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SURFACE PREPARATION OF PLATINUM GROUP METALS FOR ELECTRODEPOSITION

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This invention relates in general to the preparation of the surface of a metal of the platinum group to make it suitable as a base for electroplating and, in particular, to the preparation of a platinum group metal surfaced substrate as a base for the subsequent anodic deposition of an inert coating such as alpha or beta lead dioxide. For the sake of brevity platinum will be used in a generic sense in the following and in the claims and it is to be understood to include all members of the platinum group, namely, Ru, Rh, Pd, Os, Ir, Pt.

It has been found that an article made of platinum or having a platinum surface will serve as a base for a tightly adhering, blister-free electro-deposited coating if it is subject to a periodic reverse current treatment in a weak oxidizing acid electrolyte. During the periodic reverse treatment the several cycles are of equal length and the last half cycle must be anodic if a subsequent anodic deposition is to be achieved.

As illustrative of the utility of the invention, an electrode made of titanium base or substrate, flashcoated with a platinum group metal and having an outer lead dioxide surface is useful in electrolytic per-oxidation reactions such as the production of sodium perchlorate. As made heretofore, such electrodes suffered from peeling and blistering of the lead dioxide coating. I have found that the poor adhesion between the lead dioxide and platinum can be overcome by using the periodic reverse current procedure of this invention.

The platinum surface can be provided by the solid metal as such or the platinum can be only a surface coating on a substrate applied by flashcoating, cladding or in any other suitable manner. If a substrate other than platinum is employed, the nature of the substrate is controlled by the use to which the final article is to be put. For example, when the article is to be employed as an anode in a chlorate or perchlorate cell one desirably uses titanium or tantalum for such common metals and alloys as copper, nickel, brass, and steel will corrode if exposed in the cell. Irrespective of the substrate, the periodic reverse current activation procedure is the same. The plating of the various platinum group metals on a metal or alloy substrate is well known in the art and forms no part of this invention.

The periodic reverse current cycling activates the platinum surface in the following manner. During the cathodic half cycles, hydrogen is evolved on the platinum surface. This exerts a cleaning action by gas scrubbing and reducing any obnoxious oxide contamination on the surface or which is embedded in the base. Also during the anodic half cycles further cleaning by oxygen gas scrubbing occurs. In addition, any organic surface contamination is destroyed by the oxidation. The combination of the adsorbed hydrogen with the nascent oxygen diminishes the deleterious effect of hydrogen absorption. Finally, a uniform oxygen-containing layer forms over the anode which is only a few molecular layers thick. This cycling must be repeated several times, depending on the state of the surface. Thus articles that were platinum surfaced and then were allowed to dry out for some time before the deposition of lead dioxide coating require approximately 5 minutes' cycling, at approximately 15 seconds per half cycle, just prior to their transfer to the lead dioxide plating cell. The last half cycle being anodic, the platinum surface experiences no further change in adsorbed gas content in the plating cell where it continues as an anode.

Example 1

A titanium sheet of 4" x 8" x 1/16" dimensions was cleaned with caustic, rinsed and washed with hot hydrofluoric acid. The sheet was then anodized after removal of a major portion of the oxide film by immersion in 10% HF at room temperature for several seconds. The anodizing was effected by placing the plate in a 2% nitric acid solution at room temperature and raising the voltage from zero to about four volts whereupon a pale yellow anodic film formed on the plate. The sheet was then platinized using a known composition and technique as described in "Metal Finishing Guidebook," pages 359–362 (1957, Finishing Publications, Inc.).

The article was immediately rinsed and immersed in a 2 volume percent nitric acid solution at room temperature (approximately 18° C.). The opposite electrode was a platinized titanium sheet of like dimensions. During four cycles, at 15 seconds per half cycle, the article was alternately cathodic and anodic at 4 volts and a current density of approximately 80 amps/ft.^{2}. The article was anodic during the last half cycle, after which it was rinsed and was immediately transferred into a lead nitrate bath having the following composition:

	G./l.
Lead nitrate	200
Copper nitrate	10
Nitric acid to give a pH of 2.0.	

The temperature was maintained between 80° and 95° C. throughout the electrolysis. The anodic current density was 10 amps/ft.^{2}. The electrodeposition proceeded at the approximate rate of 0.0015 inch per hour. The adherence of the electrodeposited lead dioxide was excellent, as tested by repeated bending and hammering of the sheets.

Example 2

A titanium sheet, 4" x 8" x 1/16", was flashcoated with 0.005 mil thickness of rhodium and was activated as in Example 1. After rinsing the sheet was transferred to a lead plumbate plating solution of the following composition:

	G./l.
Sodium hydroxide	50
Lead oxide	50
Zinc acetate	2

The temperature was maintained at 60° C. The anodic current density was 10 amps/ft.^{2} and the solution was vigorously agitated throughout the electrolysis.

A tightly adhering deposit of lead dioxide was obtained, fragments of which clung tenaciously to the substrate even after shattering the deposit by heavy blows with a hammer.

Example 3

A titanium sheet of 4" x 8" x 1/16" dimensions was flashcoated with 0.01 mil thickness of palladium using a bath of the following composition and under the conditions indicated:

Sodium palladium chloride	g./l.	10
Sodium nitrate	g./l.	10
Sodium chloride	g./l.	50
pH		4–5
Temperature	°C.	50
Cathodic current density	amps/ft.^{2}	10

The resulting article was then activated and thereafter coated with lead dioxide as in Example 1. The adherence of the electrodeposited lead dioxide was excellent and resisted bending and hammering.

Examples 4–6

Three metal substrates were each coated with plates of ruthenium, osmium and iridium using baths and procedures which are well known. Following the plating with the respective members of the platinum group, each of the metal substrates was anodized and a plating of lead dioxide applied as in Example 1. The electrodeposited lead dioxide coating was quite smooth, uniform and tenacious in each instance.

While the invention has been disclosed as employed for producing a lead dioxide coated electrode suitable for use in an electrolytic per-oxidation cell for production of sodium chlorate the invention is not limited to the use of lead dioxide. Thus, coatings of other useful and generally inert oxides can be applied using known procedures, these oxides including manganese dioxide and magnetite. The invention is not limited to oxide coatings and one can apply any other material to the platinum surface. The anodizing of the platinum surface prepares it for the subsequent inferred deposition of any other coating which may desirably be applied to the platinum surface.

I claim:

1. In the method for electrolytically depositing a coating of lead dioxide on a platinum surface the improvement which comprises, making the platinum surface an electrode in an electrolyte comprising a solution of an oxidizing acid, exposing said platinum surface while in said electrolyte to periodically reversed current at a current density of from 10 to 80 a.s.f., the last half-cycle of said periodically reversed current being anodic to anodize said platinum surface, and then electrolytically depositing an anodic coating of lead dioxide upon said anodized surface.

2. In the method for producing an electro-deposited coating on a platinum surface the improvement which comprises, making the platinum surface an electrode in an electrolyte comprising a solution of an oxidizing acid, exposing said platinum surface while in said electrolyte to periodically reversed current at a current density of from 10 to 80 a.s.f., the last half-cycle of said periodically reversed current being anodic to anodize said platinum surface, thereafter making the anodized surface an electrode in a second plating bath from which a coating of another material can be electrodeposited on said surface, and passing direct current through said second bath to anodically deposit a tightly adhering coating of said material on said surface.

3. In the method for electrolytically depositing a coating of lead dioxide on a platinum surface the improvement which comprises, making the platinum surface an electrode in an electrolyte comprising a solution of an oxidizing acid, exposing said platinum surface while in said electrolyte to periodically reversed current at a current density of from 10 to 80 a.s.f. for a period per cycle of approximately 30 seconds, the last half-cycle of said periodically reversed current being anodic to anodize said platinum surface, thereafter making the anodized surface an electrode in a second plating bath from which a coating of lead dioxide can be plated on said surface, and passing direct current through said second bath to anodically deposit a tightly adhering coating of said lead dioxide on said surface.

References Cited by the Examiner

UNITED STATES PATENTS

1,897,902	2/33	Harsanyi	204—141
2,546,150	3/51	Brenner et al.	204—29
2,872,405	2/59	Miller et al.	
2,888,387	5/59	Wasserman	204—33
2,926,125	2/60	Currah et al.	204—29
2,945,791	7/60	Gibson	204—290

FOREIGN PATENTS

836,078	1/58	Great Britain.
586,846	11/59	Canada.

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