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METHOD FOR ELECTROPLATING
ON TITANIUM

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This invention relates to the anodizing of titanium and titanium alloys to provide a surface suitable for subsequent electroplating or finishing.

It is known that titanium on exposure to air or oxidizing conditions forms a surface skin consisting chiefly of oxides which interfere with the adhesion of electrodeposited coatings. The known techniques for preparation of a titanium surface for electroplating include various procedures for removal of this oxide skin to expose a clean titanium metal surface or for replacing the oxide film with a hydride film. These procedures may provide a suitable surface for cathodic deposition of metals and alloys. However, they fail as a preparatory step for anodic deposition because of the uncontrolled reformation of the oxide skin under the anodic conditions.

The present invention eliminates these restrictions. It also provides a process which has particular application in the plating of lead dioxide over a precious metal flash coated on a substrate of titanium or a titanium alloy. This process requires first a cathodic and then an anodic deposition on the metal base.

A further object is to provide a titanium surface finish which is of uniform texture and thickness and which provides excellent anchorage for dyes, paints and chemical conversion finishes.

A further object of this method is to provide a suitable titanium surface for electroplating, without strong etching of the titanium, thereby permitting close control of dimensional tolerances.

A further object is to eliminate the need for lengthy heat treatment of plated titanium articles to relieve hydrogen embrittlement.

A specific object of this invention is to provide a technique for electrodepositing anodically a metal oxide coating, such as lead dioxide, over a titanium, titanium alloy, or flash-coated titanium substrate.

In accordance with the present invention, the titanium substrate is anodized under controlled conditions to a yellow color. The resulting oxide film is sufficiently porous to permit direct substrate metal to noble metal bonding and direct noble metal to lead dioxide bonding. In addition, adhesion of the lead dioxide to the substrate by mechanical anchorage within the spongy anodized structure is improved while further growth of the oxide skin is obviated.

While a great number of alkaline, neutral and acidic media are suitable for the production of an anodized base for later cathodic depositions, the best results are obtained when the pH and anion composition of the anodizing and plating solutions are similar.

EXAMPLE I

To illustrate the practice of the invention, sheets of titanium and titanium alloy, size 8" x 4" x 1/16", were treated. The titanium sheet was relatively pure, 99+%, while the titanium alloy contained 2% molybdenum, 2% chromium and 2% iron. The substrate was first degreased by soaking in a 10% NaOH solution at 75°.

After rinsing, the substrate was freed of a major portion of its oxide film. This can be achieved in various ways, usually by treatment with a suitable non-oxidizing acid at an elevated temperature since such oxide films are

ordinarily resolvable in hot acid. In the case of the plating operation under discussion, the substrate was immersed in approximately 10% HF at room temperature for several seconds, until the surface was uniformly gray and clean.

After rinsing the substrate was placed in an electrolytic cell in which the electrolyte was a 2% nitric acid solution at ambient temperature. The voltage was slowly raised from zero to about 4 volts when formation of a pale yellow anode film became visible. This voltage was maintained for about ten minutes. The pale yellow color is a good measure of the desired thickness of the surface layer of oxide on the substrate, being an interference color of the light reflected from the substrate through the oxide layer applied, which defines a definite thickness. The color of the applied anodized surface is a function of the value of the voltage applied. For example, using the same bath at the same temperature and applying the voltage indicated for a short period gives a film of the indicated color using the same base. The color appears in a matter of seconds; in the case of the light yellow color, the film color is apparent in about 10 seconds.

Color	Approximate voltage
Slightly discolored base	1
Light yellow	4
Brown	6
Purple	8
Catastrophic corrosion	12

EXAMPLE II

The procedure of Example I was followed except that similar sheets were anodized to a yellow color in a 2% NaOH solution.

EXAMPLE III

Following the anodization of Examples I and II, each substrate was rinsed and then flashplated with platinum in the usual manner in a bath having the following composition:

Water	liter	1
Diammonium phosphate	grams	20
Disodium phosphate	do	100
Chloroplatinic acid	do	4

The substrates, now flashplated with a layer of platinum, were then coated with lead dioxide in baths of the following composition:

Bath 1

	Grams/liter
Pb(NO ₃) ₂	200
NaF	0.5
Cu(NO ₃) ₂ ·3H ₂ O	7.5
Ni(NO ₃) ₂ ·6H ₂ O	12.5
Igepal	0.75
HNO ₃	less than 1.0

Bath 2

	Grams/liter
PbO	50
NaOH	50
Zinc acetate	10
0.1/1. of a non-ionic wetting agent, Tergitol.	

The substrates could have been plated cathodically in another electroplating bath or, immediately following the anodizing step, in Baths 1 or 2 without first applying an intermediate cathodic flashcoating. The thickness of the flash intermediate coatings has no bearing on the adhesion of the final lead dioxide coating, provided the metal or alloy used for the intermediate coating is not attacked in the lead dioxide plating solution. In the above example precious metals were used.

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The trademarks Igepal and Tergitol refer respectively to an alkylphenoethylene oxide condensation product and to a higher sodium alkyl sulphate, both useful as wetting and emulsifying agents.

EXAMPLE IV

A titanium sheet was prepared as in Example I. It was then anodized in a Watts nickel bath for thirty seconds, at a constant voltage of 4. The current density was 20-100 amps. sq. ft. and the bath temperature was between 115°-160° F. The bath had the following composition:

	Ounces/gallon
Nickel sulfate	32
Nickel chloride	6
Boric acid	4

Subsequently, without removing the article from the bath, the polarity was reversed and nickel was deposited on the article for one minute. Such nickel flashcoats function well as a base for a great variety of electrodeposits, including heavy nickel coatings. The composition of the Watts nickel bath appears at page 341 in "Metal Finishing Guidebook" (1957), published by Finishing Publications, Inc., New Jersey.

In the place of titanium we can employ alloys in which titanium is a substantial alloying agent.

I claim:

1. In a process for preparing an electrode having a titanium substrate, the steps comprising:

(a) anodizing the titanium substrate in a first bath to a yellow color,

(b) cathodically applying a flash coating of platinum upon the anodized titanium substrate in a bath having substantially the same anion concentration and pH as the first bath, and thereafter

(c) electroplating a coating of lead dioxide onto the flash coated platinum.

2. In a process for preparing an electrode having a titanium substrate, the steps comprising:

(a) placing the titanium substrate, as an anode, in an electrolyte containing a cathode, applying current to the substrate-anode and increasing the voltage to deposit a yellow layer of titanium oxide upon the surface of said titanium substrate,

(b) cathodically applying a flash coating of platinum upon the layer of titanium oxide deposited in (a), and thereafter

(c) electroplating a coating of lead dioxide onto the flash coated platinum.

3. In a process for preparing an electrode having a titanium substrate, the steps comprising:

(a) placing the titanium substrate, as an anode, in an electrolyte containing a cathode, applying current to the substrate-anode and increasing the voltage to about four volts and maintaining that voltage for about 10 minutes to deposit a layer of titanium oxide upon the surface of said titanium substrate,

(b) cathodically applying a flash coating of platinum upon the layer of titanium oxide deposited in (a), and thereafter

(c) electrolytically depositing a coating of lead dioxide upon the layer of platinum deposited in (b).

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