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(72) Inventors:

- **EBIHARA, Ken, c/o Nippon Light Metal Co., Ltd.
Ihara-gun, Shizuoka 421-3203 (JP)**
- **NAGASAWA, Daisuke,
c/o Nippon Light Metal Co., Ltd.
Ihara-gun, Shizuoka 421-3203 (JP)**

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(74) Representative: **Towler, Philip Dean**

**Frank B. Dehn & Co.,
European Patent Attorneys,
179 Queen Victoria Street
London EC4V 4EL (GB)**

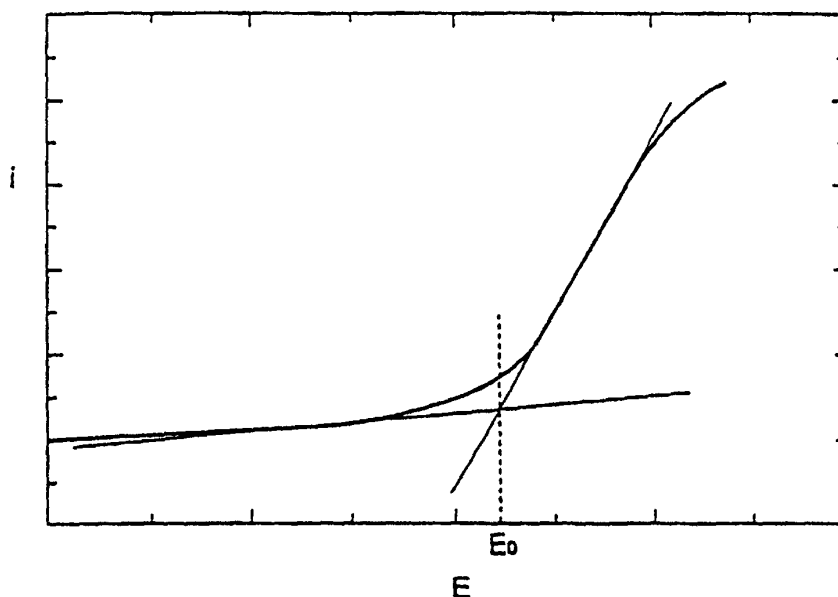
(71) Applicant: **Nippon Light Metal Company Ltd.**

Shinagawa-ku, Tokyo 140-8628 (JP)

(54) **METHOD FOR ELECTROLYTIC COLORING OF ALUMINUM MATERIAL**

(57) This invention relates to an improvement of a process for electrolytically coloring an aluminum material comprising immersing an aluminum material consisting of anodized aluminum or an anodized aluminum alloy in an electrolytic coloring bath containing a soluble metal salt, performing a pretreatment prior to coloring by passing a direct current waveform with said aluminum material serving as the anode, and performing al-

ternating current electrolytic coloring in the same electrolytic coloring bath and the improved process comprises performing said pretreatment prior to coloring until the voltage and current respectively reach the preset ultimate values. It is possible to prevent as much as possible an occurrence of irregular coloring not only in one energizing lot but also in different energizing lots and produce an aluminum material colored in a uniform tone stably and readily on a commercial scale.



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DescriptionField of Technology

5 **[0001]** This invention relates to a process for electrolytically coloring an aluminum material consisting of anodized aluminum or an anodized aluminum alloy (hereinafter simply referred to as "aluminum material"); more particularly, this invention relates to a process for electrolytically coloring an aluminum material which can attain uniformity in color tone during alternating current electrolytic coloring and, still more, to a process for electrolytically coloring an aluminum material which can keep the color tone from changing irregularly not only in a given energizing lot but also in different energizing lots during electrolytic coloring thereby producing an aluminum material colored in a uniform tone.

Background Technology

15 **[0002]** An aluminum material is used frequently in many areas such as construction materials, vehicle parts and furniture on account of its good processability and corrosion resistance and, for the purpose of enhancing the aesthetic effect of the material, electrolytic coloring has been practiced wherein an aluminum material is subjected to electrolysis in an electrolyte containing a soluble salt of metal such as Ni, Co, Cu, and Sn thereby causing the electrolysis product of the metal salt to deposit in the porous anodic oxide film.

20 **[0003]** The following processes are known for electrolytic coloring of an aluminum material; alternating current electrolytic coloring (Asada process) wherein an alternating current is passed through an electrolyte to effect electrolysis and direct current electrolytic coloring wherein a direct current is passed through an electrolyte. Each process has its own advantages and the former can utilize a low-cost power source to reduce the equipment cost while the latter can perform electrolytic coloring in a relatively short time and, in particular, is known to attain sufficiently uniform coloring in the case of electrolytic coloring in dark tone such as black.

25 **[0004]** A problem arises, however, in the aforementioned electrolytic coloring of an aluminum material, particularly in the cases in which an aluminum material has a complicated shape or aluminum materials of various shapes are treated simultaneously; irregular coloring tends to occur in the depressed and projected parts, the color tone lacks uniformity and deviates from the range approved by clients, the product yield drops and, as a result, the product cost runs up.

30 **[0005]** Such being the case, a variety of processes have been proposed to solve this problem. For example, one of them performs a pretreatment of an aluminum material prior to alternating current electrolytic coloring by passing a direct current in the same electrolytic coloring bath with the aluminum material used as the anode; constant voltage electrolysis is known as such wherein a direct current is passed for a given length of time while maintaining the voltage at a constant value [Japan Tokkyo Koho Sho 54-23,664 (1979)].

35 **[0006]** This pretreatment prior to coloring by constant voltage electrolysis aims at eliminating irregular coloring by passing a direct current at constant voltage for a certain length of time thereby making the resistance of the anodic oxide film uniform in various parts and creating a condition for a relatively uniform current to flow through the oxide film during alternating current electrolytic coloring which follows the pretreatment; this process is commercially admissible in the cases in which an aluminum material is electrolytically colored in a relatively dark tone.

40 **[0007]** Another process proposes the following procedure for electrolytic coloring of an aluminum material; a stable color tone is attained by repeating passage and stoppage of electric current in multiple stages intermittently and meanwhile setting the voltage successively higher from one stage to the subsequent stage [Japan Kokai Tokkyo Koho Hei 8-41,685 (1996)]. It is said that the process undoubtedly attains a stable color tone and additionally shortens the time required for coloring in black, and controls the influence of trace amounts of impurities thereby preventing white streak defects.

45 **[0008]** Any of the aforementioned processes can attain a relatively stable color tone in a given energizing lot, but is unable to control irregularities in color tone in different energizing lots completely and, in consequence, produces with difficulty an aluminum material colored in a uniform tone in different energizing lots.

50 **[0009]** This tendency to irregularity does not matter very much in electrolytic coloring in a relatively dark tone, but becomes pronounced in electrolytic coloring in a relatively light tone and poses a problem in commercial production of an electrolytically colored aluminum material.

55 **[0010]** Another process proposed to solve the aforementioned problem is alternating current electrolytic coloring which is effected by changing the total current density that is the sum total of the absolute values of positive and negative current densities of the current waveform stepwise from the first step to at least the fourth step [Japan Tokkyo Koho Hei 3-32,637 (1991)]. This process can somehow manage to do as much as keeping the difference in color tone from becoming real in the case of electrolytic coloring of an aluminum material in a relatively light tone.

[0011] This process, however, faces another problem in that the control of current becomes extremely complicated and the equipment cost goes up to its economical disadvantage. Moreover, in electrolytic coloring of an aluminum

material in a relatively light tone such as bronze, a slight difference in color tone becomes emphasized and conspicuous depending upon the condition of light and greatly affects the value of commodities. A case of this kind presents a big problem in commercial production of an electrolytically colored aluminum material.

[0012] Under these circumstances, the present inventors have conducted studies to develop a process for producing an aluminum material colored in a uniform tone stably and commercially advantageously while preventing irregular coloring in different energizing lots as much as possible in alternating current electrolytic coloring and found that a uniform color tone can be attained in different energizing lots even in electrolytic coloring in a relatively light tone by performing a pretreatment prior to coloring that precedes alternating current electrolytic coloring until the voltage and current respectively reach the preset ultimate values.

[0013] According to the literature survey and research works of the present inventors, irregularity in color tone in different energizing lots in alternating current electrolytic coloring of an aluminum material seems to occur for the following reasons.

[0014] For example, in case a pretreatment prior to coloring is performed by constant current electrolysis in the same electrolytic coloring bath as used for alternating current electrolytic coloring of an aluminum material, the bath voltage in the pretreatment prior to coloring is affected by the temperature and pH of the electrolytic coloring bath and, still more, by the water washing time and the pH of the water washing bath during the step for water washing of the anodized aluminum material before immersion in the electrolytic coloring bath (the aforementioned conditions are hereinafter collectively referred to as "the bath conditions") and the bath voltage changes with the bath conditions.

[0015] Now, the bath voltage in the pretreatment prior to coloring by constant current electrolysis is decided primarily by the resistance of the electrolytic coloring bath and the resistance of the anodic oxide film on the surface of aluminum material immersed in the bath. As changes in the resistance of the electrolytic coloring bath from energizing lot to energizing lot are not very large, at most 0.1-0.2 V in terms of the corresponding voltage, changes in the bath voltage in the pretreatment prior to coloring are considered to be due chiefly to the resistance of the anodic oxide film. The anodic oxide film on the surface of aluminum material consists of the so-called "barrier layer" which is a fine aluminous layer formed on the aluminum substrate of an aluminum material and a porous layer formed on the barrier layer and the resistance of the anodic oxide film is practically that of the barrier layer.

[0016] The efficiency for formation of the barrier layer in the pretreatment prior to coloring by constant current electrolysis is considered to be 60% or so in terms of apparent efficiency that is the ratio of the theoretical amount formed with the current efficiency assumed to be 100% to the actual amount increased with the dissolution of the barrier layer taken into account (amount increased/theoretical amount formed). Moreover, since the rate of chemical dissolution of the barrier layer is affected by changes in the bath conditions, the apparent efficiency changes under the influence of the bath conditions like the aforementioned bath voltage in the pretreatment prior to coloring; as a result, the resistance of the anodic oxide film on the surface of aluminum material changes from energizing lot to energizing lot.

[0017] On the other hand, in the pretreatment prior to coloring by the conventional constant current electrolysis which is effected by passing a direct current at a constant value for a given length of time, the bath voltage changed in a given energizing period under the influence of "the changes in the bath voltage in the pretreatment prior to coloring" and "the changes in the resistance of the anodic oxide film on the surface of aluminum material" caused by the changes in the aforementioned bath conditions; as a result, it was not possible to control completely the formation of the barrier layer on the surface of aluminum material and to keep the current distribution in the anodic oxide film of aluminum material constant.

[0018] In order to obtain a uniform color tone in different energizing lots, a conceivable approach is to control the aforementioned bath conditions strictly and eliminate their influence. In reality, however, strict control of the bath conditions is difficult to perform on a commercial scale and changes of the bath conditions are unavoidable within the range of control and, in particular, it is impossible to suppress completely the unevenness in color tone in different energizing lots in the case of electrolytic coloring in a relatively light tone.

[0019] The present inventors have conducted studies to find a commercially adequate solution to the aforementioned problem, found that the thickness of the barrier layer of the anodic oxide film to be formed and adjusted in the pretreatment prior to coloring is dependent on the ultimate voltage and current to be reached finally in the pretreatment, for example, the thickness in question is proportional to the ultimate voltage in the case of the pretreatment prior to coloring by constant current electrolysis, and, as a result, the thickness of the barrier layer is directly related to the color tone given to the aluminum material by alternating current electrolytic coloring, and completed this invention.

[0020] Accordingly, an object of this invention is to provide a process for electrolytically coloring an aluminum material which is capable of preventing as much as possible irregularities in coloring not only in a given energizing lot but also in different energizing lots in alternating current electrolytic coloring of an aluminum material and producing an aluminum material colored in a uniform tone stably and easily on a commercial scale.

Disclosure of the Invention

[0021] In a process for electrolytically coloring an aluminum material which comprises immersing an aluminum material consisting of anodized aluminum or an anodized aluminum alloy in an electrolytic coloring bath containing a soluble metal salt, performing a pretreatment prior to coloring by passing a direct current waveform with the aluminum material serving as the anode, and performing alternating current electrolytic coloring in the same electrolytic coloring bath, this invention relates to an improved process for electrolytically coloring an aluminum material which comprises performing said pretreatment prior to coloring until the voltage and current respectively reach the preset ultimate voltage and current.

[0022] In this invention, a particularly desirable mode of execution of the process for electrolytically coloring an aluminum material comprises performing a pretreatment prior to coloring by constant current electrolysis wherein a direct current is passed until the voltage reaches the ultimate value while maintaining the current at the preset ultimate value and then performing alternating current electrolytic coloring wherein a voltage-controlled alternating current waveform that has the peak voltage 0.55-0.8 times the final voltage in the pretreatment prior to coloring by constant current electrolysis is passed through the aluminum material.

[0023] There is no specific restriction on an aluminum material to be electrolytically colored in this invention and, as in the conventional anodizing, a direct current, an alternating current, or an alternating current superimposed on a direct current is passed through an electrolytic bath containing an aqueous solution of acid such as sulfuric acid, oxalic acid, sulfonic acid, and chromic acid with an aluminum raw material consisting of ordinary aluminum or an aluminum alloy serving as the anode to form an anodic oxide film on the surface of the aluminum raw material.

[0024] There is also no specific restriction on the electrolytic coloring bath containing a soluble metal salt intended for the pretreatment prior to coloring and for alternating current electrolytic coloring of the aluminum material obtained in the aforementioned manner and any electrolytic coloring bath similar to the conventional one is acceptable. Soluble metal salts include inorganic salts such as sulfates, nitrates, phosphates, chlorides, and chromates and organic salts such as oxalates, acetates, and tartrates of metals such as nickel (Ni), cobalt (Co), copper (Cu), tin (Sn), chromium (Cr), magnesium (Mg), iron (Fe), cadmium (Cd), titanium (Ti), manganese (Mn), molybdenum (Mo), calcium (Ca), vanadium (V), lead (Pb), and zinc (Zn).

[0025] For the purpose of improving the degree of coloring, it is allowable, if necessary, to add the following compounds including strong reducing agents as additives to the electrolytic coloring bath: dithionites such as sodium dithionite and zinc dithionite, thiosulfates such as ammonium thiosulfate and sodium thiosulfate, hydrogen sulfites such as sodium hydrogen sulfite, sulfurous acid, sulfites such as sodium sulfite, thioglycolic acid, and thioglycolates such as ammonium thioglycolate.

[0026] The pretreatment prior to coloring preceding alternating current electrolytic coloring in this invention is performed by immersing an aluminum material in the electrolytic coloring bath, passing a direct current waveform (that is, direct current or an alternating current superimposed on a direct current) with the aluminum material serving as the anode, and completing the operation at the point when the voltage (the peak voltage in case the direct current waveform is that of an alternating current superimposed on a direct current) and the current respectively reach the preset ultimate values.

[0027] In performing the pretreatment prior to coloring, for example, by constant current electrolysis which is effected by passing a current of a constant value, a concrete procedure is to pass a direct current while keeping the current at the preset value of ultimate current and terminate the pretreatment when the voltage reaches the preset value of ultimate voltage. In the initial stage of this constant current pretreatment, the current flows preferentially to the portion where the barrier layer of the anodic oxide film on the surface of aluminum material is relatively thin and offers a low resistance and to the portion near the cathode where the resistance of the bath is low; the barrier layers either get compensated for small thickness or grow relatively thicker by the amount corresponding to the difference in resistance of the bath in these portions and a constant anodic current distribution is obtained when the voltage reaches the ultimate value.

[0028] On the other hand, in case the pretreatment prior to coloring is performed by constant voltage electrolysis by passing a current at constant voltage, there is normally a danger of overcurrent if a current of the preset ultimate voltage is passed from the start in the initial stage. To prevent the flow of overcurrent, a direct current waveform is passed at a lower voltage than the preset ultimate voltage in the initial stage and, when the current stabilizes, the voltage is switched over to the ultimate voltage and the constant voltage electrolysis is continued until the current reaches the preset ultimate value.

[0029] Setting of the ultimate voltage and current in the pretreatment prior to coloring varies with what color tone is required for the aluminum material as product; the ultimate voltage is preferably set at 30-50 V for electrolytic coloring in a relatively light tone or at 20-30 V for electrolytic coloring in a relatively dark tone and the ultimate current is preferably set in the range 20-50 A/m².

[0030] Upon completion of the pretreatment prior to coloring in this manner, this invention performs alternating current

electrolytic coloring in the same electrolytic coloring bath by passing an alternating current waveform or a superimposed AC-DC waveform through the aluminum material.

[0031] In this case, there is no specific restriction on the procedure for alternating current electrolytic coloring and the conventional procedure can be adopted. For the reason given below, the peak voltage of the alternating current waveform or superimposed AC-DC waveform in use is set at a value preferably 0.55-0.8 times, more preferably 0.65-0.75 times, the value of the preset ultimate voltage in the pretreatment prior to coloring. If the peak voltage is lower than 0.55 times, coloring does not occur or the rate of coloring becomes extremely low. On the other hand, if the peak voltage exceeds 0.8 times, the current becomes difficult to stay constant in alternating current electrolytic coloring and a uniform color tone cannot be obtained even if the time for treatment is fixed.

[0032] This situation can be understood as follows according to the studies of the present inventors.

[0033] In electrolytic coloring, a metal species in the bath is reduced and deposited inside the oxide film to produce a color tone. Therefore, making the color tone uniform is nothing less than making the current distribution in the aluminum material uniform when electrolytic coloring is performed with the aluminum material serving as the anode.

[0034] In case the pretreatment prior to coloring is performed with the aluminum material as the anode by controlling the current and regulating the final voltage, the film resistance corresponding to the bath resistance in each part is generated and the current distribution of the aluminum material can be made constant and nearly uniform at the end of the pretreatment prior to coloring.

[0035] However, in case alternating current electrolytic coloring is performed thereafter by passing an alternating current waveform, the current distribution in the aluminum material becomes nonuniform and the color tone becomes nonuniform in spite of the fact that the current distribution in the aluminum material is nearly uniform at the end of the pretreatment prior to coloring if the peak voltage of the alternating current waveform is equal to or higher than the final voltage in the current-controlled pretreatment prior to coloring. This is because the film resistance itself has a property of varying with the direction of current and the resistance in the case of the aluminum material serving as the cathode is less than in the case of the aluminum material serving as the anode.

[0036] As a result of studies of this problem, the present inventors have found that the changes in film resistance in alternating current electrolytic coloring is dependent on and closely related to the ratio of the final voltage in the current-controlled pretreatment prior to coloring to the peak voltage of the alternating current waveform in alternating current electrolytic coloring. That is, the current-controlled pretreatment prior to coloring is performed first by passing a direct current while regulating the final voltage and then alternating current electrolytic coloring is performed in the same electrolytic coloring bath by passing a voltage-controlled alternating current waveform having the peak voltage 0.55-0.8 times the final voltage in the aforementioned current-controlled pretreatment prior to coloring and this procedure makes it possible to obtain a uniform current distribution corresponding to the changes in film resistance at the end of the pretreatment prior to coloring and obtain a uniform color tone.

[0037] In actual operations, it is necessary for the purpose of improving productivity to select a voltage as high as possible within the range 0.55-0.8 times the final voltage. In order to satisfy the two requirements of uniform color tone and improved productivity, a preferable procedure is to scan the aluminum material pretreated and placed in the electrolytic coloring bath with alternating current voltage to plot a voltage-current curve, determine the boundary voltage E_0 that is the intersection of the respective extension lines of the flat region and the rising region in the curve, and set the peak voltage in alternating current electrolytic coloring at this boundary voltage E_0 . The boundary voltage E_0 thus determined is normally 0.65-0.75 times the ultimate voltage preset in the current-controlled pretreatment prior to coloring and, although varying somewhat with the conditions for the pretreatment prior to coloring or other conditions (such as treatment of anodic oxide film and the subsequent water washing), it can be determined unambiguously as a suitable peak voltage of an alternating current waveform or a superimposed AC-DC waveform.

[0038] According to the process of this invention, an electric current flows with ease in the parts near the counter electrode in the initial and intermediate stages of the pretreatment prior to coloring and the barrier layer grows there preferentially. The film resistance increases as the barrier layer grows and the ease of flow of the current in this part is held in check. That is, preferential growth of the barrier layer in the part where the current flows with ease in the pretreatment prior to coloring helps to eliminate the difference in site-dependent ease of current flow in alternating current electrolytic coloring thereby causing the current to flow with a nearly uniform current distribution over the whole surface of the aluminum material in a given energizing lot and eliminating irregularities in color tone in a given energizing lot.

[0039] Moreover, according to the process of this invention, the aforementioned pretreatment prior to coloring is performed until the voltage and current reach the preset ultimate values and, even if the bath conditions change in different energizing lots, the condition of the barrier layer finally adjusted by the pretreatment prior to coloring becomes constant in different energizing lots and the current flows with a nearly uniform current distribution over the whole surface of the aluminum material in different energizing lots and this eliminates irregularities in color tone in different energizing lots.

Brief Description of the Drawing

[0040] Fig. 1 is a voltage-current curve plotted in the determination of the boundary voltage E_0 in Example 1.

5 Preferred Embodiments of the Invention

[0041] A preferable mode of execution of this invention will be described concretely with reference to test examples, examples, and comparative examples below.

10 [Example 1]

[0042] An aluminum raw material, A6063S-T5, was anodized in 20% H_2SO_4 at a current density of 100 A/m² for 30 minutes to form an anodic oxide film with a thickness of 10 μ m on the surface of the aluminum raw material and then washed in an acid bath at pH 1 for 5 minutes to prepare an aluminum material.

15 **[0043]** An electrolytic coloring bath composed of 25 g/l of $CuSO_4$ and 5 g/l of H_2SO_4 was prepared and the aforementioned aluminum material was submitted to the current-controlled pretreatment prior to coloring with the aluminum material serving as the anode at a current density of 25 A/m², a bath temperature of 25°C, and an ultimate voltage of 20 V for approximately 20 seconds.

20 **[0044]** Upon completion of the pretreatment in this manner, the pretreated aluminum material was scanned with alternating current voltage in the same coloring bath while raising the peak voltage from 0 V at a rate of 1 V/sec and a voltage-current curve was plotted.

[0045] The results are shown in Fig. 1 and the boundary voltage E_0 was 14 V when the flat region and the rising region of the curve were respectively extended and the intersection of the two extension lines was read.

25 **[0046]** Alternating current electrolytic coloring was performed in the same coloring bath by setting the peak voltage of a commercial alternating current at this boundary voltage which is 14 V and passing the current for 50 seconds, 100 seconds, and 150 seconds to give the aluminum material electrolytically colored pink.

[0047] Color measurement was made on the electrolytically colored aluminum material thus obtained and the uniformity of color tone (color difference; ΔE^*_{ab}) in a given energizing lot was examined.

30 **[0048]** The treatment of the anodic oxide film, current-controlled pretreatment prior to coloring, and alternating current electrolytic coloring were repeated under the aforementioned conditions and the electrolytically colored aluminum material was submitted to color measurement to examine the uniformity of color tone (color difference; ΔE^*_{ab}) in different energizing lots. The results are shown in Table 1.

35 [Example 2]

[0049] The current-controlled pretreatment prior to coloring and alternating current electrolytic coloring were performed as in the aforementioned Example 1 except using the the conditions and the peak voltage of a commercial alternating current shown in Table 1 to give the electrolytically colored aluminum material.

40 **[0050]** The uniformity of color tone was examined as in Example 1 on the electrolytically colored aluminum material thus obtained. The results are shown in Table 1.

[Example 3]

45 **[0051]** Using the aluminum material prepared by anodizing the same raw materil by the same method as in Example 1 and the same electrolytic coloring bath as in Example 1, the constant voltage pretreatment prior to coloring was performed by placing the aluminum material as the anode, passing a direct current at a voltage of 15 V initially, switching the voltage over to 20 V thereafter at the point when the current density dropped to 32 A/m², and continuing the operation until the final current density became 25 A/m².

50 **[0052]** Upon completion of the constant voltage pretreatment prior to coloring, the material was scanned with commercial alternating current voltage in the same electrolytic coloring bath as in Example 1 and a voltage-current curve was plotted. The results are similar to those in Example 1 and the boundary voltage E_0 determined from the intersection of the respective extension lines of the flat and rising region was 14 V.

[0053] Alternating current electrolytic coloring was performed in the same electrolytic coloring bath by setting the peak voltage of a commercial alternating current at this boundary voltage E_0 of 14 V and passing the current for 100 seconds to give the aluminum material electrolytically colored pink.

55 **[0054]** The colored aluminum material was submitted to color measurement to examine the uniformity of color tone (color difference; ΔE^*_{ab}) in a given energizing lot. The results are shown in Table 1.

[Comparative Example 1]

[0055] Alternating current electrolytic coloring was performed under the same conditions as in Example 1 without the current-controlled pretreatment prior to coloring and the electrolytically colored aluminum material thus obtained was examined for the uniformity of color tone as in Example 1. The results are shown in Table 1.

[Comparative Examples 2 and 3]

[0056] The current-controlled pretreatment prior to coloring and alternating current electrolytic coloring were performed as in the aforementioned Example 1 except applying the peak voltage of a commercial alternating current shown in Table 1 and the electrolytically colored aluminum material thus obtained was examined for the uniformity of color tone as in Example 1. The results are shown in Table 1.

[Comparative Example 4]

[0057] The constant voltage pretreatment prior to coloring was performed at a bath voltage of 30 V for 30 seconds and alternating current electrolytic coloring was performed as in Example 2 and the electrolytically colored aluminum material thus obtained was examined for the uniformity of color as in Example 1. The results are shown in Table 1.

Table I

	Conditions for pretreatment prior to coloring	Conditions for alternating current electrolytic coloring			Color difference : ΔE^*_{ab}	
		Peak voltage (*1)	Voltage ratio (*2)	Time of energizing : seconds	In a given lot	In different lots
Example	1	14 V	0.70	50	1	≤ 1
	Current density : 25 A/m ²			100	1	≤ 1
	Ultimate voltage : 20 V			150	1	≤ 1
	2	21 V	0.70	50	1	≤ 1
	Current density : 50 A/m ²			100	1	≤ 1
	Ultimate voltage : 30 V			150	1	≤ 1
3	Current-controlled pretreatment prior to coloring			50		
	Voltage set initially : 15 V					
	Voltage after switchover : 20 V	14V	0.70	100	2	≤ 2
Comparative Example	Ultimate current density : 25 A/m ²			150		
	1	14 V	—	50	9 (*3)	5
	Current-controlled pretreatment prior to coloring					
	Current density : 50 A/m ²	25 V	0.83	50	6 (*3)	3
	Ultimate voltage : 30 V			100	≥ 3 (*3)	3
	Current-controlled pretreatment prior to coloring			50	No coloring	
4	Current density : 50 A/m ²	14 V	0.50	100	No coloring	
	Ultimate voltage : 30 V					
	Constant voltage pretreatment prior to coloring					
4	Bath voltage : 30 V	21 V	0.70	100	≥ 4 (*3)	4
	Treating time : 30 seconds					

(Notes) *1) Peak voltage of alternating current during alternating current electrolytic coloring

*2) Voltage ratio=peak voltage/ultimate voltage

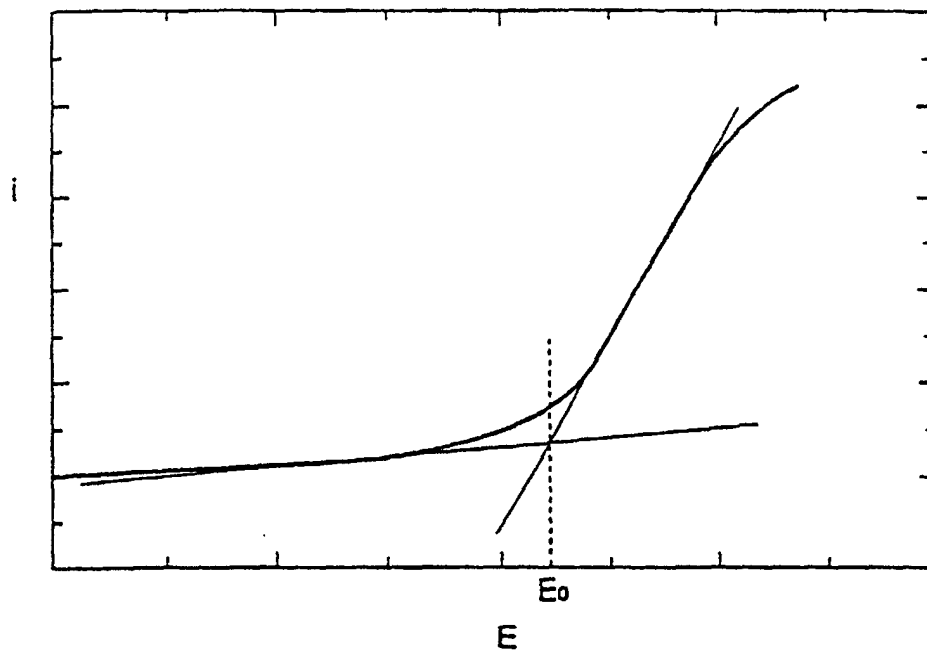
*3) Extremely large dependence on coloring time

Industrial Applicability

[0058] According to this invention, it is possible not only to secure uniformity in color tone in a given energizing lot but also prevent irregular coloring in different energizing lots as much as possible in alternating current electrolytic coloring of aluminum materials and produce aluminum materials colored in a uniform tone commercially and stably.

Claims

1. In a process for electrolytically coloring an aluminum material which comprises immersing an aluminum material consisting of anodized aluminum or an anodized aluminum alloy in an electrolytic coloring bath containing a soluble metal salt, performing a pretreatment prior to coloring by passing a direct current waveform with said aluminum material serving as the anode, and performing alternating current electrolytic coloring in the same electrolytic coloring bath, an improved process for electrolytically coloring an aluminum material which comprises performing said pretreatment prior to coloring until the voltage and current respectively reach the preset ultimate values.
2. A process for electrolytically coloring an aluminum material as described in claim 1 wherein said pretreatment prior to coloring is constant current electrolysis effected by passing a direct current waveform while maintaining the current at the preset ultimate value and the constant current electrolysis is continued until the voltage reaches the preset ultimate value.
3. A process for electrolytically coloring an aluminum material as described in claim 2 wherein said alternating current electrolytic coloring is performed by passing to the aluminum material a voltage-controlled alternating current waveform having the peak voltage which is 0.55-0.8 times the final voltage in the pretreatment prior to coloring.
4. A process for electrolytically coloring an aluminum material as described in claim 1 wherein said pretreatment prior to coloring is constant voltage electrolysis effected by starting the passage of a direct current waveform at a voltage lower than the preset ultimate value, then switching over to the ultimate value, and passing a direct current waveform and the constant voltage electrolysis is continued until the current reaches the preset ultimate value.
5. A process for electrolytically coloring an aluminum material as described in any one of claims 1 to 4 wherein the aluminum material pretreated prior to coloring and placed in the electrolytic coloring bath is scanned by alternating current voltage to plot a voltage-current curve, the boundary voltage E_0 is determined from the intersection of the respective extension lines of the flat and rising regions of the voltage-current curve, and the peak voltage in alternating current electrolytic coloring is controlled below the boundary voltage E_0 .



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/04179

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ C25D11/22		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ C25D11/00-11/24		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 58-025495, A (Mitsubishi Keikinzoku Kogyo K.K.), 15 February, 1983 (15.02.83) (Family: none)	1-5
A	JP, 59-173294, A (The Pilot Pen Co., Ltd.), 01 October, 1984 (01.10.84) (Family: none)	1-5
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search 11 September, 2000 (11.09.00)		Date of mailing of the international search report 19 September, 2000 (19.09.00)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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