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2,958,610

PRE-PLATING TREATMENT OF ALUMINOUS SURFACES

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This invention relates to surface conditioning of aluminum or aluminum-containing alloys to improve receptivity of metal deposition from aqueous chemical plating solutions. More particularly, this invention relates to pretreating the surface of aluminum or aluminum containing alloys prior to nickelizing in an aqueous chemical plating solution with an aqueous ammoniacal solution containing a complexing agent so that metal hydroxide precipitation and surface oxide formation is reduced during the nickelizing process.

In the plating of aluminum and aluminum alloys, the surface of the metal to be plated must be free from impurities such as oxide film or other impurities which form in the plating bath. Aluminum is prone to rapid oxidation which forms a hard film that must be removed before plating. If this film is not removed, the plating bridges over the oxide portion or over other impurities on the surface of the metal so that the plating only mechanically adheres to that portion of the surface of the aluminum containing the impurities. Such bridging results in a plated surface that peels, blisters, or cracks, particularly when the surface is subjected to strains such as are produced by temperature elongation, flexing, or bending.

To remove the oxide film, which quickly forms on aluminum surfaces, the aluminum article generally is subjected to an etching treatment in a strong alkaline solution, such as sodium hydroxide, followed by washing, and then is placed in the plating bath. The strong alkaline solution attacks the aluminum oxide and other impurities on the surface and cleans it preparatory to plating. Some of the hydroxide, however, is present on the surface of the etched aluminum after washing so that when it is dipped in the plating solution or bath, there is quickly formed nickel hydroxide, which deposits on the surface of the aluminum as an impurity. In addition, before the plating can be completed, the surface of the aluminum is oxidized to a small extent by the presence of oxygen releasing compounds in the solution and the air to which it has been exposed before immersion in the bath.

Although attempts have been made to accelerate plating from an aqueous chemical nickel plating solution and to eliminate blistering and cracking of the surface, such as by adding fluoride or nitrate ions to the plating solution, these and many other innovations have not resulted in a substantial improvement of plating. For example, in the nickel plating of metals, including aluminum, it is general practice to use a buffered sodium hypophosphite solution which on application to the base is reduced to phosphite liberating hydrogen. Such a process is described in United States Patent 2,532,283 Brenner et al. Improved plating solutions are described in United States Patents 2,658,839 Talmey et al., 2,658,841 and 2,658,842 to Gutzeit et al., 2,694,017 Reschan et al., and 2,694,019 Gutzeit. In these latter improved plating solutions, certain "exalting agents" consisting of agents such as short chain saturated aliphatic dicarboxylic acids

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(malonic, succinic, glutaric and adipic acids) were added to the plating solution to improve the autocatalytic action of the nickel plating solution itself. However, it was found that the special problem of nickel plating existing where plating on aluminum or aluminum alloys was concerned still remained in that the so-called "black precipitate" of nickel hydroxide occasionally formed on the surface of the base. Therefore, the present workers turned to certain improved pretreatment process steps and compositions which have been found to eliminate the difficulties found in the prior art processes and to make possible later plating of nickel without the formation of nickel hydroxide $[\text{Ni}(\text{OH})_2]$.

This present invention contemplates the pretreating of the surface of aluminum and aluminum alloys with an aqueous ammoniacal solution containing a complexing agent, prior to immersion in a chemical nickel plating bath so that, when the surface to be plated is immersed in the plating bath, nickel hydroxide precipitation and oxide film growth are greatly reduced and improved plating of the surface is accomplished. This reduction of impurities by a pretreating step provides for improved smoothness of nickelization of the surface with elimination of blistering and cracking of the plated surface. The invention provides a process for chemical nickel plating whereby accelerated plating is accomplished by a pretreatment of the etched aluminum-containing surface.

By employing an aqueous ammoniacal solution containing from about 0.1 to about 30 parts by weight of ammonia and from about 0.1 to about 5 parts by weight of a complexing agent (sequestering or chelating), aluminum-containing surfaces can be modified to reduce impurity formation thereon either before immersion in the plating bath or during chemical plating thereof. The term "complexing agent" heretofore and hereinafter in the present application and claims is defined to mean any agent which will form a complex such as a chelate to tie up or inactivate the nickel ions of the pretreatment solutions. Preferred complexing agents contemplated by the present invention include aminopolycarboxylic acids and alkaline earth metal salts thereof, such as ethylenediaminetetracetic acid and aliphatic hydroxycarboxylic acids, such as gluconic, tartaric, and citric acids and ammonium, alkali metal and alkaline earth salts thereof.

Specific operable aminopolycarboxylic acid compounds found to be operable and within the purview of this invention include diethylene triamine pentacetic acid, monosodium EDTA, disodium EDTA, trisodium EDTA, tetrasodium EDTA, trisodium triethylene tetramine hexacetic acid, propylene diamine tetracetic acid, and trisodium dipropylene triamine pentapropionic acid.

Immersion of the aluminum-containing surface in the aqueous ammoniacal solution having a complexing agent therein for a period of from about 30 to about 60 seconds produces a conditioned surface for effecting an acceleration and evenness of plating as heretofore described. Although the temperature of the plating solution may range from room temperature to a boiling temperature, optimum results have been obtained where the surface conditioned according to this invention was immersed in a plating solution maintained at a temperature of about 90° to 95° C.

Therefore, an object of this invention is to provide a pretreating process whereby the surface of aluminum and aluminum-containing alloys prior to chemical nickel plating is subjected to surface conditioning to reduce surface impurities and accelerate the nickel plating process.

Another object of this invention is to provide a process for the treatment of etched aluminum and aluminum-containing alloys to enhance the quality of the plate

deposited thereon and to accelerate the rate of plating.

A still further object of this invention is to provide a process for conditioning the surface of aluminum and aluminum-containing alloys subjecting same to an aqueous ammoniacal bath containing a chelating or sequestering agent for a period of 30 to 60 seconds prior to chemical nickel plating to accelerate plating and improve the surface qualities of the plating.

Another object of this invention is to provide an aqueous ammonium pretreating composition having a chelating or sequestering agent therein for conditioning the surface of aluminum and aluminum-containing alloys prior to immersion in a chemical plating bath to prevent formation of nickel hydroxide precipitation and oxide film growth on the aluminum surface during plating process.

These and other objects will become apparent from the following description and appended claims.

It has been found that improved nickelizing of aluminum and aluminum alloys can be produced at an accelerated rate with a high degree of adherence to the base metal and free of blisters and cracks by treating the surface to be plated subsequent to alkaline etching and prior to dipping in the plating bath with an aqueous ammoniacal solution containing a small amount of a complexing agent. For example, nickel plating can be deposited on the surface of an aluminum alloy by chemical reduction of nickel ions in a hypophosphite aqueous nickel plating solution. When the aluminum alloy surface is first treated with an aqueous ammoniacal solution containing complexing ions for a period of from about 30 to about 60 seconds, the surface has an increased receptivity to the plating reaction. This receptiveness is borne out by the fact that immediate plating occurs after transferring the dipped surface from the aqueous ammoniacal solution to the nickel chemical plating bath.

The mechanism involved in producing an activated aluminum surface is believed to be directly connected with the action produced by the ammoniated chelating or sequestering compounds, for there is a marked retarding or minimizing of oxide growth as well as the elimination of foreign hydroxide precipitation. The presence of the complexing agent near the aluminum surface limits nickel hydroxide precipitation so that a reduction of the nickel is more rapidly accomplished to provide even plating. Thus, by limiting the formation of the nickel hydroxide, there is a substantial reduction in the bridging so that the plate is bonded to the pure aluminum, thereby eliminating blisters and cracks in the plated surface.

The complexing agent may be a chelating compound, such as the ammonium salts of ethylenediaminetetracetic acid, or a sequestering compound, such as ammonium citrate. As heretofore described in detail, other chelating agents of the aminopolycarboxylic acid type and the salts thereof, or sequestering agents of the hydroxycarboxylic acid type, such as gluconic, citric, tartaric and the like and salts thereof may be used with good results to form the aqueous ammoniacal solutions of this invention.

It has been found that surface activation of cleaned aluminum can be produced when the aqueous ammoniacal solution containing a complexing agent has from about 0.1 to about 30 parts by weight ammonia and from about 0.1 to about 5 parts by weight of a complexing agent. Although the nickel plating bath can be operated at a range from room temperature to slightly below boiling, with good results, it has been found that excellent results are obtained when the plating bath is operated at a temperature between 90 and 95° C. It has also been found that the transfer of the ammoniacal treated aluminum surface to the nickel plating bath need not be interrupted by a rinse or wash as the presence of the ammonium ions on the surface of the aluminum have been found to be helpful in initiating and producing a high quality of plating.

The following examples serve to illustrate the improved results obtained when the composition and process treat-

ment of this invention are used to pretreat the surface of aluminum and aluminum-containing alloys before immersion in a chemical nickel plating bath.

Example I

The surface of a 3003 type aluminum bar was cleaned in a 30R alkaline cleaner for a period of 2 minutes. A 30R cleaner is a sodium hydroxide type alkali cleaner containing a minor amount of surfactant. The aluminum bar was then removed from the cleaning solution, washed, and dipped in an aqueous ammoniacal pretreating solution containing 3% by weight of ammonia and 2% by weight of ammonium citrate for a period of 45 seconds at room temperature. The aluminum bar was removed from the pretreating solution and placed in an aqueous chemical nickel plating bath formed from a hypophosphite solution containing nickel ions. The plating bath was maintained at a temperature of between 90° and 95° C. Plating was continued for a period of 1 hour and upon removal of the aluminum bar, it was found that an even plate had been deposited showing no cracks or blisters. Microscopic inspection of the plating produced also showed that the surface was free from normal plating defects caused by impurities and that the plating was uniform.

Example II

A 3003 aluminum bar was cleaned in a 30R alkaline cleaner for a period of 2 minutes. The aluminum bar was removed from the cleaning solution, rinsed and treated for 45 seconds in an aqueous ammoniacal pretreating solution containing 3% by weight of ammonia and 1% by weight ammonium salt of an ethylene diaminetetracetic acid. The aluminum bar was removed and immediately immersed in an aqueous chemical nickel plating bath formed from a hypophosphite solution containing nickel ions and processed as described in Example I.

After one hour, the aluminum bar was removed and inspected and it was found to have a smooth even plate with no blisters or cracks in the surface thereof. Microscopic examination showed absence of impurities and evenness of plating.

It was found that either a sequestering agent or a chelating agent can be used for tying up or making inactive impurity forming agents on or near the surface of the aluminum. It was also found that the pretreating composition of this invention and a method of treating produced equivalent results when the plating took place in other commercial buffered hypophosphite type aqueous chemical plating solutions, such as the acetate, succinate, propionate, or the like.

It will be appreciated that the treating composition for improving the quality of nickel plating as heretofore described may be utilized with other aqueous chemical solutions for plating where surface oxidation and impurity precipitation of the surface of the metal to be plated is experienced.

In the process of the invention, equivalent soluble salts such as the alkali metal, alkaline earths, and ammonias are included in the phraseology for the acids, such as (a) amino polycarboxylic acids and (b) aliphatic hydroxycarboxylic acids.

The process of the invention has the important advantage of providing immediate initiation of nickel plating, with a consequent avoidance of the undesirable formation of boehmite, a hydrated aluminum oxide. In the case of conventional plating, for example, an aluminum specimen is immersed for one to three minutes in a solution of 1% hydrochloric acid and 10% nitric acid, and then the specimen is treated in the nickel plating solution for three minutes. When practicing the present invention, on the other hand, after the same preliminary acid treatment, for example, the aluminum specimen is as fully plated in the nickel plating solution within a period of less than five seconds.

While present preferred practices and embodiments of the invention have been described above, it will be

understood that the invention may be otherwise variously embodied and practiced within the scope of the following claims:

What we claim is:

1. A pretreating composition for conditioning the surface of alkaline etched aluminum and aluminum containing alloys preparatory to nickelizing with an aqueous hypophosphite chemical plating solution, said pretreating composition comprising an aqueous ammonical solution consisting essentially of about 3% by weight of ammonia and about 1% by weight of ethylenediaminetetracetic acid chelating agent.

2. A pretreating composition for conditioning the surface of alkaline etched aluminum and aluminum containing alloys preparatory to nickelizing in an aqueous hypophosphite chemical plating solution, said pretreating composition comprising an aqueous ammonical solution consisting essentially of about 3% by weight of ammonia and about 2% by weight of ammonium citrate sequestering agent.

3. In the chemical nickel plating of aluminum and aluminum alloys by the sequential procedure of alkaline etching, pretreat rinsing and chemical hypophosphite plating, the step which consists in pretreat rinsing said aluminum with an aqueous bath consisting essentially of ammonia in the range of about 0.1 to about 30 parts by weight and a complexing agent selected from the group consisting of aminocarboxylic acids, alkaline earth metal salts of aminocarboxylic acids, ammonium salts of aliphatic hydroxycarboxylic acids, aliphatic hydroxycarboxylic acids, alkali metal salts of aliphatic hydroxycarboxylic acids and alkaline earth metal salts of aliphatic hydroxycarboxylic acids in the range of about 0.1 to 5 parts by weight.

4. In the chemical nickel plating of aluminum and aluminum alloys by the sequential procedure of alkaline etching, pretreat rinsing and chemical hypophosphite plating, the step which consists in pretreat rinsing said aluminum with an aqueous bath consisting essentially of ammonia in the range of about 0.1 to about 30 parts by weight and an aminopolycarboxylic acid complexing agent in the range of about 0.1 to 5 parts by weight.

5. In the chemical nickel plating of aluminum and aluminum alloys by the sequential procedure of alkaline etching, pretreat rinsing and chemical hypophosphite plating, the step which consists in pretreat rinsing said aluminum with an aqueous bath consisting essentially of ammonia in the range of about 0.1 to about 30 parts by weight and an aliphatic hydroxycarboxylic acid complexing agent in the range of about 0.1 to 5 parts by weight.

6. In the chemical nickel plating of aluminum and aluminum alloys by the sequential procedure of alkaline etching, pretreat rinsing and chemical hypophosphite plating, the step which consists in pretreat rinsing said aluminum with an aqueous bath consisting essentially of ammonia in the range of about 0.1 to about 30 parts by weight and an ammonium salt of ethylenediaminetetracetic acid complexing agent in the range of about 0.1 to 5 parts by weight.

7. In the chemical nickel plating of aluminum and aluminum alloys by the sequential procedure of alkaline etching, pretreat rinsing and chemical hypophosphite plating, the step which consists in pretreat rinsing said aluminum with an aqueous bath consisting essentially of 3% by weight of ammonia and 1% by weight of an ammonium salt of ethylenediaminetetracetic acid.

8. In the chemical nickel plating of aluminum and aluminum alloys by the sequential procedure of alkaline etching, pretreat rinsing and chemical hypophosphite plating, the step which consists in pretreat rinsing said aluminum with an aqueous bath consisting essentially of ammonia in the range of about 0.1 to about 30 parts by weight and ammonium citrate complexing agent in the range of about 0.1 to 5 parts by weight.

9. In the chemical nickel plating of aluminum and aluminum alloys by the sequential procedure of alkaline etching, pretreat rinsing and chemical hypophosphite plating, the step which consists in pretreat rinsing said aluminum with an aqueous bath consisting essentially of 3% by weight of ammonia and 2% by weight of ammonium citrate.

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