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PROCESS FOR ELECTROLYTIC TREATMENT
OF A METAL BY LIQUID POWER FEEDING

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This invention relates to a process for the electrolytic treatment of a metal with an electrolyte
5 containing an organic acid or a salt thereof by the liquid power feeding method.

It is widely known to effect surface treatments such as formation of oxide coatings and electrolytic etching on metals such as aluminum by subjecting such
10 metals to electrolysis. These surface treatments are carried out by methods which can be broadly classified as batchwise or continuous. Treatments of the latter type are capable of mass production and, therefore, are adopted for electrolytic treatment of various
15 metallic articles such as building materials and electrolytic capacitors.

In the continuous electrolytic treatment of a thin metallic sheet, for example, it has been customary to feed power directly to the metallic sheet
20 being treated by means of a metallic contact roll. Recently a method for the electrolytic treatment of metallic objects by liquid power feeding instead of the power feeding by direct contact has been proposed.

The term "liquid power feeding" as used herein means a method for indirectly feeding power through the medium of the electrolyte. Since this method does not require direct electric contact at any point on the object under treatment, it is sometimes alternatively called a "non-contact electrifying method". This method is described in detail, for example, in "Working Surface Technique", Vol. 29, No. 10, pp. 17-21 (1982). Electrolytic treatment by the liquid power feeding method is particularly suitable for continuous high-speed treatment of a thin sheet or foil of metal. The feasibility of this particular method of electrolysis in the commercial production of electrolytic capacitors made of Al or Ta, for example, is presently underway. In the process of electrolytic treatment using this liquid power feeding method, the treatment for the desired formation is obtained by feeding power to an anode disposed in an anodic power feeding compartment and to a cathode disposed in a forming compartment and continuously passing a metallic foil under treatment in an electrolyte which fills both compartments. The metallic foil is polarized between the two compartments and is subjected to electrolytic oxidation while functioning as a cathode within the anodic power feeding compartment and as an anode within the forming compartment. Electrolytic treatment by the liquid power feeding method, therefore,

necessitates additional use of an insoluble anode capable of withstanding use in the electrolyte.

As the electrolyte, a solution of an ammonium salt of an inorganic acid such as boric acid or phosphoric acid has been used. Recently, a solution containing an ammonium salt of an organic acid has been demonstrated to yield more desirable results (as described in the "Handbook on Metal Surface Techniques", page 677 (1976) published by Japan Industry News and in Japanese Patent Application Laid Open SHO 56(1981)-140618). So far, no anode has been reported which provides stable service over a long period in an electrolyte containing an organic acid or a salt thereof. Thus, it has been difficult to carry out an electrolytic treatment of a metallic object using the liquid power feeding method with this electrolyte.

An object of this invention is to provide an excellent process for electrolytic treatment of a metallic object by the liquid power feeding method using an electrolyte containing an organic acid or salt thereof.

This invention provides a process for the electrolytic treatment of metal with an electrolyte containing an organic acid or a salt thereof, which comprises feeding power by the liquid power feeding

method of feeding power through the medium of the electrolyte cell and using as an anode for the liquid power feeding an insoluble anode comprising a substrate of a corrosion-resistant metal and an electrode coating containing
5 at least some iridium oxide.

This invention, by the adoption of the above-described insoluble anode as the anode for liquid power feeding, enables the electrolytic treatment of a metallic object to be effectively carried out by the
10 liquid power feeding method using as the electrolyte therefor a solution containing an organic acid or a salt thereof, for example, an ammonium salt. It, therefore, provides an extremely beneficial economic effect of enabling electrolytic treatments of metallic
15 objects such as the formation of aluminium electrolytic capacitors, to be performed efficiently and easily.

The process of this invention permits effective use of known electrolytes containing various organic acids or salts thereof. Examples of organic acids
20 usable advantageously herein include saturated monocarboxylic acids such as formic acid, acetic acid, propionic acid, and N-butyric acid; saturated dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, and adipic acid; and alicyclic dicarboxylic acids such as those disclosed in Japanese
25 Patent Application Laid-Open SHO 56(1981)-140618. The

(12)

above-described electrolytes are generally prepared by adding ammonia to aqueous solutions of organic acids such as those mentioned above.

Research to find an anode which is suitable for liquid power feeding, as described above, in the electrolytic treatment of a metallic object in this electrolyte has led to the knowledge that an anode with a coating based on the presence of at least some iridium oxide meets the description satisfactorily. The present invention has resulted from this knowledge.

Platinum and lead, which have been widely used as materials for anodes, have high oxygen evolution potentials such that, in the electrolytes containing organic acids possessing carboxylate groups, they cause these types of organic acids to induce electrochemical reactions such as the Kolbe reaction. An anode possessing a coating based on the presence of ruthenium oxide and used in the electrolysis of sodium chloride, for example, possesses a relatively low hydrogen evolution potential but offers insufficient resistance to corrosion in the electrolytes used in the present invention. By contrast, an anode possessing an electrode coating containing at least some iridium oxide has been demonstrated to possess an oxygen evolution potential low enough to preclude the organic acid in the electrolyte

from inducing an undesired electrochemical reaction of itself, exhibits an outstanding resistance to corrosion under working conditions, and provides ample stability to withstand long-term use in commercial operation.

5 The amount of iridium oxide in the coating is not particularly limited. However, 40 mol% or more of iridium oxide in the oxides in the oxide coatings is preferred.

10 The insoluble anode possessing the coating containing at least some iridium oxide can be constructed by coating a substrate of a corrosion-resistant metal (usually a "valve metal" such as Ti, Ta or Nb) with iridium oxide, alone or in the form of a mixture or solid solution together with a platinum group metal (Pt, Ir, Os, Pd, Rh or Ru) such as rhodium, an oxide of another platinum group metal, 15 or an oxide of a non-platinum group metal. It is preferred to also include in the coating an oxide of Ti, Ta, Nb, Co or Mn. The mixing proportion of such metal oxide is not specifically limited but is not more than 60 mol% of the total coated metal oxides.

20 The coating on the anode can be produced by the method of thermal decomposition of a salt of the metal of which the oxide is to be formed, as disclosed in Japanese Patent Publication SHO 46 (1971)-21884 (corresponding to U.S.P. 3,632,498) and Japanese Patent Publication SHO 25 48(1973)-3954 (corresponding to U.S.P. 3,711,385), or by any other known method.

Each metal oxide in the coating can be a non-stoichiometric oxide, an oxide possessing lattice defects or

(13)

- 7 -

a stoichiometric metal oxide. If desired, the resistance of the anode to corrosion can be enhanced by interposing, between the metal substrate and the coating oxide, an intermediate layer of an oxide of Pt, SnO_2 , or an oxide of a valve metal.

The electrolytic treatment of a metallic object in the present invention is carried out by using the above-described insoluble anode as the anode for liquid power feeding.

In the electrolytic oxidation of aluminium foil, iron or an alloy thereof is generally used as a cathode, a suspension type plate-shaped insoluble anode is used as an anode for liquid power feeding, an organic acid salt such as ammonium adipate at a concentration of about 5 to about 200 g/liter is used as an electrolyte, and the conditions of a temperature of 10° to 60°C and a current density of 1 to 20 A/dm^2 are adopted.

Of course, these electrolytic conditions may be suitably varied, depending on the kind of metal subjected to treatment and the composition of the electrolyte used.

The following non-limiting examples and comparative examples are given to illustrate further the present invention.

EXAMPLES

Ten insoluble electrodes were each prepared by coating a titanium plate, measuring 100 mm x 100 mm x 1.5 mm, with various metal oxide compositions having iridium oxide as a main component.

The coating of the electrode was effected by the thermal decomposition method, i.e., by applying a hydrochloric acid solution of the chloride of the metal used for coating on the titanium substrate and heating the substrate with the deposited coating thereon in air to a temperature exceeding 400°C.

Each electrode produced was tested for performance as the anode for liquid power feeding, under the above-described conditions for electrolytic oxidation of aluminium foil. For comparison, various plate-shaped electrodes of Ti plated with Pt, Pb, Ni and Ti plated with Pt-Ir, and Ti coated with $\text{RuO}_2\text{-TiO}_2$ were prepared and put to the same test.

The electrodes prepared according to this invention and those prepared for comparison were tested in an electrolytic treatment at varying current densities, using as electrolyte an ammonium adipate aqueous solution of a concentration of 50 g/liter, as normally used for the electrolytic oxidation of aluminium foil, as the electrolyte and a plate of 18-8 stainless steel (SUS 304) as the cathode at 40°C. Aluminium foil was fed continuously through the electrolyte and subjected to anodic oxidation.

The results obtained are shown collectively in Table 1 below.

Table 1

		Coating on Anode (mol ratio composition)	Current Density (A/dm ²)	Service Life of Anode (days)
5	Example			
	1	IrO ₂ /Ti	10	60
	2	IrO ₂ /Pt/Ti	5	135
10	3	IrO ₂ -Ta ₂ O ₅ /Ti (70:30)	10	80
	4	Same as above	5	213
	5	Same as above	3	360
	6	IrO ₂ -TiO ₂ /Ti (60:40)	10	60
15	7	IrO ₂ -MnO ₂ /Ti (75:25)	10	95
	8	Same as above	5	180
	9	IrO ₂ -Nb ₂ O ₅ /Ti (65:35)	5	198
20	10	IrO ₂ -CoO/Ti (95:5)	5	120

(18)

Table 1, continued

	Coating on Anode (mol ratio composition)	Current Density (A/dm ²)	Service Life of Anode (days)
5	Comparative Example		
	1 Pt/Ti	10	7
	2 Pb	10	3
10	3 Ni	10	7
	4 Pt/Ir/Ti (70:30)	10	1
	5 RuO ₂ -TiO ₂ /Ti (55:45)	10	5

15 When the anodes of Comparative Examples 1-5 were used, they invariably had very short service life spans and the electrolyte became colored and emitted an offensive odor due to the electrochemical reaction of adipic acid such that continued use of the anodes

20 became impossible. In contrast, when the anodes of Examples 1-10 according to the present invention were used, they exhibited sufficiently long service life spans and enabled the electrolysis to be continued without any difficulty.

25 From the foregoing results, it is evident that the electrolytic treatment of a metallic object in an electrolyte containing an organic acid or a salt

thereof can be carried out in a stable manner for a long time when an insoluble anode possessing an electrode coating containing at least some Ir oxide was used as the anode for liquid power feeding.



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- 12 -

CLAIMS

1. A process for the electrolytic treatment of a metal with an electrolyte containing an organic acid or a salt thereof, comprising feeding power by the liquid power feeding method of feeding power through the medium of the electrolyte and using for said liquid power feeding an insoluble anode comprising a substrate of a corrosion-resistant metal and an outer electrode coating containing some iridium oxide.
2. A process according to Claim 1, wherein said insoluble anode has an electrode coating composed of a mixture of iridium oxide and the oxide of a metal selected from titanium, tantalum, niobium, cobalt, manganese and mixtures thereof.
3. A process as claimed in Claim 1 or 2, wherein the iridium oxide constitutes 40 mol% or more of the oxide in the electrode coating.
4. A process as claimed in Claim 1 or 2, wherein the coating was formed by thermal decomposition of a salt of the metal of the oxide.
5. A process as claimed in any preceding claim, wherein an intermediate oxide layer is formed between the electrode coating and the metal substrate..
6. A process as claimed in any preceding claim, wherein the metal being treated is aluminium.
7. A process according to any preceding claim, wherein said electrolyte contains the ammonium salt of an organic carboxylic acid.
8. A process for the electrolytic treatment of a metal, substantially as hereinbefore described in any of the Examples 1 to 10.
9. A metal article which has been electrolytically treated by a process as claimed in any preceding claim.