APPARATUS AND PROCESS FOR APPLYING ELECTRODEPOSITION PAINTING BY ALTERNATING CURRENT

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3,392,101 7/1968 Barrett et al................. 204/181

ABSTRACT

Apparatus and process for electroddeposition painting of a metallic material by using alternating current (hereinafter designated as A.C.). The apparatus comprises the conventional resin bath and uses the metallic material as an electrode. A counter-electrode is formed of a film-forming metal upon which an oxide film is formed, the oxide film having a thickness no less than 0.2 μ. Additionally, a third electrode is utilized for preventing pin holes in the coating film.

23 Claims, 15 Drawing Figures

![Graph showing Coulombic efficiency ratio and Al oxide film thickness](image-url)
FIG. 1

(i) Bath voltage
- Bath voltage graph with peaks labeled A and B.
- Metal is positive → anode, counter-electrode is negative → cathode.
- Metal is negative → cathode, counter-electrode is positive → anode.

(ii) Bath current
- Current in the direction (+) to the order of electrodeposition coating.
- Current in reverse direction to electrodeposition coating – loss of current due to paint redissolution etc.
- Current in reverse direction to electrodeposition coating.

(iii) Bath current
- Current in the direction (+) to the order of electrodeposition coating.
- Current in reverse direction to electrodeposition coating.
**FIG. 2**

Acrylic resin bath
Solid content 15%
Coulombic efficiency ratio of D.C. electrodeposition = 18.8\%_{out}

**FIG. 3**

Coulombic efficiency ratio (%) = \frac{\text{Coulombic efficiency of A.C. deposition}}{\text{Coulombic efficiency of D.C. deposition}} \times 100

Thickness of Ta oxide film (Å)
FIG. 4

Al material with 0.12 μm oxide film

Coulombic efficiency (m%) = 18.8%

Solid content 15%

Coulombic efficiency ratio of D.C. electrodeposition = 18.8 m%

FIG. 5

Al material with 0.12 μm oxide film

Coulombic efficiency ratio (%) = \frac{\text{Coulombic efficiency of A.C. deposition}}{\text{Coulombic efficiency of D.C. deposition}} \times 100(\%)

Al oxide film thickness (μ)
FIG. 6
Alkyd resin bath
pH = 8.50 Solid content 15%
Coulombic efficiency 12.52 %

200 Amount of Deposited point m^2/m^2
100
Electro deposition Coating Time (Sec)
0 5 10
Bath Voltage 300V
Bath Voltage 200V
Bath Voltage 100V

FIG. 7
Alkyd resin bath
pH = 8.50 Solid content 15%
Coulombic efficiency 12.81 %

200 Amount of Deposited point m^2/m^2
100
Bath Voltage (V)
0 100 200
5 second Electro deposition
10 second Electro deposition
FIG. 8

\[
\text{Coulombic efficiency ratio (\%)} = \frac{\text{Coulombic efficiency of present process}}{\text{Coulombic efficiency of D.C. process}} \times 100(\%)
\]

Acrylic resin  Solid content 15\%
Bath temperature 20°C  pH=7.90  Bath Voltage 100V
5 second electrodeposition
Ta oxide film electrode

Coulombic efficiency

Sine waved A.C. frequency (f)
FIG. 9

Bath Voltage (V)

Triangle wave

Bath Current (A)

Echelon wave

Bath Voltage (V)

Bath Current (A)
FIG. 10
FIG. 11

- Bath Voltage (V)
- Total bath current (I₀)
- Third electrode current (I₁)
- Current passing through metal to be coated (I₂)

\[ I₀ = I₁ + I₂ \]

Current actually used for electrodeposition
**FIG. 12**

![Graph showing number of pinholes in metal before and after baking.](image)

**Equation:**

\[ \alpha = \log x \]

\[ \alpha : \text{Area ratio} = \frac{\text{Surface Area of Third Electrode}}{\text{Surface Area of Metal to be Coated}} \]

**FIG. 13**

![Graph showing Coulombic Efficiency.](image)

**Equation:**

\[ \alpha = \log x \]

\[ \alpha : \text{Area ratio} = \frac{\text{Surface Area of Third Electrode}}{\text{Surface Area of Metal to be Coated}} \]
APPARATUS AND PROCESS FOR APPLYING ELECTRODEPOSITION PAINTING BY ALTERNATING CURRENT

The present invention relates to a process for electrodeposition painting by alternating current or by using an a.c. source. This invention is for a process of electrodeposition painting by an a.c. voltage to popularize the technique of electrodeposition painting and to permit a converter from a.c. to direct current (designated hereinafter as d.c.) to be omitted and therefore to simplify the necessary electric devices.

The present invention may be summarized to be a process for applying electrodeposition painting by a.c. comprising applying painting by an a.c. voltage in a resin bath for the electrodeposition painting using an oxide film electrode as counter-electrode of a film-forming metal such as Ta, Al, Ti, Zr and Nb and an alloy thereof.

In principle, processes for electrodeposition painting so far used comprises applying an external d.c. voltage between a metallic matter to be coated as anode and a counter-electrode or cathode in a bath for the electrodeposition painting containing an electrodeposition paint material, and painting the surface of the metallic matter with the deposited paint material. Most other processes are modifications of the above process.

Although some processes for electrodeposition painting using an a.c. voltage have been devised in which an a.c. voltage is applied between a metallic matter to be coated and a counter-electrode to coat the surface of the former with the paint material deposited, these processes are of almost no practical use because of the following difficulties:

1. A special bath of paint material is used for the a.c. electrodeposition painting. In this case, the paint material is deposited on the counter-electrode, though it does not need to be coated, and a device is necessary to remove the paint material which, to the contrary, loses the merit of the electrodeposition coating method by a.c.

2. The amount of deposited paint material per unit time is so small that profitable application of the technique is questionable.

3. The coulombic efficiency, or amount of paint material deposited in mg/dm² per unit coulomb, is small relative to that in the method using d.c.

4. A measure should be taken to the gas which is evolved at the cathode.

However, if the above difficulties could be solved, the process for the electrodeposition painting by a.c. is apparently more profitable in equipments and devices than the corresponding processes by d.c.

The present invention has succeeded in solving these difficulties profitably and developing a practical process for the electrodeposition painting by a.c.

Difficulties generally accompanying with the processes for the electrodeposition painting by a.c., such that a thick coating film is not obtained and that the coulombic efficiency is low, arise from the mode of treatment in which the a.c. voltage is directly applied between a metallic material to be coated and the counter-electrode, where the metallic material is alternately polarized as anode and cathode in accordance with the cycle of the a.c. voltage source so that the coating film that is formed when the material is anodic is inevitably dissolved or peeled in part when the polarity is reversed.

In this invention, however, the electrical resistance between both electrodes is made lower, hence the bath current larger, when the metallic material to be coated is anodic and the counter-electrode is cathodic, and therefore the coating process to the metal surface proceeds regularly. On the other hand, when the metallic material is cathodic and the counter-electrode is anodic, the resistance between both electrodes is made higher and hence the bath current smaller so that the deposited coating film on the surface of the metallic material is not easily dissolved or peeled. Furthermore, a more perfect process for the electrodeposition painting has been completed by compensating the undesired current which flows when the metallic matter to be coated is cathodic and the counter-electrode is anodic.

The characteristic feature of the process of this invention is that all the requirements in realizing electrodeposition painting by an a.c. voltage have been met solely by modifying the counter-electrode without introducing a sophisticated set of apparatus.

Subsequently, performance of the counter-electrode of this invention as well as the consequence in which the process for the electrodeposition painting by a.c. has been realized will be explained in the following paragraphs.

The feature of the counter-electrode employed in the process of the present invention is that the electrical resistance and the electrostatic capacitance between the electrode and the paint material bath are large when the electrode is anodic while they are small when cathodic.

The present invention shall be described in detail referring to the attached drawings.

FIG. 1 shows the relation between the bath voltage and the bath current when a sinusoidal a.c. voltage is used in the process of this invention, where (i) shows the bath voltage, (ii) the bath current depending on the polarity of voltage and (iii) the bath current when ineffective current is compensated with electrostatic capacity.

FIG. 2 shows the coulombic efficiency in the a.c. electrodeposition coating when the tantalum oxide film electrode is used.

FIG. 3 shows the ratio in coulombic efficiency of the a.c. electrodeposition painting with the tantalum oxide film electrode to the d.c. method.

FIG. 4 shows the coulombic efficiency in the a.c. electrodeposition painting when the tantalum oxide film electrode is used.

FIG. 5 shows the ratio in coulombic efficiency of the a.c. electrodeposition painting with the tantalum oxide film electrode to the d.c. method.

FIG. 6 shows the relation between the time for electrodeposition and the amount of paint material deposited in the period when a tin-plated iron plate is coated by the a.c. electrodeposition using the tantalum oxide film electrode.

FIG. 7 shows the relation between the bath voltage and the amount of paint material deposited when a tin-plated iron plate is coated by electrodeposition using the tantalum oxide film electrode.

FIG. 8 shows the relation between the cycle of the sinusoidal alternating current and the ratio in the coulombic efficiency.
FIG. 9 shows the relation between the bath voltage and the bath current in electrodeposition coating when alternating currents of various wave forms are used.

FIGS. 10 - 15 show a modification of the present invention. FIG. 10 shows the principle of the modification of the present invention. FIG. 11 is a graph for explaining the bath current. FIG. 12 shows the relation between the area ratio of the third electrode and pin holes in the coating film. FIG. 13 is a graph for explaining the area ratio of the third electrode and the coulombic efficiency. FIG. 14 shows the position of the third electrode and FIG. 15 explains the behavior of the third electrode in relation to the current elements.

The electrical resistance between the counter-electrode and the paint material bath is high and low when the electrode is anodic and cathodic, respectively. As shown as (ii) in FIG. 1 when the metallic material to be coated is positive and the counter-electrode is negative or, in other words, the paint material is deposited on the surface of the metallic material, the resistance between the counter-electrode and the solution is low enough to allow a large bath or a forward current to flow. When the metallic material is negative and the counter-electrode is positive, respectively, high resistance between the counter-electrode and the solution causes the bath current or the current in the inverse direction to be low and suppress the re-dissolution and peeling of the paint coating films formed on the surface of the metallic material to be coated.

However, re-dissolution and peeling of the coating films which cause a loss, due to the current in the inverse direction, though small, can not be avoided.

The loss can be compensated by the electrostatic capacitance when the counter-electrode is anodic. Namely, when the counter-electrode is anodic, the phase of the bath current leads the bath voltage due to the capacitance. As a result, as shown as (ii) in FIG. 1, while the counter-electrode is positive and the metallic material to be coated is negative according to the bath voltage (interval B on (i) or under the voltage favorable to re-dissolution of films), current flows in the direction to deposit the paint material for a time period on the metallic material (interval C on (iii)). Thus, additional coating is applied to the metallic matter to compensate the loss due to the current in the inverse direction.

In the above, the coulombic efficiency is emphasized, but a different requirement should be met with the counter-electrode. If the paint material is deposited on the counter-electrode itself, a thick film will be formed on the surface which increases the electrical resistance between the electrode and the solution, requiring a higher bath voltage for the coating to proceed. A counter-electrode free from such trouble is desired.

In this connection, the counter-electrode of the present invention has an oxide film on the surface prevents the coating resin from completely depositing on the electrode surface. As an anode, the electrode forms a current leading in phase due to the electrostatic capacitance so that the coating film once formed is dissolved while acting as anode and, therefore, the loss in bath voltage due to the resistance of coating film can be kept low.

As has been explained, the counter-electrode having the specified properties outlined above permits electrodeposition painting by a.c. to be performed with much simpler apparatus in comparison with conventional processes.

In following the process and apparatus of this invention, the counter-electrode having the above properties is required. Such an electrode can be prepared from a film-forming metal such as Ta, Al, Ti, Nb, Zr, Y, Hf, Cr, Mo, W, Bi, Mg, Ge, V and Si and alloys thereof by forming an oxide film on the surface by a chemical or electrochemical manner.

For example, a tantalum plate, after a pre-treatment (immersing for about 10 sec. in a solution containing H₂SO₄, HNO₃ and HF in the ratio 5:2:2), is anodically treated for 10 to 120 min. by d.c. voltage using a carbon cathode in a 15 percent solution of boric acid at 70°C. The oxide film formed on the surface has the thickness as shown in Table 1 depending on the voltage applied to the bath.

Table 1 shows the oxidation treatment of the tantalum and the film thickness.

<table>
<thead>
<tr>
<th>Voltage of anodic treatment (V)</th>
<th>Film thickness (A)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>about 500</td>
<td>dark pale blue</td>
</tr>
<tr>
<td>70</td>
<td>1000</td>
<td>golden</td>
</tr>
<tr>
<td>90</td>
<td>1300</td>
<td>reddish violet</td>
</tr>
<tr>
<td>100</td>
<td>1500</td>
<td>blue</td>
</tr>
<tr>
<td>130</td>
<td>1900</td>
<td>golden</td>
</tr>
<tr>
<td>160</td>
<td>2400</td>
<td>red</td>
</tr>
<tr>
<td>180</td>
<td>2700</td>
<td>green</td>
</tr>
</tbody>
</table>

Using tantalum as a counter-electrode which was coated by an oxide film, an aluminum material (oxide film being 0.12µ thick) was coated by electrodeposition in a coating resin bath of the d.c. anodically deposition type by an a.c. voltage from the commercial source. If the tantalum electrode had been sufficiently treated to form the oxide film, the coulombic efficiency was almost equal to that in the d.c. electrodeposition painting process as shown in FIG. 2. The result illustrates the benefits of the present invention in comparison with the low coulombic efficiency, less than 10 percent of the d.c. process, due to low efficiency of deposition of the paint material. This low efficiency is obtained when electrodes of stainless steel (SUS 27), platinum, carbon and aluminum (carrying less than 0.2µ thick oxide film) were used as the counter-electrode and electrodeposition coating was performed by the identical a.c. voltage. (see Table 2).

Similar property of the tantalum oxide film electrode mentioned can be obtained by the anodic oxidation treatment in various electrolysis solutions such as H₂SO₄, CrO₃, HNO₃, NaOH, Na₂SO₄ and many others.

When the counter-electrode is prepared from aluminum, the procedure is the same as for tantalum. The oxide film forming process is followed for 5 to 300 min. in an electrolysis solution containing substances of moderate dissolving power such as H₂SO₄ and under a 3.0 to 200 V d.c. or a.c. voltage, so as to achieve sufficiently high resistance between the electrode and the solution when the former is anodic. At the same time, the electrostatic capacitance is ensured therebetween. The coulombic efficiency of the electrode thus formed is close to that of the electrodeposition painting by a d.c. process if sufficient treatment of the oxide film formation has been performed, as shown in FIGS. 4 and 5.
In other words, the ratio of the coulombic efficiency in the electrodeposition coating processes conducted in identical baths by d.c. and a.c. approaches 100 percent. This ratio can never be attained with the previously cited electrodes, namely stainless steel (SUS 27), platinum, carbon and aluminum with less than 0.2 µ thick oxide film, when these electrodes are used as counter-electrode and an aluminum material (10 cm x 10 cm, 0.12 µ thick oxide film) is coated by electrodeposition using an a.c. voltage.

An aluminum electrode can be provided with the property of the counter-electrode of this invention by treating to form an oxide film on the surface by many procedures, as is the case with tantalum. For example, electrolytic oxidation in solutions of sulfuric, chromic and boric acids. The methods are not restricted to those mentioned above.

Film-forming metals such as Ti, Zr and Nb and alloys thereof could provide the counter-electrode which have necessary properties required to achieve the process of this invention by being treated to form oxide films in fundamentally the same way as before.

In the oxide film electrodes of this invention, the oxide film should be especially stable and uniformly formed on the electrode surface. If otherwise, the oxide film may be deteriorated or broken to fall off due to evolution of hydrogen gas when serving as a cathode and likely deposition of resin on the electrode surface and deterioration of the electrostatic capacity may result when serving as an anode. Anodic general, thickness of oxide films is important with the oxide films which is required to form the electrodes of the present invention. In particular, for the metals of the first group, that is Ta and Nb, an oxide film thicker than 0.2 µ is sufficient and the film can be obtained with relative ease in an acid, neutral or alkaline solution. With the second group metals, that is Zr and Hf, oxide film thickness more than 0.35 µ for Zr and 0.4 µ for Hf is necessary, which could be prepared by an anodic treatment in almost any acid, neutral or alkaline electrolysis solution, except that of hydrofluoric acid. With film-forming metals of the third group, that is Al, Ti and others, a thickness of oxide films more than 1 µ is necessary. The electrode could be prepared by chemically treating in an electrolyte which is mostly acid having moderate dissolving power against the oxide films (dilute sulfuric, nitric, chromic and oxalic acids being contained). With the fourth group metals consisting of alloys of oxide film-forming metals such as Ta, Nb, Zr, Hf, Al and Ti, the actual thickness of the oxide films should be greater than the summed products of thicknesses of oxide films and the contents with respect to all composing elements.

Finally with the fifth group metals which consist of alloys of one or more elements of the oxide film-forming metals belonging to groups 1 through 4 above such as Ta, Nb, Zr, Hf, Al and Ti as the major constituent with elements other than the oxide film-forming metals, the thickness of the oxide films should be larger than product of the reciprocal of content of the major constituent and the minimum film thickness of the film-forming metals. In these cases the procedure to treat the oxide films may be similar to that for the oxide film-forming metal contained as the major constituent.

In the above statement, the structure and quality of the counter-electrode were explained with regard to the coulombic efficiency. However, further typical requirements that follow should be met with the counter-electrode in order for the electrodeposition painting process by a.c. to be extensively applicable in industry.

1. The process should be applicable to various metals. When applied to Al, zinc-plated iron plate, tin-plated iron plate, Fe, tin-free sheet and many other materials, it should exhibit excellent performance and high coulombic efficiency as a process for electrodeposition painting.

2. Any desired resin type coating materials such as acrylic, polyester, alkyd, epoxyester and maleic oil resins could be applied with the high coulombic efficiency as could be encountered in the electrodeposition painting process by d.c.

3. Time required for the electrodeposition painting could be varied as desired. In other words, a coating layer of the desired thickness could be obtained within a certain time interval which is predetermined as desired.

4. As a.c. voltage sources, not only the commercially supplied sinusoidal a.c. source of 50 or 60 c.p.s but also any a.c. sources of higher or lower cycles could be used for the purpose. Further, saw-tooth or square wave a.c. could be satisfactorily used for the coating.

All the requirements above have been met by the process of the present invention with satisfactory results as illustrated below.

1. Table 2 shows the performance of the process of the present invention as a coating process applicable to various metallic materials including Al, zinc-plated iron plate, tin-plated iron plate, Fe and tin free sheet.

<table>
<thead>
<tr>
<th>Electrode of the process of this invention</th>
<th>Counter-electrodes other than that in the process of this invention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tantalum oxide film electrode</td>
<td>Stainless Steel oxide film electrode</td>
</tr>
<tr>
<td>Aluminum (SUS 27)</td>
<td>Aluminum</td>
</tr>
<tr>
<td>Zinc-plated iron plate</td>
<td>Tin plate</td>
</tr>
<tr>
<td>100 µ</td>
<td>100 µ</td>
</tr>
</tbody>
</table>

Table 2

Coulombic efficiency at the electrodeposition coating of various metallic materials
3,878,078

1. Tantalum oxide film electrode: 2700 (Å) thick oxide film
2. Aluminum oxide film electrode: 10.5 (μ) thick oxide film

[Conditions under which the electrodeposition coating was performed]

A counter-electrode of the same dimension 10cm × 10cm as a metallic material to be coated was placed at a 10cm distance from the latter in an electrodeposition painting bath. The coating was conducted for 5 sec. by the commercial a.c. (50 c.p.s. sinusoidal) of 100V, and the coulombic efficiency was calculated. Subsequently, the corresponding coulombic efficiency for the d.c. coating was obtained when the same material was treated by electrodeposition painting process under application of 70V d.c. source in the same bath for 3 sec. using a stainless cathode. Ratio of the coulombic efficiencies shows the relative performance of the electrodeposition coating of each counter-electrode.

[Bath for the electrodeposition painting]

Acrylic resin: the solid content of the bath being 15 percent

Bath temperature: 25°C

The coulombic efficiency of the process of this invention was in all cases close to that of the d.c. method, and therefore the ratio in the coulombic efficiencies was 100 percent. Such values of coulombic efficiency were never obtained in the a.c. electrodeposition coating with electrodes other than the counter-electrode of the present invention.

2. As for the coulombic efficiency when a coating material of an arbitrary resin type was used, the same coulombic efficiencies as those by d.c. electrodeposition painting processes were obtained by the a.c. process for a varieties of coating materials including those containing as major constituent acrylic, polyester, alkyd, epoxyester and maleic oil resins, as shown in Table 3.

3. As for the time required to complete the electrodeposition coating to obtain a desired thickness of the coated films, FIGS. 6 and 7, which illustrate the deposition rate of the coating materials of this invention, show that the deposition rate may be arbitrarily varied by changing the bath voltage to meet any requirement.

This is one of the important requirements which the process of this invention should meet in order to be generally used as a painting process for industrial purpose. The reason for it is self-evident, since a paint coating process to be used in industrial purposes should proceed at a rate comparative with that of other operations in a sequence. For example, in coating automobile bodies the coating should proceed at the same rate as that of body-forming operation prior to the coating, and in coil coating very rapid coating is required to attain a desired thickness of the coating film in a short time.

4. With regard to the a.c. sources to be applicable to the present invention, this invention exhibits the high performance in the electrodeposition painting, as shown in FIG. 8, by using a.c. of a very wide range of frequency and, in addition to sinusoidal waves, by saw-tooth or square waves shown in FIG. 9 with higher coulombic efficiencies than in other a.c. electrodeposition painting processes.

According to a modification of the present invention, a third electrode is provided in addition of the metal to be painted by electrodeposition and the coupled electrode is electronically connected to the metal to be painted by electrodeposition.

This modification of the present invention further enhances the advantages of the alternating current electrodeposition paint coating and particularly enhances the paint film quality.

The third electrode in the modification of the present invention has its objects to prevent gas generation at the metal to be painted by electrodeposition and to effect precision control of the paint film thickness, and is an "oxide film electrode" or may be an ordinary electrode commonly used for electrolysis connected with a rectifying element of silicon, germanium selenium, etc. in such a manner that the current flows in the direction from the electrode to the rectifying element.

Table 3

<table>
<thead>
<tr>
<th>Resin</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic</td>
<td>7.90</td>
<td>18.8</td>
<td>18.9</td>
<td>18.7</td>
</tr>
<tr>
<td>Polyester</td>
<td>6.47</td>
<td>14.8</td>
<td>14.9</td>
<td>14.8</td>
</tr>
<tr>
<td>Maleic oil</td>
<td>7.60</td>
<td>6.2</td>
<td>6.2</td>
<td>6.3</td>
</tr>
<tr>
<td>Epoxyester</td>
<td>9.10</td>
<td>17.8</td>
<td>17.9</td>
<td>17.7</td>
</tr>
<tr>
<td>Alkyd</td>
<td>8.50</td>
<td>12.5</td>
<td>12.5</td>
<td>12.5</td>
</tr>
</tbody>
</table>

The oxide film electrode referred to above is composed of metals which form an oxide film such as Ta, Al, Ti, Zr, Nb, etc. or their alloys on which an oxide film is formed.
The modification of the present invention shall be described in details referring to FIGS. 10 – 15.

In FIG. 10, 1 is a bath filled with electrodeposition paint, 2 is an oxide film electrode used as a coupled electrode, 3 is a metal to be painted by electrodeposition, connected to an alternating current source, 4 is another oxide film electrode used as the third electrode connected to the side of the metal to be painted through a resistor 5.

When the alternating current is supplied, the metal 3 to be painted coated and the third electrode are impressed with positive and negative voltages alternatively in respect to the counter-electrode 2. As an oxide film electrode is used for the counter-electrode, a large bath current passes under the bath voltage condition in which the counter-electrode is negative and the metal 3 to be painted coated and the third electrode 4 are positive, and electrodeposition paint coating is effected thereby. Since the third electrode is the oxide film electrode, the current is hard to pass and passes mainly through the metal to be painted coated, thus using most of the current for electrodeposition paint coating on the surface of the metal to be painted coated.

Next, when the counter-electrode 2 is positive and the metal to be coated 3 and the third electrode 4 are negative, a small amount of current flows in a direction reverse to that for effecting the electrodeposition paint coating. If this reverse current passes through the metal to be coated, not only the electrodeposited film is redissolved, but also hydrogen is generated by the cathodic electrolysis. In the modification of present invention, this reverse current is made to pass through the third electrode, thus eliminating the above defect. Namely, because the third electrode is an oxide film electrode, the current easily passes when it serves as a cathode while the current does not easily pass through the surface of the metal to be coated because of the electrodeposited coating film. Thus, the bath current passes mainly through the third electrode. Therefore, the hydrogen gas generation due to the cathodic electrolysis is caused on the surface of the third electrode.

In this way, pin holes in the paint coating film due to the gas generation on the surface of the metal to be painted coated, or foams in the coating film are remarkably reduced.

However, when the third electrode is used, a small amount of current passes from the third electrode when it serves as anode, and this current is of use for electrodeposition paint coating, thus lowering the amount of coating electrodeposited per unit current passage. Thus there is an optimum range for the ratio of the surface area of the third electrode to the metal to be painted coated. FIG. 12 shows the relation between the ratio of the surface area α and the number of the pin holes in the coating film. The solid line represents the relation before the baking and the dotted line represents the relation after the baking. From this figure, it is clear that the ratio α should be log $10^{10} \leq -5$. The relation between the coulombic efficiency (the amount of electrodeposited coating (mg) per unit current passage (per 1 coulomb)) and the area ratio of the third electrode is shown in FIG. 13. It is clear that the increased area ratio lowers the efficiency, and particularly when the ratio is larger than $-1 (=\log 10) \equiv 0$, a rapid lowering is caused and the lowering is moderated when the ratio is $1 (=\log 10^0)$ or more. From a view point of industrial value, $\log 10^\alpha \leq 0$ is better, thus the range of the area ratio is: $-5 \leq \log 10^\alpha \leq 0$.

As shown in FIG. 10, the connection of the third electrode to the metal to be coated may be preferably done through a variable resistor for better current balance between the third electrode and the metal to be coated, and in some cases for precision control of the amount of the electrodeposited paint coating. The capacity of the resistor may be $0 - 200 \text{K}\Omega$ for presently available paints and it is enough if the resistor can flow the current corresponding to 10 percent of the bath current.

Lastly, regarding the shape and position of the third electrode, it is preferable from better efficiency that the third electrode is positioned up to $3/5 L(m)$ (corresponding to the slant lined portion in FIG. 14) from the metal to be coated supposing the distance between the metal and the counter-electrode is $L(m)$. Regarding the shape of the third electrode, it is preferable that the electrode has some measures such as perforation because if a plate-form electrode is positioned in parallel with the current for electrodeposition, a point of equipment efficiency, a round bar form of electrode is preferred for stability and draining of the bath solution at the suspension of the operation. FIG. 14 shows one example.

As explained above, with the use of the third electrode pin holes or foams are prevented from taking place in the paint coating film, thus solving one of the big problems of the a.e. electrodeposition paint coating.

Meanwhile, when an electrode commonly used for electrolysis is used as the third electrode, it is necessary that a rectifying element 107 such as of silicon, germanium, selenium, etc. and a variable resistor 105 by orienting the rectifying element are connected in series in such a direction that the current flows in the direction 108 as shown in FIG. 15. In this case, the capacity of the rectifying element or the resistor should be large enough to pass the current corresponding to 1/10 of the bath current.

The electrode commonly used for electrolysis referred to above means an electrode of a metal which does not react with water such as stainless steel, lead, nickel, chromium, iron, silver, platinum, etc. or of non-metallic material such as carbon.

As has been explained above, the electrodeposition painting by a.c. of the present invention is a very excellent as well as practical process with a wide range of application.

EXAMPLE 1

A tantalum oxide film electrode having a 2700 A thick oxide film to be used in the process of this invention was prepared as follows: A 10cm x 10cm plate of tantalum was treated by immersing for 10 sec. in a mixed solution of $H_2SO_4$, $HNO_3$ and $HF$ in a ratio of 5 : 3 : 2, and an oxide film was formed on the surface by the anodic oxidation with a carbon cathode in a 15 per cent boric acid solution at 70°C, applying a voltage of about 5V at the beginning which was increased gradually up to 180V in 60 min. and maintained at the voltage for 20 min. Subsequently the plate was washed with water and then dried.

With the above tantalum oxide film electrode as counter-electrode, a 10cm x 10cm aluminum material
3,878,078

(1) with one side sealed and having a 0.12μ thick oxide film placed at a distance of 10cm from the counter-electrode was coated by electrodeposition for 5 sec. using the commercial sinusoidal a.c. voltage of 100V and 50 c.p.s. in a coating bath containing acrylic resin of the d.c. anode deposition type. As a result, the coating material was deposited by 58.1 mg/dm² and the quantity of electricity involved in the treatment, as measured from the current form on an oscilloscope, was calculated according to the following expression, to be 3.09 coul/dm² (see (iii) in FIG. 1),

\[ Q = Q_e + Q_b - Q_f \]

where \( Q \) is the effective quantity of electricity, \( Q_e \) and \( Q_b \) are the quantity of electricity of the current in phase with the applied bath voltage, and \( Q_f \) is the quantity of electricity of the current in inverse phase with the applied bath voltage (or the quantity of electricity once charged in the electrode and then discharged).

\[ Q_e = 3.10 \text{ (coul/dm²)} \]
\[ Q_b = 0.10 \text{ (coul/dm²)} \]
\[ Q_f = 0.11 \text{ (coul/dm²)} \]

therefore, \( Q = 3.10 + 0.10 - 0.11 = 3.09 \text{ (coul/dm²)} \)

Consequently, the coulombic efficiency of the process of the present invention was 58.1 (mg/dm²)/3.09 (coul/dm²) = 18.8 (mg/coul), which was equal to the coulombic efficiency in the d.c. electrodeposition coating.

**COATING BATH OF ACRYLIC RESIN**

1. Acrylic resin was the major constituent with the solid content of the bath being 15 percent. Bath temperature 20°C. Emulsion type.

2. The coulombic efficiency when an aluminum material having a 0.12μ thick oxide film was coated by electrodeposition for 5 sec. using a 70V d.c. applied bath voltage was 18.8 mg/coul.

For the sake of comparison, a platinum plate, stainless steel (SUS 27) and pure aluminum (having a 0.12μ thick oxide film) which had not the quality required for the process of this invention were used as counter-electrode, and the electrodeposition painting was performed by a.c. under the same conditions of bath as well as painting. In any case, the coulombic efficiency remained below 0.2 percent.

**EXAMPLE 2**

An aluminum oxide film electrode (having 10.5μ thick oxide film) to be used in the present invention was prepared as follows: A 10cm x 10cm pure aluminum plate was kept for 3 min. in a 5 percent oxalic acid solution with a 5V voltage applied until the current decreased to a steady state. The voltage was then elevated, under the precaution not to change the current seriously, to 100V in about 60 min. Kept standing for 10 min., washed with water and dried.

With the said aluminum oxide film electrode as counter-electrode, a 10cm x 10cm aluminum material (with one side sealed and having a 0.12μ thick oxide film) placed oppositely at a distance of 10cm from the counter-electrode was coated by electrodeposition for 5 sec. using the commercial sinusoidal a.c. voltage of 100V and 50 c.p.s. in a coating bath containing acrylic resin of the d.c. anode deposition type. As a result, the paint material was deposited by 60.3 mg/dm².

**EXAMPLE 3**

A titanium oxide film electrode to be used as counter-electrode of the process of this invention was prepared as follows: A 0.1mm thick 10cm x 10cm foil of pure titanium was treated, after degreasing, with 2 percent hydrofluoric acid for 3 min. to dissolve impure oxide, electrolytically cleansed (with the current density 0.5A/dm²) in an aqueous solution containing 10 percent sulfuric, 7 percent phosphoric and 18 percent acetic acids, anodically oxidized by a current of 0.1A/dm² in a 10 percent solution of phosphoric acid in glacial acetic acid, and then electrolytically oxidized by a current of 0.1A/dm² followed by heating at 300°C in the air to coat the surface with an oxide film, the film being 2μ thick.

With the titanium oxide film electrode as a counter-electrode, a 10cm x 10cm aluminum material (with one side sealed and having a 0.12μ thick oxide film) placed oppositely at a distance of 10cm from the counter-electrode was coated by electrodeposition for 5 sec. using the commercial sinusoidal a.c. voltage of 100V and 50 c.p.s. in a coating bath containing acrylic resin of the d.c. anode deposition type. As a result, the coating material was deposited by 46.3 mg/dm².

**COATING BATH OF ACRYLIC RESIN**

<table>
<thead>
<tr>
<th>Major constituent:</th>
<th>Acrylic resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid content of bath:</td>
<td>15%</td>
</tr>
<tr>
<td>State of bath:</td>
<td>Emulsion type</td>
</tr>
<tr>
<td>pH of bath:</td>
<td>7.90</td>
</tr>
</tbody>
</table>
The quantity of electricity involved in the treatment, as measured from the current form on an oscilloscope, was calculated according to the following expression, to be 3.21 (coul/dm$^2$).

\[ Q = Q_a + Q_b - Q_c \]

(see (iii) in FIG. 1), where $Q$ is the effective quantity of electricity, $Q_a$ and $Q_b$ are the quantity of electricity of the current in phase of the applied bath voltage, and $Q_c$ is the quantity of electricity of the current in inverse phase of the applied bath voltage, and $Q_a = 3.17, Q_b = 0.10$ and $Q_c = 0.06$.

Consequently, the coulombic efficiency in the electrodeposition coating by a.c. using the counter-electrode of this invention was 46.3 (mg/dm$^2$/coul) / 3.21 (coul/dm$^2$) = 14.4.

The ratio of the coulombic efficiencies was calculated to be 76 percent by the following expression.

\[ \text{Ratio of coulombic efficiency} = \frac{\text{Coulombic efficiency in the process of this invention}}{\text{Coulombic efficiency in the d.c. process}} \times 100 \]

\[ = \frac{14.4}{18.8} \times 100 = 76 \% \]

**EXAMPLE 4**

Using the tantalum oxide film electrode (with 0.27$\mu$m thick oxide film) prepared according to Example 1 and a platinum electrode for the purpose of comparison as counter-electrodes, electrodeposition painting was conducted by a.c. with the following four materials.

1. Bonderized zinc-plated iron plate: Amount of bonde film (1.2 g/m$^2$) Amount of zinc plated (183 g/m$^2$)
2. Tin-plated iron plate (ET No. 25): Commercial tin-plated iron plate Amount of tin plated (lb/BB)
3. Fe (substrate for plating): Cold rolled in steel plate, with oil application
4. Tin-free sheet: Amount of chromium plated (metallic chromium 1.00 mg/m$^2$, chromate chromium 4.0 mg/m$^2$)

The acrylic resin bath was used as the coating bath and the electrodeposition coating was performed for 5 sec. with a distance of 10cm between electrodes by the commercial 100V and 50 c.p.s. sinusoidal a.c. source.

**ACRYLIC RESIN COATING BATH**

<table>
<thead>
<tr>
<th>Major constituent</th>
<th>Acrylic resin 15%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid content of bath</td>
<td>Emulsion type</td>
</tr>
<tr>
<td>pH of bath</td>
<td>7.00</td>
</tr>
<tr>
<td>Bath temperature</td>
<td>25°C</td>
</tr>
</tbody>
</table>

Coulombic efficiency by the d.c. method in this bath : 18.8 mg/coul when an aluminum material having a 0.12$\mu$m thick oxide film was coated by electrodeposition for 5 sec. at a d.c. bath voltage 70V.
15 COATING BATH OF ACRYLIC RESIN

Major constituent: Acrylic resin
Solid content of bath: 15% Emulsion type
pH of bath: 7.90
Bath temperature: 25°C

Coulombic efficiency by the d.c. method in this bath: 18.9 mg/coul when a tin-plated iron plate (ET No. 25) was coated by the electrodeposition for 5 sec. at d.c. 70V.

After the plate was baked for 20 min. at 210°C, the amount of the coating material deposited was measured and the coulombic efficiency was calculated from the quantity of electricity passed. The coulombic efficiency only when the aluminum oxide film electrode was used was equal to that for the d.c. method, as observed in Table 6.

Table 6

<table>
<thead>
<tr>
<th>Electrode of this invention</th>
<th>Electrode other than this invention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum oxide film electrode</td>
<td>Stainless steel (SUS 27) electrode</td>
</tr>
<tr>
<td>Coating material deposited (mg/dm²)</td>
<td>60.9</td>
</tr>
<tr>
<td>Quantity of electricity (coul/m²)</td>
<td>3.22</td>
</tr>
<tr>
<td>Coulombic efficiency (mg/coul)</td>
<td>18.9</td>
</tr>
<tr>
<td>Ratio of coulombic efficiency (%)</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table 8 shows the results. The same coulombic efficiencies as those by the d.c. method are obtained for different baths of coating materials.

Table 8

| Electrodeposition coating by a.c. voltage using a tantalum oxide film electrode |
|-------------------------------|--------|--------|--------|--------|
| Coating material deposited (mg/dm²) | Polyester | Maleic oil | Epoxyester | Alkyd |
| Quantity of electricity (coul/m²) | 4.8 | 5.2 | 5.0 | 6.0 |
| Coulombic efficiency (mg/coul) | 3.3 | 8.4 | 2.8 | 4.8 |

EXAMPLE 6

Using the tantalum oxide film electrode (having a 0.27μ thick oxide film) prepared according to Example 1 as counter-electrode, an aluminum material (having a 0.12μ thick oxide film) of a dimension 10cm × 10cm (one side sealed) placed oppositely at a 10cm distance from the counter-electrode was coated for 5 sec. by the electrodeposition in 4 different baths of coating materials shown in Table 7 by the commercial 100V and 50 c.p.s. sinusoidal a.c. voltage. The plate was then washed with water, baked for 20 min. at 210°C and the amount of the coating material deposited was measured in mg/dm². The quantity of electricity passed was calculated as in Example 1 to obtain the coulombic efficiency.

Table 7

| Baths of coating materials (in outline) |
|-----------------------------|--------|--------|--------|
| Polyester | Maleic oil | Epoxyester | Alkyd |
| Major constituent | Oil-free polyester resin | Maleated resin | Epoxyester resin |
| Solid content of bath (%) | 10% | 15% | 15% |
| State of bath | Water-soluble | Water-soluble | Water-soluble |
| pH of bath | 6.47 | 7.70 | 9.10 |
| Coulombic efficiency by d.c. method (mg/coul) | 14.8 | 6.2 | 17.8 |

Coulombic efficiency by d.c. method:
Coulombic efficiency observed when an aluminum material (having a 0.12μ thick oxide film) was coated for 5 sec. by the electrodeposition using 70V d.c. voltage.

EXAMPLE 7

Using the aluminum oxide film electrode (having a 10.5μ thick oxide film) appearing in Example 2 as counter-electrode, a 10cm × 10cm (one side sealed) aluminum material (commercially available material with an oxide film not thicker than 0.12μ) placed oppositely at a 10cm distance from the counter-electrode was coated by electrodeposition for 5 sec. in a coating bath of alkyd resin (shown in Table 7) using the commercial 100V 50 c.p.s. sinusoidal a.c. voltage. The aluminum plate after the above treatment was washed with water, baked for 20 min. at 210°C and then the amount of the coating material deposited was measured. The quantity of electricity passed was calculated as in Example 1, from which the coulombic efficiency was calculated.

For the sake of comparison with the process of the present invention, a stainless steel plate, a platinum plate and an aluminum plate (non-treated pure aluminum with an oxide film not thicker than 0.2μ) of the same dimension, 10cm × 10cm, were used as counter-electrode. and the electrodeposition coating by a.c. were performed under the identical condition to obtain the coulombic efficiency. Table 9 shows the result. As seen in the table, only the aluminum oxide film electrode of the process of this invention shows the same coulombic efficiency, 12.5 mg/coul, as by the d.c. method.
Table 9

<table>
<thead>
<tr>
<th>Coating material deposited (mg/dm²)</th>
<th>Quantity of electricity (coul/dm²)</th>
<th>Coulombic efficiency (mg/coul)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum oxide film electrode</td>
<td>Stainless steel electrode</td>
<td>Platinum electrode</td>
</tr>
<tr>
<td>52.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
</tbody>
</table>

Table 11

<table>
<thead>
<tr>
<th>Process of the present invention</th>
<th>20 c.p.s.</th>
<th>150 c.p.s.</th>
<th>300 c.p.s.</th>
<th>600 c.p.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of coating material deposited (mg/dm²)</td>
<td>58.3</td>
<td>59.2</td>
<td>60.1</td>
<td>58.3</td>
</tr>
<tr>
<td>Quantity of electricity passed (coul/dm²)</td>
<td>3.19</td>
<td>3.13</td>
<td>3.18</td>
<td>3.13</td>
</tr>
<tr>
<td>Coulombic efficiency</td>
<td>18.3</td>
<td>18.9</td>
<td>18.9</td>
<td>18.6</td>
</tr>
</tbody>
</table>

EXAMPLE 8

Using the tantalum oxide film electrode (having a 2700A thick oxide film) prepared in the manner as described in Example 1 as counter-electrode, a plate of electrolytically tin-plated iron (commercial material having tin plated in 0.24 lb/B.B) of a dimension 10cm x 10cm (one side sealed) placed oppositely against the counter-electrode at a 5cm distance was coated for 5 sec. by the electrodeposition in an acrylic resin bath (the same as in Example 1) at a 100V a.c. voltage by means of a source which generated sinusoidal a.c. of 20, 150, 300 and 600 c.p.s. The plate was then washed with water, baked for 20 min. at 210°C, and the amount of the coating material deposited was measured in mg/dm². On the other hand, the quantity of electricity passed was measured as in Example 1, which gave the coulombic efficiency. The results are shown in Table 11. Apparently, sufficiently high coulombic efficiencies in the practical sense are maintained regardless of varied frequencies.

EXAMPLE 9

0.27μ thick oxide film) prepared according to the process in Example 1 as counter-electrode, an electrolytically tin-plated iron material with an amount of tin-plated 0.24 lb/B.B) of a dimension 10cm x 10cm (one side sealed) placed oppositely at a distance of 10cm from the counter-electrode was coated by the electrodeposition for 5 sec. using the commercial 100, 200 and 300V a.c. voltage (50 c.p.s.) in an alkyd resin coating bath (bath temperature 20°C, see Table 7), washed with water, baked for 20 min. at 210°C, and then the amount of the coating material deposited (mg/dm²) was measured.

The quantity of electricity passed (coul/dm²) was calculated in the manner as explained in Example 1 to obtain the coulombic efficiency.

Table 10 shows the result. Obviously, the rate of deposition of coating material could be improved without lowering the coulombic efficiency by elevating the applied bath voltage.

Table 10

| Rate of deposition of coating material controlled by the applied a.c. bath voltage |
|----------------------------------------|------------------------------------------|
| Bath voltage                           | 100V | 200V | 300V |
| (effective value)                      |      |      |      |
| Amount of coating material deposition  | 50.1 | 110.1| 160.3|
| (mg/dm²)                               |      |      |      |
| Quantity of electricity (coul/dm²)     | 3.94 | 8.46 | 12.6 |
| Coulombic efficiency                   | 12.7 | 13.0 | 12.7 |

EXAMPLE 10

Using the aluminum oxide film electrode (having a 10.5μ thick oxide film) shown in Example 2 as counter-electrode, an aluminum material (commercially available untreated pure aluminum with an oxide film not thicker than 0.12μ) of a dimension 10cm x 10cm (one side sealed) placed oppositely against the counter-electrode at a 10cm distance was coated by the electrodeposition for 5 sec. in an epoxyester resin bath (the same bath as shown in Example 1) by the saw-tooth a.c. voltage shown in FIG. 10. The aluminum was washed with water, baked for 20 min. at 210°C, and the amount of the coating material deposited was measured to be 50.0 mg/dm².

The quantity of electricity passed Q was estimated as the difference of the quantity of electricity (Q_a + Q_b) due to current in phase with the applied bath voltage and the quantity of electricity Q_c due to current in inverse phase with the applied bath voltage. Thus,

Q = Q_a + Q_b - Q_c = 2.82 + 0.05 - 0.06 = 2.81 (coul/dm²)

The amount of the coating material deposited divided by the above quantity of electricity passed gave the coulombic efficiency,

50.0 (mg/dm²) / 2.81 (coul/dm²) = 17.8 (mg/coul)

This value being almost equal to the coulombic efficiency 17.8 by the d.c. method.

EXAMPLE 11

A tantalum oxide film electrode having a 2.1μ thick oxide film to be used in the process of this invention
was prepared as follows: A 0.2 mm thick tantalum plate of a dimension 10 cm x 10 cm was treated by immersing for 10 sec. in a mixed solution of H$_2$SO$_4$, HNO$_3$, and HF in a ratio of 5:2:2, and an oxide film was formed on the surface by the anodic oxidation with a carbon cathode in a 7 percent sulfuric acid solution at 25°C, applying a voltage of about 5 V at the beginning which was increased gradually up to 120 V in 30 min. and maintained at the voltage for 120 min. Subsequently, the plate was washed with water and then dried.

With the above tantalum oxide film electrode as counter-electrode, a 10 cm x 10 cm aluminum material (with one side sealed having an oxide film less thicker than 0.02 μm) was coated by electrodeposition for 5 sec. using the commercial sinusoidal a.c. voltage of 100 V and 50 c.p.s. in a coating bath containing acrylic resin of the d.c. anode deposit type. As a result, the coating material was deposited by 56.4 mg/dm$^2$ and the quantity of electricity involved in the treatment, as measured from the current form on a synchroscope, was calculated according to the following expression, to be 3.00 (coul/dm$^2$) (see (iii) in FIG. 1),

\[ Q = Q_e + Q_a = Q_e \]

where \( Q \) is the effective quantity of electricity, \( Q_e \) and \( Q_a \) are the quantity of electricity of the current in phase with the applied bath voltage, and \( Q_a \) is the quantity of electricity of the current in inverse phase with the applied bath voltage (or the quantity of electricity once charged in a condenser and then discharged).

\[ Q_a = 3.00 \text{ (coul/dm}^2\text{)}, Q_e = 0.07 \text{ (coul/dm}^2\text{)}, Q_r = 0.07 \text{ (coul/dm}^2\text{)}\]

Therefore,

\[ Q = 3.00 + 0.07 - 0.07 = 3.00 \text{ (coul/dm}^2\text{)} \]

The coulombic efficiency 18.8 mg/coul was equal to the obtained with the electrodeposition coating by d.c. voltage.

The coating bath of acrylic resin used was the same as used in Example 1.

For the sake of comparison, a platinum plate, a stainless steel (SUS 27) and pure aluminum having a 0.05 μm thick oxide film) which had not the quality required for the process of this invention were used as counter-electrode, and the electrodeposition coating was performed by a.c. under the identical condition of bath as well as coating. In any case the coulombic efficiency remained below 0.2 percent.

**EXAMPLE 12**

A 2.5 mm thick niobium plate (purity over 96 percent) of a dimension 10 cm x 10 cm was treated by immersing for 10 sec. in a mixed solution of H$_2$SO$_4$, HNO$_3$, and HF in a ratio of 5:2:2, and an oxide film was formed on the surface by the anodic oxidation with a carbon cathode (10 cm x 4 cm) in a solution which was 4 percent with boric acid and 0.2 percent with sulfuric acid at a temperature 2°C, applying a voltage of about 3 V at the beginning which was gradually increased to 50 V in 30 min. and to 100 V in further 50 min. Thus, a tantalum oxide film electrode having a 0.8 μm thick oxide film was prepared.

With the above niobium oxide film electrode as counter-electrode, a 10 cm x 10 cm iron plate (cold rolled steel for plating with one side sealed) was coated by electrodeposition for 10 sec. using the commercial sinusoidal a.c. voltage of 70V and 50 c.p.s. in a coating bath containing acrylic resin of the d.c. anode deposition type. As a result, the coating material was deposited by 80.1 mg/dm$^2$. The quantity of electricity involved in the treatment, as calculated as in Example 1, was 4.26 coul/dm$^2$ (\( Q = Q_e + Q_a - Q_r = 4.26 + 0.09 - 0.09 = 4.26 \text{ (coul/dm}^2\text{)} \)). The coulombic efficiency, obtained by dividing the amount of the coating material deposited by the quantity of electricity, was 18.8 mg/coul, which was equal to that in the d.c. electrodeposition coating. No deposition of the coating material in the oxidized niobium oxide film electrode.

**EXAMPLE 13**

A 0.2 mm thick zirconium plate (99 percent pure) of a dimension 10 cm x 10 cm was treated by immersing for 10 sec. in a mixed solution of H$_2$SO$_4$, HNO$_3$, and HF in a ratio of 5:2:2, and an oxide film was formed on the surface by the anodic oxidation with a carbon cathode (5 cm x 10 cm) in a 7 percent solution of sulfuric acid at 18°C, applying a voltage of about 5 V at the beginning which was gradually increased to 120 V in 60 min. and the voltage was maintained for 20 min. Then the plate was washed with water, and dried to obtain a zirconium oxide film electrode (having a 1.9 μm thick oxide film) to be used as counter-electrode in the process of this invention.

With the above zirconium oxide film electrode as counter-electrode, a 10 cm x 10 cm iron plate (cold rolled steel for plating with one side sealed) was coated by electrodeposition for 5 sec. using the commercial sinusoidal a.c. voltage of 70V and 50 c.p.s. in a coating bath containing acrylic resin of the d.c. anode deposition type (the same as in Example 1). As a result, the coating material was deposited by 42.3 mg/dm$^2$. The quantity of electricity \( Q \) (coul/dm$^2$) consumed in the treatment, as measured from the wave form of current on a synchroscope and calculated with the same expression as in Example 1, was 2.25 coul/dm$^2$. (See (iii) in FIG. 1 \( Q = Q_e + Q_a - Q_r, Q_e = 2.26 \text{ (coul/dm}^2\text{)}, Q_a = 0.05 \text{ (coul/dm}^2\text{)}, Q_r = 0.06 \text{ (coul/dm}^2\text{)} \)).

The coulombic efficiency obtained when the present oxide film electrode was used was 42.3 (mg/dm$^2$) = 2.25 (coul/dm$^2$) = 18.8 (mg/coul), and it became apparent that the electrodeposition coating with the same coulombic efficiency as by the d.c. method could be attained by using the oxide film electrode. Almost no deposition of the coating material was observed on the oxide film electrode.

**EXAMPLE 14**

Two 2 mm thick plates of pure aluminum of a dimension 10 cm x 10 cm were electrolytically treated in a 7 percent solution of sulfuric acid at 20°C with a 10 cm x 5 cm stainless steel cathode, applying at first a bath voltage of 3 V which was raised to 22V in 30 min. and the voltage was maintained for 5 and 25 min. The plates were washed with water, and then dried to obtain oxide film electrodes having 3.0 μm and 6.3 μm thick oxide films.

With the above oxide film electrodes as counter-electrode, 10 cm x 10 cm plates of aluminum (having an oxide film not thicker than 0.02 μm) was coated for 5 sec. by electrodeposition using the commercial sinusoidal a.c. voltage of 70V and 50 c.p.s. in an acrylic resin electrodeposition coating bath (the same as in Example 1).

As a result, the amounts of the coating material were 52 mg/dm$^2$ for the oxide film electrode having a 3.0 μm thick oxide film and 50.8 mg/dm$^2$ for the oxide film electrode having a 6.3 μm thick oxide film. The quantity of electricity, as measured from the wave form of the cur-
rent on a synchroscope, was $Q = 2.76$ (coul/dm$^2$) for the oxide film electrode having a 3.0$\mu$m oxide film ($Q_r = Q_{ox} + Q_{s} = 2.75$ (coul/dm$^2$), $Q_{s} = 0.08$ (coul/dm$^2$), $Q_r = 0.07$ (coul/dm$^2$)) and $Q = 2.70$ (coul/dm$^2$) for the oxide film electrode having a 3.4$\mu$m oxide film ($Q = Q_s + Q_{ox} - Q_r = 2.70$ (coul/dm$^2$), $Q_r = 0.07$ (coul/dm$^2$), $Q_s = 0.07$ (coul/dm$^2$)). The coulombic efficiencies obtained by dividing the amount of the deposited coating film by the quantity of electricity were for both cases 18.8 mg/coul, which was equal to that by the d.c. method. No deposition of the coating material on the oxide film electrodes was observed.

The present electrodes were successively used for 100 treatments of electrodeposition coating, each for 5 sec. For both electrodes, neither lowering of the coulombic efficiency nor deterioration phenomena were observed such as growth of the oxide films, deposition of the coating material on the surfaces of the oxide film electrodes and the lowered effect of compensation due to electrostatic capacity.

**EXAMPLE 15**

A 3 mm thick and 10 cm $\times$ 10 cm plate of a Zr-Nb alloy containing 89.2 percent of Zr, 10 percent of Nb and 0.8 percent of other constituents was treated by immersing for 10 sec. in a mixed solution of $\text{H}_2\text{SO}_4$, $\text{HNO}_3$ and HF in a ratio of $5:2:2$, and then an oxide film was formed on the surface by anodically electrolyzing in a 7 percent solution of sulfuric acid with a carbon cathode, applying at first a bath voltage of 5V which was raised to 100V in 60 min. After maintained at the voltage for 5 min., the plate was washed with water and then dried to obtain a Zr-Nb oxide film electrode having a 2.1$\mu$m thick oxide film to be used as counter-electrode in the process of this invention.

With the above Zr-Nb oxide film electrode as counterelectrode, a 10 cm $\times$ 10 cm plate of iron (cold rolled steel for plating, and with one side sealed) was coated for 10 sec. by electrodeposition in a coating bath of acrylic resin of the d.c. anodic deposition type (the same as in Example 1), applying 70V, 50 c.p.s. commercial sinusoidal a.c. voltage. As a result, 80.3 mg/dm$^2$ of the coating material was deposited. The quantity of electricity $Q$ consumed in the treatment, as measured from the wave form of the current on a synchroscope and calculated according to the same expression as in Example 1, was 4.26 coul/dm$^2$ ($Q = Q_s + Q_{ox} - Q_r = 4.27$ (coul/dm$^2$), $Q_r = 0.10$ (coul/dm$^2$), and $Q = 0.11$ (coul/dm$^2$)). The coulombic efficiency when the oxide film electrode was used was therefore 80.3 (mg/dm$^2$) + 4.26 (coul/dm$^2$) = 84.8 (mg/coul). Thus, the present oxide film electrode proved to give the equal coulombic efficiency as given by the d.c. method in the electrodeposition coating. Almost no deposition of the coating material was observed on the oxide film electrode.

**EXAMPLE 16**

As shown in FIG. 10, a metal plate (one side is shielded) 3 of 10 cm $\times$ 12 cm was connected with a third electrode 4 in 5 mm diameter round form of tantalum having an oxide film of 0.27$\mu$m thickness through a resistor 5 of 100$\Omega$ and the third electrode 4 was arranged in parallel with the metal 3 to be coated. Only the surface area of 10 cm $\times$ 10 cm of the metal to be coated and only the length of 5 cm of the third electrode were immersed in the bath solution and the electrodeposition paint coating was effected by giving a sine waved a.c. voltage of 100V, 50 c.p.s. for 5 minutes between a counter-electrode 2 of tantalum (surface area: 10 cm $\times$ 10 cm, oxide film thickness: 0.27$\mu$m) and the metal to be coated 3. The distance between the counter-electrode 4 and the metal 3 was 10 cm. The following electrodeposition paint coating solution was used.

<table>
<thead>
<tr>
<th>Major constituent</th>
<th>Acrylic resin</th>
<th>15% Emulsion type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid content</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bath state</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>7.96</td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td>35°C</td>
</tr>
</tbody>
</table>

The condition of baking the coating was 200°C $\times$ 20 minutes.

As the result, the electrodeposited coatings as shown in Table 12 were obtained.

**Table 12**

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tin-plated iron plate</td>
<td>Steel plate substrate</td>
<td>Binderized zinc</td>
</tr>
<tr>
<td></td>
<td>(ET No. 25)</td>
<td>for plating</td>
<td>plated plate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(binderized film</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>of 1.2g/m$^2$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(deposition of 18g/m$^2$)</td>
</tr>
<tr>
<td>Amount of coating mate</td>
<td>61.0</td>
<td>60.0</td>
<td>58.4</td>
</tr>
<tr>
<td>material deposited</td>
<td>(mg/dm$^2$)</td>
<td>(mg/dm$^2$)</td>
<td>(mg/dm$^2$)</td>
</tr>
<tr>
<td>Quantity of electricity</td>
<td>3.49</td>
<td>3.46</td>
<td>3.37</td>
</tr>
<tr>
<td>(coul/dm$^2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coulombic efficiency</td>
<td>17.5</td>
<td>17.4</td>
<td>17.3</td>
</tr>
<tr>
<td>(mg/coul)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of pin holes</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(per dm$^2$) in coating</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The quantity of currency was measured in a similar way as in Example 3.*
EXAMPLE 17

The metal plate (one side shielded) of 10 cm x 12 cm was connected with four third electrodes of 5 mm diameter round bar of tantalum having 0.27 μ thick oxide film through a resistor of 100Ω and these third electrodes were arranged at a position of 1/5 L in the direction from the metal to the counterelectrode as shown in FIG. 14.

The surface area of 10 cm x 10 cm of the metal to be coated and the length of 10 cm of the third electrodes were immersed in the bath solution. The distance between the metal and the counter-electrode of tantalum (surface area 10 cm x 10 cm) was 10 cm. A sine wave a.c. voltage of 100V, 50 c.p.s. was given for 5 sec. between the metal and the counter-electrode to effect electrodeposition paint coating. The following bath solution was used.

The condition for baking the coating was 200°C for 20 minutes.

As the result, the electrodeposited coatings as shown in Table 13 were obtained for various metals to be coated.

<table>
<thead>
<tr>
<th>Tin-plated iron plate (ET No. 25)</th>
<th>Steel plate (substrate for plating)</th>
<th>Bonderized zinc plated iron plate (substrate for plating)</th>
<th>Tin-free sheet metallic Cr: 100 mg/m², chromate Cr: 40 mg/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major constituent:</td>
<td>Acrylic resin</td>
<td>Solid content: 15%</td>
<td>Emulsion type</td>
</tr>
<tr>
<td>Number of pin holes per dm² in coating film:</td>
<td>23</td>
<td>29</td>
<td>22</td>
</tr>
<tr>
<td>Amount of coating material deposited (mg/dm²):</td>
<td>65.0</td>
<td>64.5</td>
<td>62.5</td>
</tr>
<tr>
<td>Quantity of electricity (coul/dm²):</td>
<td>3.49</td>
<td>3.47</td>
<td>3.34</td>
</tr>
<tr>
<td>Coulombic efficiency (mg/coul):</td>
<td>13.2</td>
<td>13.1</td>
<td>13.3</td>
</tr>
<tr>
<td>Number of pin holes in coating film:</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The number of the pin holes in the coating film includes that of foams (after the baking).

What is claimed is:

**1. A process for applying electrodeposition paint coating by alternating current comprising applying paint coating to a metallic material with an alternating current voltage in a resin bath using an electrode having an oxide film and forming said film thicker than 0.2 μ.**
2. A process according to claim 1 in which the electrode is composed of a metal selected from the group consisting of Ta, Nb and their alloy.

3. A process according to claim 1 in which the electrode is composed of a metal selected from the group consisting of Zr and Hf and their alloys, and the oxide film is thicker 0.35μ-0.35μ.

4. A process according to claim 1 in which the electrode is composed of a metal selected from the group consisting of Al and Ti and their alloys, and the oxide film is thicker than 1μ.

5. A process according to claim 1 in which a third electrode is used.

6. A process according to claim 5 in which the third electrode is composed of a metal selected from the group consisting of Ta, Al, Ti, Zr, Nb, Hf and their alloys and the oxide film is thicker than 0.2μ.

7. Apparatus for electrodeposition painting on a metallic material comprising an A.C. voltage source, said metallic material serving as an electrode in a resin bath, and a counter-electrode comprising a film-forming metal having an oxide film of a thickness of at least 0.2μ.

8. An apparatus of claim 7, wherein said film-forming metal is selected from the group consisting of Ta, Nb and their alloys.

9. An apparatus of claim 7, wherein said film-forming metal is selected from the group consisting of Zr and Hf and their alloys and said film has a thickness of at least 0.35μ.

10. An apparatus as set forth in claim 7, wherein said film-forming metal is selected from the group consisting of Al and Ti and their alloys, and said film has a thickness of at least 1μ.

11. An apparatus as set forth in claim 7, wherein said film-forming metal is selected from the group consisting of the alloys of Ta, Nb, Zr, Hf, Al and Ti.

12. An apparatus as set forth in claim 7, further comprising a third electrode, electrically connected to said metallic material.

13. An apparatus as set forth in claim 12, comprising a variable resistor connected between said metallic material and said third electrode.

14. An apparatus as set forth in claim 12, comprising rectifier means connected between said third electrode and said metallic means.

15. An apparatus as set forth in claim 12, wherein said third electrode comprises a film-forming metal and an oxide film thereon.

16. An apparatus as set forth in claim 15, wherein said film-forming metal is selected from the group consisting of Ta, Al, Ti, Zr, Nb, Hf and their alloys and the thickness of said oxide films at least 0.2μ.

17. Apparatus for electrodeposition painting on a metallic material adapted to form an electrode in a resin bath, comprising a counter electrode adapted to be placed in the resin bath, means to apply an A.C. voltage to the electrode and counter electrode, coating means formed at said counter electrode for permitting more current to flow in one direction in said resin bath between said electrodes than in the opposite direction and forming capacitor means said counter electrode.

18. Apparatus as set forth in claim 17, wherein said capacitor means comprises electrostatic capacitance having a large value when said resistor means permits more current to flow and a low value when said resistor means permits less current to flow in said opposite direction.

19. Apparatus as set forth in claim 17, comprising a third electrode adapted to be electrically connected to said metallic material for carrying said current flowing in said opposite direction and causing said current flowing in said opposite direction to bypass said metallic material.

20. Apparatus as set forth in claim 19, comprising a variable resistor adapted to be connected between said metallic material and said third electrode.

21. Apparatus as set forth in claim 19, comprising rectifier means adapted to be connected between said third electrode and said metallic materials.

22. Apparatus as set forth in claim 19, wherein said third electrode comprises a film forming metal and an oxide film thereon.

23. Apparatus as set forth in claim 22, wherein said film forming metal is selected from the group consisting of Ta, Al, Ti, Zr, Nb, Hf and their alloys and the thickness of said oxide film is at least 0.2μ.