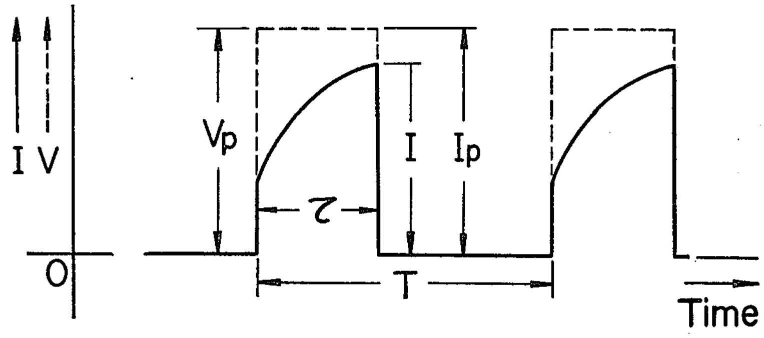
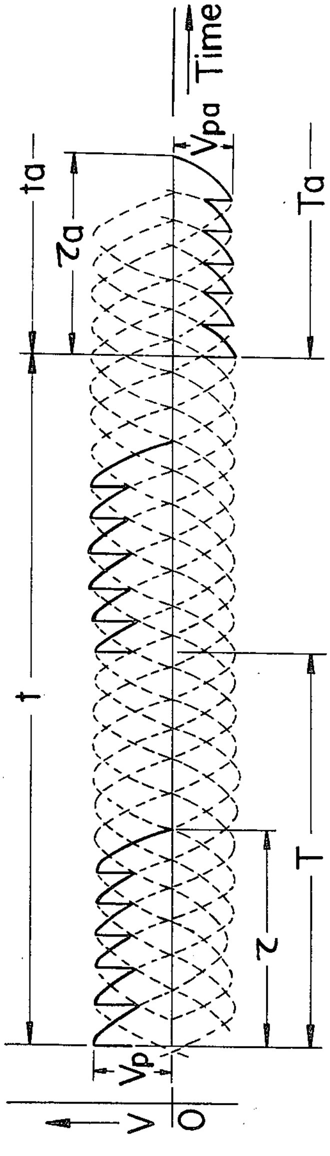


Fig. 12



# METHOD OF FORMING COLORED OXIDE FILM ON ALUMINUM OR ALUMINUM ALLOY MATERIAL

## BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of forming a colored oxide film or the surface of an aluminum or aluminum alloy material (hereinafter referred to simply as an aluminum material), and more particularly to a method of forming a colored oxide film on the surface of an aluminum material by electrolyzing the aluminum material in an electrolytic bath containing a metallic salt to thereby color the oxide film in color tone characteristic of the metal in the metallic salt.

2. Description of the Prior Art

Herertofore, a variety of methods have been employed for forming a colored oxide film on the surface of an aluminum material by electrolyzing the aluminum material by applying thereto a predetermined voltage in an electrolytic bath containing a metallic salt. In one such method, an oxide film is formed first by electrolyzing the aluminum material used as an anode and then colored by applying an AC voltage to the aluminum material in an aqueous solution containing a metallic salt.

With this method, however, the colored oxide film forming process is composed of two steps and, further, it is necessary that the second step using the AC field be achieved in relation to the oxide film formation of the first step. This introduces defects such as difficulty in bath control, low productivity, a narrow range of color tone of the colored oxide film and poor reproducibility of color tone, making it difficult to obtain uniform colored oxide films at all times.

## SUMMARY OF THE INVENTION

It is one object of this invention to provide a colored oxide film forming method that, in an electrolytic bath containing a metallic salt, an aluminum material with no oxide film formed thereon or an aluminum material having an oxide film previously formed thereon, used as one or each of electrodes, is electrolyzed by supplying the aluminum material with a voltage of pulse waveform which is positive or negative for a period of time longer than one pulse period at the shortest, whereby an oxide film colored over a wide range of color tone is formed on the surface of the aluminum material.

It is another object of this invention to provide a colored oxide film forming method that, in an electrolytic bath containing a metallic salt, an aluminum material with no oxide film formed thereon or an aluminum material with an oxide film previously formed thereon, used as one or each of electrodes, is electrolyzed by supplying the aluminum material with a pulse voltage of rectangular waveform which is positive or negative for a period of time longer than one pulse period at the shortest, thereby to form a colored oxide film on the surface of the aluminum material.

Other objects, features and advantages of this invention will become apparent from the following description taken in conjunction with the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a waveform diagram of a pulse voltage which is obtained by half-wave rectification of a single-phase sine-wave voltage and whose polarity is inverted at every predetermined conduction;

FIG. **2** is a waveform diagram of a pulse voltage which is obtained by phase-controlling the waveform of FIG. **1** with a silicon controlled rectifier;

FIG. **3** is a waveform diagram of a rectangular-wave pulse voltage whose polarity is inverted at every predetermined conduction and whose positive and negative pulses are both of rectangular shape;

FIG. **4** is a graph showing the interrelationships of a pulse period T/a, pulse duration $\tau a$, a peak voltage and color tone of the resulting colored oxide film in an electrolysis which is effected in an electrolytic bath containing a metallic salt by applying a rectangular pulse voltage whose polarity is inverted at every predetermined conduction;

FIG. **5** is a graph showing the same relationships as in FIG. **4** in the case of using a silver salt as a metallic salt;

FIG. **6** shows an equivalent circuit of an aluminum material electrolytic cell;

FIGS. **7** and **8** show voltage variations between both electrodes due to a discharge from an electrolytic cell during an electrolysis employing such a rectangular-wave pulse voltage as depicted in FIG. **3**;

FIGS. **9** and **10** are circuit diagrams illustrating means for preventing the influence of the discharge from the electrolytic cell such as shown in FIGS. **7** and **8**;

FIG. **11** shows the mode of a current flowing between both electrodes in an electrolytic bath which is caused by the influence of accessories to an electrolyzing equipment such as leads or the like during an electrolysis using such a rectangular-wave pulse voltage as shown in FIG. **3**; and

FIG. **12** is a waveform diagram of a rectangular-wave pulse voltage produced by half-wave rectification and phase control of a commercial AC.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will hereinafter be described in detail.

At first, an aluminum material is subjected to pretreatment as is the case with ordinary electrolysis. This pretreatment is not related directly to the present invention and may be mechanical or chemical pretreatment. Further, an aluminum material having an oxide film previously formed thereon can also be used and, in this case, the mechanical or chemical pretreatment is achieved prior to the formation of the oxide film, so that such pretreatment need not be effected again.

Then, in an electrolytic bath containing a metallic salt, the aluminum material with no oxide film formed thereon or the aluminum material with an oxide film previously formed thereon is electrolyzed by applying a voltage of the following characteristics to it, the aluminum material being used as one or both electrodes.

The voltage used in this case is a voltage of pulse waveform, which is applied to the aluminum material for a period of time longer than one pulse period in its positive and negative cycles alternately.

Further, this voltage of pulse waveform is one that the duration of each pulse is short, the initial and final values of the pulse are equal to each other and the pulse rises up to a predetermined level. This voltage may be such as shown in FIG. **1**, which is obtained by halfwave rectification of a single-phase sine-wave voltage, or as shown in FIG. **2**, which is obtained by phase-controlling the voltage of FIG. **1** with a silicon controlled rectifier or like rectifier, or such as shown in FIG. **3**, which is a rectangular-wave voltage, or may be a triangular-wave, exponential-wave or a partly sinewave voltage. Of these voltages, the pulse voltage of rectangular waveform is the easiest to obtain industrially and, by changing the characteristic values of the rectangular-wave as required, oxide films colored over a wide range of color tone can be obtained.

The characteristic values of the rectangular-wave pulse voltage are pulse durations $\tau$ and $\tau_a$, pulse periods T and $T_a$, peak voltages $V_p$ and $V_{pa}$ and conduction times $t$ and $t_a$, as shown in FIG. **3**. The metallic salt, which is contained in the electrolytic bath, is selected in relation to the color tone of the colored oxide film which is desired to obtain and it may be a sulfate, nitrate or any other salt. Further, the electrolytic bath is required only to be conductive and a sulfuric acid aqueous solution is the most inexpensive, and hence economical.

By electrolyzing the aluminum material under such conditions as described above, an oxide film which is composed of an aluminum oxide and colored, that is, a colored oxide film is formed on the surface of the aluminum material.

Now, a description will be given of the colored oxide film forming mechanism mainly in connection with the case of electrolyzing an aluminum material by applying thereto the rectangular-wave pulse voltage shown in FIG. **3**. In the rectangular-wave pulse shown in FIG. **3**, the positive and negative pulse waveforms are different from each other but the characteristic values of the bath pulse waveforms, for example, the peak voltages $V_p$ and $V_{pa}$, the pulse periods T and $T_a$, the pulse durations $\tau$ and $\tau$ and the conduction times t and $t_a$, can be selected identical or symmetrical with each other, respectively. Accordingly, the rectangular-wave pulse voltage will hereinafter be described on the assumption that the characteristic values of both pulse waveforms are identical to each other. However, this invention is not limited specifically to the above. For example, by selecting the conduction times of the positive and negative pulses to be different from each other, color tone of the colored oxide film can be changed as required and, also by selecting the peak voltage, the period and the duration of the positive pulse to be different from those of the negative pulse respectively, color tone of the colored oxide film can be changed as desired.

Namely, in the present invention, if alternately supplied with the positive and negative pulses such as depicted in FIG. **3**, the aluminum material serving as one or each of the electrodes becomes positive and negative alternately with the predetermined conduction times t and ta. In this case, while the polarity of the aluminum material remains positive, the aluminum material is oxidized as the anode to form an oxide film. Then, when the polarity of the aluminum material becomes negative, metallic ions dissociated and a metal ionized in the form of a metallic salt in the electrolytic bath enter into the oxide film. (The above metallic ions and metal will hereinafter be referred to simply as the metallic salt.) Next, when the polarity of the aluminum material becomes positive again, an oxide film is formed as mentioned above and, in addition, the metallic salt having entered into the oxide film is also oxidized and the resulting products are electro-precipitated in the oxide film when the polarity of the aluminum material becomes negative again, thus forming a colored oxide film.

With such a mechanism, the colored oxide film is formed on the aluminum material and the conditions for the above coloring mechanism are satisfied by the electrolysis using the pulse voltage. The use of such a rectangular-wave voltage as shown in FIG. **3** facilitates fulfillment of such conditions.

Thus, while the negative rectangular-wave pulse voltage is applied to the aluminum material to electrolyze it, the metallic salt invades the oxide film formed on the aluminum material during the application of the positive rectangular-wave pulse voltage or the oxide film formed previously. Since the applied pulse voltage is of rectangular waveform, predetermined invading energy is obtained and the metallic salt invades the oxide film to the vicinity of the bottom of each pore therein.

The positive pulse voltage, $V_p$ in particular, the rectangular-wave pulse voltage, has practically no rise time as shown in FIG. **3** and the negative peak voltage $V_{pa}$ also acts on the aluminum material with practically no rise time, so that the invading energy of the metallic salt is provided simultaneously with rising of the pulse voltage. Hence, the metallic salt enters deeply into the pores of the oxide film, that is, down to the bottoms of the pores.

The metallic salt thus driven into the oxide film by the electrolysis by the application of the negative rectangular-wave pulse voltage is electrolyzed and oxidized again by the application of the positve rectangular-wave pulse voltage. While the positive rectangular-wave pulse voltage is applied, oxidation of the metallic salt is promoted to provide an excellent colored oxide film.

When the oxide film into which the metallic salt has entered is electrolyzed by the application of the positive pulse voltage, the metallic salt is oxidized but one part of the resulting product is eluted and, further, one part of the metallic salt is eluted before oxidized. During the next application of the negative pulse voltage, the remaining oxidized metallic salt is electro-precipitated in the oxide film and serves as a coloring source. Accordingly, in order that the colored oxide film may be of clear and deep color tone when it is gradually formed by repeatedly effecting the above processes, it is necessary that electro-precipitation and elution of the product are balanced with each other. The rectangular-wave pulse voltage satisfies this requirements most easily and, in the electrolysis using the rectangular-wave pulse voltage, it is easy to control the voltage to fulfill the requirement.

The amount of the metallic salt oxidized during electrolysis by the application of the positive pulse voltage increases in proportion only to the magnitude of the applied voltage $V_p$ as shown in FIG. **3**. The amount of the oxidized product re-eluted is in proportion to the product of the value of the applied voltage and the duration thereof, that is, the amount of positive charges. For example, in the case of the voltage of the waveform of FIG. **3**, it is in proportion to $(V_p \times \tau)$ and, at the same time, the oxide film is formed in proportion to the amount of positive charges or current flowed.

Consequently, for electrolyzing the aluminum material in such a manner as to oxidize the metallic salt and to increase the electro-precipitated product within a range in which the oxide film can be formed on the aluminum material and to prevent re-elution of the product, it is preferred that the value of the applied voltage be as large as possible and that the amount of positive charges or the amount of current is small.

In the case of the rectangular-wave pulse voltage, it is possible to apply a high voltage instantaneously.

In the case of controlling the amount of positive charges and the peak voltage at will as described above, the rectangular-wave pulse voltage shown in FIG. **3** is easier to control than the other pulse voltages and has an advantage that a colored oxide film of desired color tone can be obtained.

FIG. **4** generally shows the relationships of the pulse durations $\tau$ and $\tau_a$, the pulse periods T and $T_a$ and the peak voltages $V_p$ and $V_{pa}$ to color tone of the oxide film in the case where an aluminum material A.A**6063** was electrolyzed by the rectangular-wave pulse voltage of FIG. **3** in a sulfuric acid aqueous solution containing a metallic salt. FIG. **5** shows similar relationships in the case of an electrolysis in a sulfuric acid aqueous solution containing $Ag_2SO_4$. As is apparent from both graphs, the relationships of FIG. **4** and those of FIG. **5** employing a special metallic salt ($Ag_2SO_4$) are substantially the same but there are some occasions when chemical and physical properties of the metallic salt used differ a little in accordance with the kind of metallic salt added. In FIG. **5,** triangles, white circles, black circles and crosses indicate yellow, light reddish orange, reddish orange and unclear reddish orange colors, respectively.

In FIGS. **4** and **5,** n=pulse period/pulse duration $(=T/\tau>1$ or $T_a/\tau_a>1)$.

In FIG. **4**, the ordinate represents the peak voltage and the abscissa represents *n*. Reference characters A, B, C and D indicates zones of color tone of the oxide film. As is seen from a comparison of FIGS. **4** and **5,** for example, in the case of an electrolysis using the pulse voltage in a sulfuric acid aqueous solution containing $Ag_2SO_4$, the zones A,B and C correspond to yellowish, light reddish orange and partly deep reddish orange colors, respectively, and the zone E is one in which the oxide film is destroyed even if any kind of metallic salt is employed.

As shown in FIG. **4**, in the zone E above the line I—I, the peak voltage is high and a current flows excessively, so that the oxide film is broken and its color tone becomes unclear. Hence, it is not preferred to raise the peak voltage above the line I—I. In the zones lower than the line I—I, by electrolyzing with the pulse voltage at different values of *n* and the peak voltage, colors such as shown in FIG. **4** can be obtained with ease.

Further, the zone below the line II—II is divided into the zones A,B and C in accordance with the values of *n* and the peak voltage. In each zone, the oxide film is colored only by the balance between the amount of the invaded metallic salt oxidized and electro-precipitated and its eluted amount. For example, as the value of *n* increases, the color tone of the oxide film changes from A to B and C one after another. For example, in the zone A in which the value of *n* is small, the amount of current flowed is large and the amount of metallic salt eluted is larger than that oxidized and electro-precipitated and, as a result of this, the color tone of the oxide film becomes light and, in the case of FIG. **5**, the oxide film becomes yellowish. In the zone B in which the value of *n* is a little larger than that in the zone A, the amount of metallic salt eluted is a little smaller than that in the zone A and the color tone of the oxide film becomes a little deeper. For example, in the case of FIG. **5**, the oxide film becomes of a light reddish orange color. Further, in the zone C in which the value of *n* is larger than that in the zone B, the pulse width $\tau$ is small but the quiescent time $h=T-\tau$ is short, so that the amount of positive current flowed decreases and the thickness of the oxide film decreases but the peak value remains as it is. Accordingly, in the zone C, since the eluted amount decreases as compared with the oxidized and electroprecipitated amount, the oxide film becomes deeper in color than in the other zones. In the case of FIG. **5**, the oxide film becomes of a reddish orange color and is partly in a deep reddish orange color. In FIG. **4**, the lines III—III and IV—IV between adjacent zones below the line II—II are inclined upwardly. this indicates that the amount of current flowed contributes to coloring of the oxide film.

Moreover, the line II—II separating the zones A, B and C from the zone D is also inclined upwardly. This indicates that the line II—II exists in the presence of a certain energy level, considering that when the amount of current flowed is decreased by an increase in *n*, even if the amount of current flowed is increased by an increase in the peak voltage $V_{pa}$, the overall energy level is lowered.

Further, in the zone D above the line II—II in FIG. **4**, the color of the oxide film becomes deep and its thickness greatly increases regardless of the value of *n*. In this zone D, the peak voltage is high and the current density increases, so that the balance between the electroprecipitation and oxidation and the elution is remarkably different from those in the zones A,B and C. Particularly, over a wide range of *n*, in other words, over a wide range of current density zone, oxide films of generally deep colors can be obtained and, for example, in the case of FIG. **5**, a deep reddish orange color can be obtained.

In the foregoing, *n* and the peak voltage which are color control factors have been described in connection with the pulse voltage.

In particular, the magnitude of the positive peak voltage $V_p$ is related mainly to oxidation of a metal and the magnitude of the negative peak voltage $V_{pa}$ is related mainly to invasion of the metallic salt into the oxide film. Considering that coloring of the oxide film in this invention is achieved by invasion, oxidation and electro-precipitation of the metallic salt, any peak voltage, whether it is positive or negative, has a close relation directly to the depth of color tone of the oxide film.

In the present invention, the depth of color tone of the oxide film is dependent upon the energy balance between the amount of the invaded metallic salt oxidized and its eluted amount. Whether the pulse voltage is positive or negative, in the zones below the line II—II in FIG. **4**, when the values of the peak voltage, *n*, etc. are controlled in such a direction as to decrease the current, the color of the oxide film becomes deeper and when the above values are controlled in such a direction as to increase the current, the color of the oxide film becomes lighter.

As described above, in the present invention, the aluminum material is electrolyzed by applying between both electrodes, at least one of which is the aluminum material, positive and negative rectangular-wave pulse voltages such, for example, as depicted in FIG. **3**, for the predetermined conduction times t and ta (refer to FIG. **3**), respectively, whereby oxide films of various colors are formed.

In the case of electrolyzing the aluminum material as described above, unlike in the conventional anodic oxidation or AC electrolysis, the peak voltages $V_p$ and $V_{pa}$ rise practically instantaneously and they are impressed for the durations $\tau$ and $\tau_a$, respectively, and stopped for the predetermined quiescent times [h=(T-$\tau$ and Ta-$\tau$)], respectively, and then impressed again (refer to FIG. 3).

However, even if the rectangular-wave pulse voltage of such a characteristic is applied to the aluminum material from a power source such, for example, as a pulse generator, there are some occasions when exactly the same voltage as the rectangular-wave pulse voltage is not applied between the both electrodes, at least one of which is the aluminum material, under the influence of the amount of charges stored in the electrolytic cell. An electrolytic cell **1** for electrolyzing the aluminum material has a predetermined electric capacitance *c* and an internal resistance *r* as shown in its equivalent circuit diagram of FIG. **6**. Therefore, even if the power source is cut off at the time of decay of the rectangular-wave pulse voltage, since charges are stored in the electrolytic cell **1** at the time of impression of the peak voltages $V_p$ and $V_{pa}$, the charges are discharged even after decay of the pulse voltage and the pulse voltage does not fall from the point **2** to **3** but falls from the point **2** to **4**, as indicated by the solid and broken lines, respectively, in FIG. **7**. Further, the decay time H of the pulse voltage in this case is longer than the pulse interval or quiescent time *h*, so that the next pulse starts to rise before the preceding pulse reaches the zero level. Accordingly, in theory, the pulse voltage should rise from the zero potential to the peak voltage $V_p$ but, in practice, the pulse only rises from $V_1$ to the peak voltage $V_p$, so that if the value of $V_1$ is large, the aforementioned effect resulting from sharp rise of the pulse voltage is lost. Therefore, it is necessary to select the value of $V_1$ as small as possible.

To this end, it is preferred to control the conditions for electrolysis in accordance with the capacitance *c* and the internal resistance *r* of the electrolytic cell **1** so as to ensure that each pulse starts to rise after the preceding one falls down to substantially zero potential.

In this case, however, the capacitance *c* and the internal resistance *r* of the electrolytic cell **1** do not remain constant during electrolyzing of the aluminum material. Especially, the value of the capacitance *c* is dependent upon the surface area of the aluminum material and the thickness of a barrier layer of the oxide film and it is almost impossible, in practice, to detect the instant when the pulse voltage lowers down to substantially zero potential.

If the time necessary for lowering of the pulse voltage down to about ¼ of the peak voltage $V_p$ is shorter than ⅓ of the quiescent time *h*, a sufficiently colored oxide film can be obtained regardless of the value of the capacitance *c* of the electrolytic cell. Further, by changing the voltage applied between the both electrodes in the electrolytic cell under such condition as mentioned above, color tone of the colored oxide film can also be controlled as desired.

Such a control of the applied voltage can be effected only by connecting an impedance between the output terminals of a pulse generator or like pulse source in the following manner.

Namely, as illustrated in FIGS. **9** and **10**, an impedance **7** is connected in parallel or in series between output terminals **5** and **6** of a pulse generator or like pulse source. With such an arrangement, the impedance **7** is connected in parallel or in series with the capacitance *c* and the internal resistance *r* of the electrolytic cell **1**.

When the pulse voltage is applied to the electrolytic cell **1** and the power source is cut off, charges in the electrolytic cell **1** by-pass the impedance **7**, so that the mode of voltage drop is changed with a change in the time constant of the impedance **7**. Therefore, only by setting the value of the impedance **7** such that the time necessary for lowering of the pulse voltage down to ¼ of the peak voltage $V_p$ may be shorter than ⅓ of the quiescent time *h*, the pulse voltage can be controlled as described above.

In the above, the influence of the electric capacitance *c* and the internal resistance *r* of the electrolytic cell **1** has been described mainly in connection with the voltage which is applied or detected between both electrodes, at least one of which is the aluminum material. The reason therefore is that even if the influence of the current during electrolyzing is not considered, it is sufficient, in practice, only to consider the applied or detected voltage as a coloring control factor and that, in actual electrolysis, control by the applied or detected voltage is the easiest and best from the industrial viewpoint.

However, where the pulse voltage of such a wave form as shown in FIG. **3** is applied to the aluminum material to electrolyze it in the presence of a large electrolyzing current, a large difference occurs between the applied pulse voltage and the current and it is necessary to achieve the electrolysis taking this difference into account.

Namely, an equivalent circuit of the electrolytic cell containing an electrolytic bath containing a metallic salt is regarded to have the electric capacitance *c* and the internal resistance *r* connected to each other as shown in FIG. **6**. Accordingly, in the case of applying the rectangular-wave pulse voltage to electrolyze the aluminum material in the presence of a large electrolyzing current, the influence of the load of a lead in addition to the electric capacitance *c* and the internal resistance *r* of the electrolytic cell is produced, by which although a pulse voltage indicated by the broken line in FIG. **11** is applied, the current rises as indicated by the solid line and does not reach a peak value $I_p$ in some cases.

Consequently, before the current I reaches the peak value $I_p$, the power source is cut off and the pulse voltage rapidly falls. This appreciably lessens the effect of the pulse voltage impression.

In the present invention, in the case of the impressed voltage, particularly in the case of the rectangular-wave pulse voltage, it is sufficient, in practice, only to properly control the relationships of the peak voltages $V_p$ and $V_{pa}$ to the pulse durations $\tau$ and $\tau_a$. Especially, it is advisable to control the peak voltages $V_p$ and $V_{pa}$ in the range of 5 to 150V, preferably 10 to 80V and to control the pulse durations $\tau$ and $\tau_a$ of the pulse voltages to be longer than $10\times10^{116\ 3}$ sec. in the presence of a large electrolyzing current. In the presence of an ordianry electrolyzing current, it is sufficient that the pulse durations are shorter than $10\times10^{-3}$ sec.

In other words, where the peak voltages $V_p$ and $V_{pa}$ and the pulse widths $\tau$ and $\tau_a$ of the pulse voltage are controlled as described above and the aluminum material is electrolyzed by such pulse voltage in the electrolytic bath containing a metallic salt, the values of the loads of the electrolytic cell 1 and the lead need not be considered and the current rises up to its peak value and then falls. Thus, the effect of application of the pulse voltage, that is, the effect of rapid rise and fall of the voltage or current can be sufficiently produced.

As described in detail in the foregoing, according to this invention, the aluminum material is electrolyzed in an electrolytic bath containing a metallic salt by applying to the aluminum material a pulse voltage whose polarity changes from positive to negative and vice versa alternately with a predetermined period, thereby to form a colored oxide film on the surface of the aluminum material. In this case, it is preferred from the industrial point of view to obtain the rectangular-wave pulse voltage by half-wave rectification and phase control of individual AC components of, for example, a three-phase or other commercial AC voltage by means of, for example, a silicon controlled rectifier or the like.

In FIG. **12**, a six-phase commercial AC voltage is shown by broken lines and voltages obtained by half-wave rectification and phase control of its individual AC components are shown by solid lines. The rectangular pulse voltage depicted in FIG. **12** has six ripple components in the unit period T, $T_a$ or the unit pulse duration $\tau, \tau_a$ and the ripple components are saw-tooth in wave form. Consequently, when a positive pulse is applied to the aluminum material, the applied voltage on the aluminum material rises from zero level to the peak voltage $V_p$ in a moment and, by the impulsive energy resulting from this abrupt rise of the voltage, the metallic salt is oxidized and electro-precipitated. Since the six ripple components of the saw-tooth wave form are intermittently applied to the aluminum material, the impulse energy is intermittently provided, by which oxidation and electro-precipitation of the metallic salt is further promoted. However, while the electro-precipitation proceeds, the metal is eluted but, in the case of such a wave form as shown in FIG. **12**, the oxidation and electro-precipitation are promoted by the presence of the ripple components, so that the pulse width $\tau$ need not be so large. Therefore, the amount of positive charges applied to the aluminum material can be decreased and the amount of the metal eluted can be inevitably held small, with the result that the balance between the electro-precipitation and the elution can be well maintained.

Then, in the negative conduction time $t_a$ after the positive one *t*, a negative pulse voltage having the same characteristics as the positive pulse voltage is applied. This negative pulse voltage also rises from the zero level up to the peak value $V_{pa}$ in a moment as is the case with the positive pulse voltage and the invading energy is applied to the metallic salt and, further, by the presence of the six saw-tooth ripple conponents, invasion of the metallic salt into the oxide film is promoted, thereby to further enhance the coloring effect.

Further, in the case of rectifying the commercial AC as shown in FIG. **12**, it is preferred that the pulse interval or the quiescent time ($T-\tau$ or $T_a-\tau_a$) is determined based on the unit period of the commercial AC. For example, in the waveform shown in FIG. **12**, its unit period is used as the pulse period.

In the case of applying the rectangular-wave pulse voltage, the following values are appropriate.

| | |
|---|---|
| $V_p/V_{pa}/$ | 5 to 150 (10 to 80V) |
| $f.f_a$ ($f=1/T$, $f_a=1/T_a$) | 5 to 500Hz (5 to 150Hz) |
| $t$, $t_a$ | 0.2 to 2.40 sec. (3 to 50 sec.) |

In the above, the bracketed values indicate optimum ranges. The time for sufficient electrolysis is usually about 60 minutes.

The reason why the above values are proper is as follows:

For example, where the peak voltages are lower than 5V, coloring is deteriorated and where they are higher than 150V, it is difficult to control the rate of forming the oxide film.

From the viewpoint of the coloring effect, it is preferred, in general, to select the values of the peak voltages $V_p$ and $V_{pa}$ as large as possible. However, the values of the peak voltages $V_p$ and $V_{pa}$ are determined dependent upon the kind of the metallic salt in the electrolytic bath selected in accordance with color tone which is desired to be ultimately obtained. For example, in the case of the silver salt, optimum values of the peak voltages $V_p$ and $V_{pa}$ for forming an oxide film of clear and deep color tone are about 20V or more and, in this case, the electrolysis can be achieved at relatively low peak voltages $V_p$ and $V_{pa}$.

For convenience' sake, the foregoing description has been given mainly in connection with the case of applying the rectangular-wave pulse voltage that the characteristic values of its positive and negative waveforms are partly or entirely equal to each other. With the method of this invention however, even if the characteristic values of the positive and negative waveforms are entirely different from each other, a colored oxide film can be formed by electrolyzing an aluminum material and, in addition, the color of the oxide film can also be changed as desired. Especially, by increasing the amount of charges of the negative waveform component in the case of electrolyzing the aluminum material in the sulfuric acid aqueous solution containing a metallic salt, degreasing or the like of the aluminum material (except the aluminum material previously anodized can also be achieved.

Further, the foregoing description has been made mainly with regard to the case where the electrolytic bath is one containing only sulfuric acid but, even if one or more of malonic acid, malic acid, maleic acid, sulfosalicylic acid, sulfamic acid, tartaric acid and oxalic acid are contained in the electrolytic bath, the effect does not change. The electrolytic bath may be any aqueous solution containing any of the above acids other than sulfuric acid, so long as it is conductive.

In FIGS. **1, 2, 3, 7, 8, 11** and **12**, the abscissa represents time and the ordinate represents the peak voltage.

Now, this invention will be further described by the following Examples.

## EXAMPLE 1

Aluminum materials **1100**, degreased and rinsed with water in usual manner, were electrolyzed in an electrolytic bath composed of 150g of $H_2SO_4$ per liter of water and **60** mg of $AgNO_3$ per liter of water, with aluminum material used as both electrodes. Pulse voltages of rectangular-waveform having a duration of **2** msec. shown in the following Table **1** were applied, by which colored oxide films of such color tone as shown in Table 1 were formed on the aluminum materials. In the cases shown in Table 1, the time for electrolysis was 60 minutes and the positive and negative waveforms of the pulse voltages were the same.

The relationships between the pulse durations $\tau$ and $\tau_a$ of the positive and negative pulse voltages obtained (a) based on the results given in Table 1 are shown in the following Table 2. Further, (b) by our experiments in which the aluminum material was electrolyzed under the same conditions as those in Table 1, with the aluminum being used as one electrode and a carbon electrode as the counter electrode, it was found that substantially the same colored oxide films as shown in Table 1 could be obtained. In the both cases (a) and (b), the time for electrolysis was also 60 minutes.

Table 1.

| Conditions for electrolysis | | | | Formed oxide film | | |
|---|---|---|---|---|---|---|
| Frequency $f=1/T$ or $1/T_a$ (Hz) | Peak Voltage $V_p, V_{pa}$ (V) | Mean current density (A/dm²) | Conduction Time of Positive and negative pulses $t, t_a$ (sec) | Film thickness (μ) | Color tone (Color indication of the Munsel solid) | |
| 50 | 30 | 1.2 | 5 | 11.3 | 1.4Y | 5.6/7.2 |
| | 20 | 0.6 | | 3.9 | 5.6YR | 4/8.8 |
| | 10 | 0.2 | | 1.3 | 2Y | 4.1/5.1 |
| 40 | 30 | 1.1 | 5 | 10.3 | 10YR | 5.2/4.8 |
| | 20 | 0.5 | | 3.0 | 6.8YR | 4.1/6.9 |
| 30 | 30 | 10.6 | 5 | 7.1 | 2.5Y | 5.7/7.9 |
| | 20 | 0.5 | | 3.0 | 3.8YR | 3.4/0.1 |
| | 10 | 6.16 | | 1.0 | 1.5Y | 4.2/4 |
| 20 | 30 | 1.0 | 5 | 4.2 | 0.9Y | 5.3/8.7 |
| | 20 | 0.5 | | 2.5 | 5.4YR | 3.8/8.7 |
| 10 | 30 | 0.8 | 5 | 3.3 | 7YR | 3.9/8.7 |
| | 20 | 0.4 | | 2.0 | 2.4YR | 3.1/5.8 |

Table 2.

| Conditions for electrolysis | | | | | Formed oxide film | | |
|---|---|---|---|---|---|---|---|
| Duration $\tau, \tau_a$ (m sec) | Frequency $f=1/T$ or $1/T_a$ (Hz) | Peak voltage $V_p, V_{pa}$ (V) | Mean current density (A/dm²) | Conduction time of positive and negative pulses $t, t_a$ (sec) | Film thickness (μ) | Color Tone (Color indication of the Munsel Solid) | |
| 2 | 100 | 40 | 1.9 | 5 | 22.6 | 7.8YR | 4.6/5.4 |
| | | 30 | 1.6 | | 17.2 | 9.9YR | 6.9/1/5 |
| | | 20 | 0.6 | | 3.8 | | |
| 3 | | 40 | 3.6 | 5 | 28.3 | 3.4Y | 5.8/2.9 |
| | | 30 | 2.1 | | 12.8 | 8.9Y | 5.2/5.8 |
| | | 20 | 0.7 | | 5.9 | 5Y | 7.4/6.1 |
| 2 | 50 | 40 | 1.4 | 5 | 13.5 | 7.4YR | 4.5/8.5 |
| | | 30 | 1.2 | | 11.3 | 1.4Y | 5.6/7.2 |
| | | 20 | 0.6 | | 3.9 | 5.6YR | 4/8.8 |
| 3 | | 40 | 2.0 | 5 | 20.0 | 2.7G | 4.9/5.6 |
| | | 30 | 1.3 | | 6.8 | 3.5Y | 6.1/5.6 |
| | | 20 | 0.6 | | 4.3 | 5Y | 6.3/2.4 |

It appears from Table 2 that color tone of the colored oxide film can also be changed only by changing the pulse duration as required.

## EXAMPLE 2

Aluminum materials **6063**, degreased and rinsed with water in usual manner, were electrolyzed by applying the same rectangular pulse voltage as that used in Example 1 under such conditions as shown in the following Table 3, with the aluminums being used as both electrodes. As a result of this, colored oxide films with color tone as shown in Table 3 were formed on the aluminum materials. The for each electrolysis was 60 minutes. In Table 3, additive components in the electrolytic bath are shown in their weights per liter of water.

Table 3.

| Bath Composition | | Conditions for electrolysis | | | | | Formed oxide film | |
|---|---|---|---|---|---|---|---|---|
| Basic liquid | Added Metalic Salt | Duration T, $T_a$ (msec) | Frequency f=1/T or $1/T_a$ (Hz) | Peak Voltage $V_p$, $V_{pa}$ (V) | Mean current density (A/dm²) | Conduction time of positive and negative pulses t, $t_a$ (sec) | Film thickness (μ) | Color tone (Color indication of the Munsel Solid) |
| $H_2So_4$ 150 g/l | $HA_uCl_4$ 100 mg/l | 2 | 50 | 25 | 0.98 | 5 | 6 | 3.5RP 4.2/7.1 |
| $H_2SO_4$ 150 g/l | $Na_3SeO_3$ 5 g/l | 2 | 40 | 25 | 0.6 | 5 | 4.6 | 1γ 6.7/2.4 |
| | | 6 | | 25 | 11.0 | 5 | 10.4 | 8YR 7.2/2 |

## EXAMPLE 3

Aluminum materials of the same kind as employed in Example **1**, similarly degreased and rinsed with water, were electrolyzed in the electrolytic bath of the same composition as that in Example 1, with the aluminum materials being used as both electrodes. In this case, a voltage obtained by half-wave rectification of a single-phase sine-wave, shown in FIG. **1**, and a voltage obtained by controlling the above voltage with a silicon controlled rectifier (refer to FIG. **2**), were applied as positive and negative pulse voltages to the aluminum materials. The electrolysis was achieved under the conditions shown in the following Table 4.

Colored oxide films of such color tone as shown in Table 4 were formed on the aluminum materials. The time for each electrolysis was 60 minutes and the frequency used was 60 Hz.

## EXAMPLE 4.

Aluminum materials A.**A6063,** subjected to pretreatment in known manner, were electrolyzed in an electrolytic bath containing 150g of $H_2SO_4$ per liter of water and 50mg of $Ag_2SO_4$ (at a bath temperature 23°C) under the conditions shown in Table 5 for 60 minutes. The pulse width used was 16 msec. By changing the values of the peak voltage and $n(=T/\tau)$ during electrolyzing, colored oxide films shown in Table **5** were formed.

By rearranging the results in relation to the peak voltage and $n(=T/\tau)$, the relation-ships shown in FIG. **5** were obtained.

Further, when the aluminum materials were electrolyzed under the conditions shown in Table 6 with different pulse durations, such colored oxide films shown in Table **6** were obtained.

The distribution of the depth of color tone of the colored oxide films obtained in this case was substantially the same as shown in FIG. **5.** Even when the pulse duration was changed based on the above, the variation in the depth of color tone of the oxide films was substantially the same as the basic tendency shown in FIG. **4.**

The current density values given in Tables **5** and **6** are all those obtained with a moving-coil ammeter.

Table 4.

| | Conditions for electrolysis | | | | | Formed oxide film |
|---|---|---|---|---|---|---|
| Kind of applied voltage | Duration T, $T_a$ (msec) | Peak Voltage $V_p$,$V_{pa}$ (γ) | Mean current density (A/dm²) | Conduction time of positive and pulses t, $t_a$ (sec) | Film thickness (μ) | Color tone (Color indication of the Munsel solid) |
| Voltage obtained by half-wave rectification single-phase sine wave (FIG. 1) | 5.7 | 30 | 2.4 | 5 | 15.0 | 2.9Y 6.2/8.2 |
| | | 20 | 1.14 | 5 | 4.8 | 3.0Y 5.9/7.6 |
| | | 10 | 0.64 | 5 | 1.5 | 4.1Y 5.7/3.5 |
| Voltage obtained by controlling the above voltage with SCR (FIG. 2) | 2.6 | 30 | 1.8 | 5 | 14.8 | 9.4YR 5.2/8.8 |
| | 1.4 | 20 | 0.24 | 5 | 1.5 | 3.1YR 3.8/7.4 |
| | 1.6 | 10 | 0.30 | 5 | 0.8 | 8.5YR 4.1/6.3 |

Table 5.

| Conditions for electrolysis | | | | Formed oxide Film | |
|---|---|---|---|---|---|
| peak Voltage $V_p$ (V) | n | Period T | Mean current density (A/dm²) | Film thickness ($\mu$) | Color tone |
| 20 | 10 | 100 | 0.32 | 1.7 | Reddish orange |
| | 8 | 80 | 0.37 | 2.0 | " |
| | 6 | 60 | 0.44 | 2.5 | " |
| | 4 | 40 | 0.64 | 4.0 | Right reddish orange |
| | 2 | 20 | 1.18 | 7.8 | Yellow |
| 25 | 10 | 100 | 0.54 | 4.0 | Reddish orange |
| | 8 | 80 | 0.60 | 5.0 | " |
| | 6 | 60 | 0.80 | 5.2 | Light reddish orange |
| | 4 | 40 | 1.12 | 6.7 | " |
| | 2 | 20 | 2.04 | 15.0 | Yellow |
| 27.5 | 8 | 80 | 0.88 | 6 | Light reddish orange |
| | 4 | 40 | 1.60 | 11.5 | Yellow |
| | 2 | 20 | 2.52 | 19 | " |
| 30 | 10 | 100 | 0.88 | 6.7 | Light reddish orange |
| | 8 | 80 | 0.98 | 7.5 | " |
| | 6 | 60 | 1.32 | 10.7 | " |
| | 4 | 40 | 1.64 | 15.1 | Reddish orange |
| | 2 | 20 | 2.46 | 21.7 | " |
| 32.5 | 6 | 60 | 1.16 | 11 | Unclear reddish orange |
| | 4 | 40 | 3.04 | 24 | " |
| | 2 | 20 | 3.28 | 30 | Reddish orange |
| 35 | 10 | 10 | 1.50 | 17.8 | " |
| | 8 | 80 | 2.28 | 24.4 | " |
| | 6 | 60 | 2.86 | 28.2 | Unclear reddish orange |
| | 4 | 40 | 3.08 | 29 | " |

Table 6.

| Conditions for electrolysis | | | | | Formed oxide film | |
|---|---|---|---|---|---|---|
| Pulse width $\tau_p$ (msec) | Peak voltage $V_p$ (V) | n | Frequency T (msec) | Mean current density (A/dm²) | Film thickness ($\mu$) | Color tone |
| 5 | 15V | 2 | 10 | 0.7 | 3.9 | Yellow |
| | 20 | 8 | 40 | 0.5 | 2.2 | Reddish orange |
| | 25 | 4 | 20 | 1.4 | 10.5 | Light reddish orange |
| | 30 | 2 | 10 | 3.0 | 25.7 | Reddish orange |
| | 35 | 10 | 50 | 1.52 | 21.5 | " |
| 16 | 25 | 3 | 48 | 0.69 | 5.5 | Yellow |
| | 25 | 7 | 118 | 0.4 | 2.5 | Light reddish orange |
| | 30 | 2 | 32 | 2.3 | 11.5 | Reddish orange |
| | 33 | 2 | 32 | 2.2 | 22.0 | " |
| | 33 | 4 | 64 | 1.8 | 10.0 | " |

When metallic salts such as $HAuC1_4$, $Na_2SeO_3$, $CuSO_4$, $SnSO_4$, $NiSO_4$ and $CoSO_4$ were added in a $H_2SO_4$ aqueous solution in place of the aforesaid metallic salt and the peak voltage $V_p$ and *n* were changed, colors shown in the following Table 7 were obtained.

Table 7.

| No. | Coloring metal | Metallic Salt | Color of oxide film |
|---|---|---|---|
| 1 | Au | $HAucl_4$ | Purple |
| 2 | Se | $Na_2SeO_3$ | Cream |
| 3 | Cu | $CuSO_4$ | Deep red to brown |
| 4 | Sn | $SnSO_4$ | White to dark brown |
| 5 | Ni | $NiSO_4$ | Amber to black |
| 6 | Co | $CoSO_4$ | " |

When aluminum materials A.A**1099**, **1100**, **2011**, **2014**, **2024**, **3003**, **4043**, **5005**, **5086**, **5357** **6061** and **7075** other than **6063** were electrolyzed during which the peak voltage $V_p$ and *n* were controlled, substantially the same results as those in FIGS. **4** and **5** were obtained, although colors of the oxide films formed were a little different from one another because these aluminum materials were of different compositions and because their electrical properties differed in accordance with the contents and kinds of alloy elements contained in them.

The relationships of the peak voltage and the value *n* to the distribution of color tone showed the same tendency as shown in FIG. **4**, though a little affected by such factors as the power source, voltage adjusting means and the geometrical shape of the electrolytic cell used (for example, distance between electrodes, capacitance, etc.) used, a leakage current, etc. in addition to the quality of each aluminum material and the kind of each metallic salt used.

For example, when one or more of the above factors were changed, there were some occasions when the sizes and shapes of the zones A, B and C in FIG. **4** were changed, or the zone D became so narrow that it was not necessary to distinguish the zone D between the zones A, B and C and the zone E in actual electrolysis, or the width of the zone D increased. Further, the aforesaid factors had relation to at least some of the conditions for electrolysis, so that when one or more of the factors were altered, the levels of the lines I—I and II—II became higher or changed in inclination in some cases.

In any case, however, according to the method of this invention the basic tendency shown in FIG. **2** can be maintained, in which one of the features of the method of this invention resides.

## EXAMPLE 5

Aluminum materials **1100,** degreased and rinsed with water and then neutralized in known manner, were electrolyzed by applying the rectangular pulse voltage shown in FIG. **3** is an electrolytic bath containing 150g of $H_2SO_4$ per liter of water and 50mg of $Ag_2SO_4$ per liter of water (at a bath temperature of 25°C), with the aluminum materials being used as both electrodes.

In this case, an impedance was connected as shown in FIG. **9** and the impedance used was a resistor. By changing its resistance value, the by-pass current was changed. The results shown in the following Table **8** were obtained.

Table 8

| Sample No. | Pulse duration $\tau = \tau_a$ (sec) | Pulse interval h=ha (sec) | Peak voltage $V_p = \lvert V_{pa} \rvert$ (V) | Surface area of sample (cm²) | Resistance Value (Ω) |
|---|---|---|---|---|---|
| 1 | $2\times10^{-3}$ | $18\times10^{-3}$ | 20V | 50 | 10 |
| 2 | '' | '' | '' | '' | 40 |
| 3 | '' | '' | '' | '' | 54 |
| 4 | '' | '' | '' | '' | 100 |
| 5 | '' | '' | '' | '' | 150 |
| 6 | '' | '' | '' | '' | 220 |
| 7 | '' | '' | '' | '' | 500 |
| 8 | '' | '' | '' | 100 | 10 |
| 9 | '' | '' | '' | '' | 150 |
| 10 | '' | '' | '' | '' | 500 |

-continued

| Sample No. | Mean current: Electrolytic cell (A) | Mean current: By-pass circuit (A) | Time for lowering to ¼ $V_p$ or $V_{pa}$ (sec) | Color of film |
|---|---|---|---|---|
| 1 | 0.21 | 0.22 | $0.3\times10^{-3}$ | Dark brown |
| 2 | 0.23 | 0.07 | $0.85\times10^{-3}$ | '' |
| 3 | 0.20 | 0.06 | $1.1\times10^{-3}$ | '' |
| 4 | 0.22 | 0.04 | $2.0\times10^{-3}$ | A little dark brown |
| 5 | 0.25 | 0.03 | $2.5\times10^{-3}$ | '' |
| 6 | 0.23 | 0.03 | $4.3\times10^{-3}$ | Brown |
| 7 | 0.23 | 0.02 | $9\times10^{-3}$ | Light dark yellow |
| 8 | 0.44 | 0.27 | $0.5\times10^{-3}$ | Dark brown |
| 9 | 0.39 | 0.04 | $5\times10^{-3}$ | Light brown |
| 10 | 0.41 | 0.015 | $14.5\times10^{-3}$ | Light dark yellow |

The frequency of the applied voltage was 50Hz.

As seen from the above Table, when the resistance value was changed, especially in the case of the surface area of the specimen being 50cm², when the resistance value was 500Ω, the time for lowering of the applied voltage to ¼ of the peak voltage was longer than ⅓ of the pulse duration and the coloring mode of the oxide film was not good. The same was true of the case of the specimen surface area being 100cm².

## EXAMPLE 6

Aluminum materials **A.A6036,** chemically pretreated, in known manner were electrolyzed in an aqueous solution containing 150g of sulfuric acid per liter of water and 50mg of $Ag_2SO_4$ per liter of water, with the aluminum materials being used as both electrodes. In this case, a pulse voltage, obtained by half-wave rectification of a six-phase AC of the waveform shown in FIG. **12** was applied.

The results shown in the following Table 9 were obtained.

Table 9.

| No. | Characteristics of pulse voltage | | | | Mean Current density (A/dm²) | Color of oxide film |
|---|---|---|---|---|---|---|
| | Peak Voltage $V_p = V_{pa}$ (V) | Pulse width $\tau = \tau_a$ (sec) | Pulse period $T = T_a$ (sec) | Conduction time $t = t_a$ (sec) | | |
| 1 | 25 | $16\times10^{-3}$ | $48\times10^{-3}$ | 5 | 0.63 | A little deep yellow |
| 2 | 25 | $33\times10^{-3}$ | $132\times10^{-3}$ | '' | 0.62 | '' |
| 3 | 20 | $16\times10^{-3}$ | $48\times10^{-3}$ | '' | 0.44 | A little light yellow |
| 4 | 20 | $33\times10^{-3}$ | $132\times10^{-3}$ | '' | 0.43 | '' |
| 5 | 33 | $16\times10^{-3}$ | $16\times10^{-3}$ | '' | 1.50 | Deep orange |
| 6 | '' | $33\times10^{-3}$ | $33\times10^{-3}$ | '' | 1.40 | '' |
| 7 | '' | $50\times10^{-3}$ | $50\times10^{-3}$ | '' | 1.50 | '' |
| 8 | 20 | $16\times10^{-3}$ | $64\times10^{-3}$ | '' | 1.20 | Light orange |
| 9 | '' | $33\times10^{-3}$ | $132\times10^{-3}$ | '' | 1.00 | '' |
| 10 | '' | $50\times10^{-3}$ | $200\times10^{-3}$ | '' | 1.30 | '' |
| 11 | 25 | $16\times10^{-3}$ | $64\times10^{-3}$ | '' | 1.00 | Orange |

It appears from Table 9 that an increase in the values of the peak voltages $V_p$ and $V_{pa}$ causes the color of the oxide film to become deeper and that, in the case of the same frequency, that is, when the pulse periods T and $T_a$ are equal to each other, an increase in the pulse widths $\tau$ and $\tau_a$ causes the color of the oxide film to become lighter.

## EXAMPLE 7

Aluminum materials **1100** were degreased and rinsed with water and then neutralized to clean the surfaces of the aluminum materials. These aluminum materials were electrolyzed in an aqueous solution containing 150g of $H_2SO_4$ per liter of water and 50mg of $Ag_2SO_4$ per liter of water, with the aluminum materials being used as both electrodes. The pulse voltage shown in FIG. 3 was applied and the electrolysis was effected with a current of 1000A for 60 minutes.

The results shown in the following Table 10 were obtained. The positive and negative waveforms of the applied voltages were the same and the peak voltages and the pulse widths were all the same in their absolute values, respectively.

Table 10.

| Conditions for electrolysis | | | |
|---|---|---|---|
| Frequency $f=1/T$ or $1/T_a$ (Hz) | Peak voltage $V_p = V_{pa}$ (V) | Pulse width $\tau = \tau_a$ (sec) | Color of oxide film |
| 10 | 20 | $20\times10^{-3}$ | Yellow |
| 5 | 25 | $40\times10^{-3}$ | Light Orange |
| 3 | 30 | $60\times10^{-3}$ | A little light orange |
| 1 | 30 | $200\times10^{-3}$ | Deep orange |

In all cases of the above Table, the currents all reached the peak values and sufficiently colored oxide films were formed.

In the method of this invention, the frequency used is determined in relation to the pulse width but it was sufficient to be lower than 100Hz.

Although the foregoing description has been given mainly, in connection with the cases in which the aluminum materials A.**A1100** and A.**A6063** are employed, the present invention can also be easily applied to other aluminum materials.

However, a change in the composition and electrical properties of the aluminum materials used causes a change in the color of the oxide film. For example, under the conditions for electrolysis that when the aluminum material A.**A1100** is electrolyzed in the sulfuric acid aqueous solution, an oxide film of an orange color is formed, when the aluminum materials A.**A3003**, A.**A4043**, A.**A5052**, A.**A6061** and A.**A6063** are electrolyzed in the above electrolytic bath, oxide films of grayish orange, dark orange, light orange, dark reddish orange and orange colors are formed, respectively.

It will be apparent that many modifications and variations may be effected without departing from the scope of the novel concepts of this invention.

We claim as our invention:

**1.** A method of forming a colored oxide film on an aluminum material by electrolyzing said aluminum material in an aqueous electrolytic bath containing a metallic salt by supplying said aluminum material serving as each electrode with a pulse voltage consisting of a plurality of unipotetial pulses whose polarity is inverted after every predetermined conduction time.

**2.** The method according to claim **1**, wherein said aluminum material has an oxide film previously formed thereon.

**3.** The method according to claim **1**, wherein said aluminum material is electrolyzed by applying a pulse voltage whose positive and negative pulse waveforms are rectangular ones.

**4.** The method according to claim **1**, wherein said aluminum material is electrolyzed by applying a pulse voltage which is obtained by phase-controlling an AC wave.

**5.** The method according to claim **1**, wherein said aluminum material is electrolyzed in an aqueous sulfuric acid solution containing a metallic salt.

**6.** The method according to claim **3**, wherein said aluminum material is electrolyzed in an aqueous sulfuric acid solution containing a metallic salt.

**7.** The method according to claim **4**, wherein said aluminum material is electrolyzed in an aqueous sulfuric acid solution containing a metallic salt.

**8.** The method according to claim **3**, wherein the positive and negative pulse wave forms are symmetrical.

**9.** The method according to claim **6**, wherein the positive and negative pulse waveforms are symmetrical.

**10.** The method according to claim **3**, wherein said aluminum material is electrolyzed by applying a rectangular pulse voltage which is obtained by rectifying AC and whose pulse intervals of the positive and negative pulse waveforms are determined based on the unit period of said AC.

**11.** The method according to claim **6**, wherein said aluminum material is electrolyzed by applying a rectangular pulse voltage which is obtained by rectifying AC and whose pulse intervals of the positive and negative pulse waveforms are determined based on the unit period of said AC.

**12.** The method according to claim **3**, wherein the ratio of the unit pulse period to the pulse duration and the peak value of said pulse voltage are independently selectively controlled.

**13.** The method according to claim **3**, wherein the pulse duration of the positive rectangular pulse voltage and that of the negative rectangular pulse voltage are controlled to be $10\times10^{-3}$ sec. or longer.

**14.** The method according to claim **3**, wherein the time for the positive rectangular pulse voltage and the negative rectangular pulse voltage to fall to the value of ¼ of its peak voltage value is selected to be ⅛ of the pulse interval or shorter than it.

* * * * *