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ELECTROPLATING

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The invention relates to electroplating, and is more particularly concerned with the conditioning or special preparation of a base metal preliminary to plating to provide a tightly adherent bond between the electrodeposit and the base metal.

The invention is applicable to electroplating on metals which are difficult to plate directly, examples of such metals being aluminum, titanium, zinc, lead and their respective alloys. "Aluminum," "titanium," "zinc," and "lead," as hereinafter used in the specification and claims is intended in a generic sense to include both a commercially pure metal and alloys of the metal which are predominantly, or contain a substantial amount of, aluminum, titanium, zinc or lead, respectively. Also, reference to an article of aluminum, titanium, zinc or lead is intended to include a base metal which is entirely of aluminum, titanium, zinc or lead, or some other metal which is clad with, or has a surface layer of, aluminum, titanium, zinc or lead.

Great difficulty exists in obtaining tightly adherent electrodeposits on aluminum. The difficulty apparently stems from the highly oxidizing character of the metal, resulting in an ever-present aluminum oxide film on the surface. Various methods have been suggested for preparing or conditioning an aluminum surface to make it receptive for electroplating.

The process in widest commercial use today for preparing an aluminum surface for plating is the "zinc immersion process." In this process, a thin and adherent film of metallic zinc or alloy of zinc replaces the aluminum oxide film. The zinc provides a surface which is more readily plated with other metals than the aluminum. Not all metals, however, may then be simply deposited onto the zinc surface. Where it is desired to deposit chromium upon the zinc coated aluminum, special precautions are necessary, because the zinc layer is very thin, and any treatment which penetrates the zinc layer and attacks the underlying aluminum will result in a poor deposit. When depositing chromium on the zincated surface, the plating bath must be kept at a low temperature, and then, only a very thin layer of chromium may be applied. In order to produce thick and hard deposits of chromium, a transition must be made to plate at a higher temperature. The zinc immersion process for preparing an aluminum article for chromium plating has procedural limitations and is expensive.

One of the primary objects of the invention is to provide a simple and inexpensive process for plating chromium directly onto aluminum with the resultant deposit so tightly adherent to the base metal that the finished product is capable of withstanding the rugged and severe conditions encountered in industrial or engineering applications or uses.

It has been proposed to prepare the aluminum for direct plating by preliminarily etching the aluminum, the idea being to develop a keying or mechanical interlocking between the roughened aluminum surface and the overlying plate. This method is difficult to control, and

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has not furnished uniformly satisfactory adherence between the plate and the base metal.

It has also been proposed to replace the natural aluminum oxide by a relatively thick, porous oxide film formed by anodic treatment of the aluminum. This approach to the problem is based on the idea that the plating metal will adhere better to the aluminum through the medium of a controlled oxide film. The results of this method, however, have not afforded maximum adhesion of plated metal to base metal.

Special plating solutions have been devised to permit the direct plating on aluminum; however, none of the electrodeposits resulting from such solutions have furnished a truly satisfactory bond of the plate to base metal.

Another process for plating aluminum involves immersing the aluminum in a molten metallic salt bath preliminary to plating. Such process, however, because of the degree of heat involved, frequently has a deleterious effect upon the aluminum, and has proved to be less than satisfactory for many applications.

In accordance with my invention, chromium, or other metals such as nickel, copper or brass may be directly plated onto aluminum without impairing the physical properties of the aluminum, while permitting the attainment of a strong bond between the electrodeposit and the underlying aluminum. I have found that the foregoing may be accomplished by subjecting the aluminum article to the action of hydrogen chloride gas, vapor or fumes prior to plating. After plating, the deposited metal is strongly adherent and will withstand the severe mechanical abrasion, flexure, and other types of distortion encountered in rigid industrial applications. For reasons which I cannot fully explain at this time, hydrogen chloride gas somehow modifies an aluminum surface to make it highly receptive to deposits from common and well-known plating solutions.

Titanium is similar to aluminum in that it is also high in the electrochemical series, very active and highly oxidizing in character. Attempts to plate titanium, particularly with chromium, have met with repeated failure. I have found, however, that subjecting titanium to the action of hydrogen chloride gas effectively conditions the surface of the metal for the acceptance of a direct and tightly adherent plate. By firmly bonding a surface layer of chromium to titanium, this metal becomes useful for applications requiring a low coefficient of friction, a property in which titanium is most deficient, in addition to furnishing an end product that is resistant to heat and corrosion. Nickel, copper and brass may also be plated on titanium after conditioning the metal with the hydrogen chloride gas treatment.

Prior to the present invention, zinc alloy base die castings could only be satisfactorily plated with chromium after having been previously plated with nickel, or copper and nickel. In accordance with my invention, zinc may be prepared for direct plating with chromium by subjecting the zinc base metal to the action of hydrogen chloride gas. Also, lead may be simply and effectively prepared for direct plating with chromium, nickel, copper, or brass, by subjecting the lead article to the action of hydrogen chloride gas, vapor or fumes.

Describing the invention in greater detail, the article to be conditioned and plated is degreased and cleaned in accordance with accepted practices for the particular metal. Aluminum may be degreased in trichloroethylene, and cleaned with any suitable commercial cleaner, such as hot caustic soda. The alkaline cleaning step may be followed by a dip in dilute sulfuric acid, a rinse in water, or immersion in nitric acid and rinsing. Titanium may be cleaned by liquid honing (a pressure blast of

chemical emulsion and fine abrasive in solution), or by immersing the titanium in a hot, strongly alkaline bath, followed by rinsing in water, dipping a mixture of nitric and hydrofluoric acids and rinsing. Zinc and lead may be cleaned in accordance with established and well-known cleaning practices. After cleaning, the article, which is substantially at room temperature, is racked and placed in a chamber or vessel containing hydrogen chloride gas, vapor or fumes. The racks or article holding wires should be of a metal which is not readily attacked by the gas, such as copper.

The hydrogen chloride gas may be supplied in any suitable manner, as by heating hydrochloric acid in the same chamber or vessel, in which the article is suspended to receive the gas treatment, or by reacting sodium chloride with sulfuric acid, and piping the gas into the chamber. Preferably, the hydrogen chloride gas is in a heated state when the article being prepared for plating is subjected to its action. For purposes of economy, the gas may be condensed for reuse.

When hydrogen chloride gas is formed by heating hydrochloric acid in the same chamber in which the article is treated, care must be exercised not to allow an aluminum article to come in contact with the liquid acid, because the reaction is violent. A sufficiently large area may be left above the level of the liquid acid to permit suspension of the article some distance above its surface. The acid may be fully concentrated or diluted. Commercial muriatic acid having a concentration of 18° Bé. will furnish satisfactory results.

The time of treatment of the article in the hydrogen chloride gas depends upon the type and kind of metal being treated, and the temperature of the gas. Some alloys of aluminum require more time in the chamber than other alloys. For a given area of article, titanium requires a longer period of treatment than aluminum, zinc or lead. Some aluminum alloys have been activated in as little as five (5) seconds, and a titanium article having an equal surface area required fifteen (15) minutes in the gas of the same temperature. The hotter the gas, the shorter the period of treatment necessary. A gas temperature of 140° F. in the vicinity of the article is desirable, and higher temperatures are preferred for rapid processing. Adequate activation by the gas may be visually observed. The article appears to "sweat," so to speak, that is, tiny droplets or bubbles appear on the surface. The article is then removed from the gaseous medium and thoroughly rinsed. Rinsing may be done in cold running water, or where the conditioned article is to be chromium plated, in an aqueous chromic acid-sulphate solution.

Any commercial plating solution of chromium, nickel, copper or brass may be used to plate the hydrogen chloride gas conditioned article, and the article may be in the form of a machined part, casting, plate, sheet or strip.

Hydrogen chloride gas treated strips of aluminum and titanium, only one-sixteenth ($\frac{1}{16}$) inch in thickness were plated in a hard chromium plating bath containing thirty-three (33) ounces per gallon of chromic acid and 0.33 ounce per gallon of sulfate in the form of sulphuric acid. The bath was maintained at a temperature of approximately 132° F., and a current density of approximately three (3) amperes per square inch was used. The strips were variously plated from ten (10) to thirty (30) minutes. The resulting chromium deposit was hard and dense, and upon reverse-bending the strips, the plate showed no signs of cracking at the bent areas. Where the article will not encounter reverse-bending in use, it may be plated for a longer period, an hour or more, thereby depositing a thicker layer of plated metal.

Where a heavy deposit of chromium on titanium is desired, it is preferred to put the chromium on in stages, and heat treat the article intermediate plating operations. For example, a titanium article, after conditioning with

the hydrogen chloride gas, may be placed in a hard chromium plating bath at a temperature and current density such as hereinbefore described, and plated for a period up to thirty (30) minutes. The article is removed from the bath and air dried. The plated article is then heated to a temperature of between 1000° and 1700° F. A temperature of 1650° F. is preferred. When the piece is cherry red, it is removed from the heat source and allowed to cool to room temperature, after which the oxide film formed on the chromium surface during heating is removed in any suitable manner, as by liquid honing, or by immersion in dilute hydrochloric acid. If the latter cleaning method is used, care must be exercised to remove the article from the solution before the chromium is attacked to any degree. The article is thoroughly rinsed, and put back in the chromium plating bath. Any suitable procedure for plating chromium on chromium may be followed to build up to final desired thickness of plate.

A procedure which I have found to be preferable comprises placing the article back in the described chromium plating bath, and leaving it in the bath for a period of twenty (20) to thirty (30) minutes before applying any current. Current is then gradually applied to furnish a current density of one-fourth ($\frac{1}{4}$) ampere per square inch, which is applied for a period of approximately ten (10) minutes. The current density is increased another one fourth ($\frac{1}{4}$) ampere per square inch for another period of approximately ten (10) minutes, after which the current density is increased in increments of one-half ($\frac{1}{2}$) ampere for approximately fifteen (15) minute periods each until a current density of three (3) amperes per square inch is reached. Plating is then continued for a period of time depending upon thickness of plate desired. With a bath composition and temperature of plating as described, and with a current density of approximately three (3) amperes per square inch, a plate thickness of approximately 0.001 inch per hour is deposited.

After final deposition of the plating metal on the article, whether of aluminum, titanium, zinc or lead, and with or without an intermediate heat treatment, it is preferred to heat the plated article at approximately 300° F. for one (1) to two (2) hours in a furnace, or by immersing the article in hot oil.

Aluminum, titanium, zinc and lead articles conditioned and plated in the manner above described withstand grinding, bending, sawing and distortion with a prick punch without exhibiting cracking or peeling of the plate.

It is believed that the novel processes of the present invention, as well as the advantages thereof, will be apparent from the foregoing detailed description. Base metals which are difficult to plate, such as aluminum, titanium, zinc and lead, may be plated with chromium, and other metals, such as nickel, copper and brass, after conditioning the base metal with hydrogen chloride gas, vapor or fumes, with the achievement of an unusually strong bond between the plated metal and the base metal. It will also be apparent that while the invention has been described in several preferred forms, changes may be made without departing from the spirit and scope of the invention, as sought to be defined in the following claims.

I claim:

1. A process of electroplating an article formed of a metal selected from the group consisting of aluminum, titanium, zinc, and lead comprising subjecting the article having a temperature substantially equal to room temperature to the action of hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating the article.

2. A process of electroplating an article formed of a metal selected from the group consisting of aluminum, titanium, zinc and lead with a plating metal selected from

the group consisting of chromium, nickel, copper and brass comprising subjecting the article having a temperature substantially equal to room temperature to the action of hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating said plating metal on the article.

3. A process of electroplating an article formed of a metal selected from the group consisting of aluminum, titanium, zinc and lead with a plating metal selected from the group consisting of chromium, nickel, copper and brass comprising subjecting the article having a temperature substantially equal to room temperature to the action of heated hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating said plating metal on the article.

4. A process as set forth in claim 3, wherein the hydrogen chloride gas is formed by heating hydrochloric acid in a chamber or vessel in which the article is suspended.

5. A process of electroplating an aluminum article with a plating metal selected from the group consisting of chromium, nickel, copper or brass comprising subjecting the article having a temperature substantially equal to room temperature to the action of hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating said plating metal on the article.

6. A process of electroplating an aluminum article with chromium comprising subjecting the article having a temperature substantially equal to room temperature to the action of hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating chromium on the article.

7. A process of electroplating an aluminum article with chromium comprising subjecting the article having a temperature substantially equal to room temperature to the action of heated hydrogen chloride gas, removing the article from the hydrogen chloride gas medium when the article appears to sweat and electroplating chromium on the article.

8. A process as set forth in claim 7, wherein the hydrogen chloride gas is formed by heating hydrochloric acid in a chamber or vessel in which the article is suspended.

9. A process of electroplating a zinc article with a plating metal selected from the group consisting of chromium, nickel, copper, and brass comprising subjecting the article having a temperature substantially equal to room temperature to the action of hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating said plating metal on the article.

10. A process of electroplating a zinc article with chromium comprising subjecting the article having a temperature substantially equal to room temperature to the action of hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating chromium on the article.

11. A process of electroplating a zinc article with chromium comprising subjecting the article having a temperature substantially equal to room temperature to the action of heated hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating chromium on the article.

12. A process as set forth in claim 11, wherein the hydrogen chloride gas is formed by heating hydrochloric acid in a chamber or vessel in which the article is suspended.

13. A process of electroplating a lead article with a metal selected from the group consisting of chromium,

nickel, copper, and brass comprising subjecting the article having a temperature substantially equal to room temperature to the action of hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating chromium on the article.

14. A process of electroplating a lead article with chromium comprising subjecting the article having a temperature substantially equal to room temperature to the action of hydrogen chloride gas, removing the article from the hydrogen chloride gas medium when the article appears to sweat and electroplating chromium on the article.

15. A process of electroplating a lead article with chromium comprising subjecting the article having a temperature substantially equal to room temperature to the action of heated hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating chromium on the article.

16. A process as set forth in claim 15, wherein the hydrogen chloride gas is formed by heating hydrochloric acid in a chamber or vessel in which the article is suspended.

17. A process of electroplating a titanium article with a plating metal selected from the group consisting of chromium, nickel, copper or brass comprising subjecting the article having a temperature substantially equal to room temperature to the action of hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating said plating metal on the article.

18. A process of electroplating a titanium article with chromium comprising subjecting the article having a temperature substantially equal to room temperature to the action of hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating chromium on the article.

19. A process of electroplating a titanium article with chromium comprising subjecting the article having a temperature substantially equal to room temperature to the action of heated hydrogen chloride gas removing the article from the hydrogen chloride gas medium when the article appears to sweat, and electroplating chromium on the article.

20. A process as set forth in claim 19, wherein the hydrogen chloride gas is formed by heating hydrochloric acid in a chamber or vessel in which the article is suspended.

21. A process as set forth in claim 19, wherein the temperature of the gas in the vicinity of the article is more than approximately 140° F.

22. A process as set forth in claim 3, wherein the temperature of the gas in the vicinity of the article is more than approximately 140° F.

23. A process as set forth in claim 7, wherein the temperature of the gas in the vicinity of the article is more than approximately 140° F.

24. A process as set forth in claim 11, wherein the temperature of the gas in the vicinity of the article is more than approximately 140° F.

25. A process as set forth in claim 15, wherein the temperature of the gas in the vicinity of the article is more than approximately 140° F.

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