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ALUMINUM PLATING PROCESS

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ABSTRACT OF THE DISCLOSURE

A process for plating aluminum substrates involving the principal steps of depositing a coating of zinc on the aluminum and subsequently anodizing the zinc-coated workpiece in phosphoric acid to consume the zinc and oxidize the aluminum prior to subsequent plating operations.

This invention is directed toward a process for the electrodeposition of metals, such as chromium, onto aluminum and alloys thereof. Herein alloys of aluminum are intended to mean alloys having an aluminum content in excess of 50 percent.

Two processes for the electrodeposition of metals onto aluminum substrates are in common usage today. These two processes can be broadly referred to as the zincate process and the anodizing process. The zincate process involves the initial formation of a zinc coating on the aluminum substrate prior to the electrodeposition steps. The zinc coating is usually formed by dipping the aluminum part into a zincate solution from which the zinc deposits on the aluminum. In the anodizing process the aluminum is anodized prior to the electrodeposition steps. These processes are used alternatively.

The zinc layer produced by the zincate process initially adheres to the aluminum surface and forms a base upon which other coatings may be deposited. However, the zinc layer is quite fragile. The zinc layer will not resist tensile loads. The zinc layer dissolves in the acid nickel solutions and so one cannot nickel electroplate directly without the use of intermedite layers of copper. Both zinc and copper tend to aggravate galvanic corrosion of the aluminum more so than do other metals such as nickel. Over a period of time, i.e., in excess of one year, the Zn and Cu layers diffuse one into the other forming a Cu-Zn alloy layer. This layer is extremely brittle. This gives rise to blistering after the parts have been in use for a while. The blistering causes a disruption of the inner and outer metal layers. Rapid deterioration follows.

In the anodizing process an anodized layer forms the surface for the subsequent electrodeposits. The anodized layer is itself a good layer upon which to adherently plate other materials. However, the anodized layer itself is not sufficiently adherent for many applications.

Neither of the processes outlined above produce a part that exhibits excellent corrosion resistance and adherence over a long period of time.

It is, therefore, an object of my invention to provide a new and improved process for the electroplating of aluminum parts.

A further object of my invention is to provide a process which produces not only a tenacious but also an exceptionally long-lasting corrosion resistant electrodeposited coating on aluminum.

Another object of my invention is to provide an improved electrodeposited coating on aluminum that is tenacious and does not form a brittle inner layer to undermine the coating and decrease its long-term durability.

Briefly stated, my invention resides in a process comprising generally the steps of cleaning an aluminum part, immersing the part in a chemical zinc deposition bath,

anodizing the part in a phosphoric acid solution to consume the zinc and oxidize the aluminum, nickel plating the part, and subsequently treating the part in any desired plating sequence.

In this process any acceptable aluminum cleaning technique may be employed as long as the part is adequately degreased and all loose metal or buffing compound has been removed. The part is subsequently dipped in an acid solution to remove any smut and oxides formed on the surface.

In the case of aluminum die castings containing alloying metals such as silicon and iron, etching should also be used to deplete the surface of same. These alloying materials complicate the subsequent processing steps and hence should be removed. Either acid or caustic etching solutions may be employed. When using an acid etch, a single combined nitric-sulfuric-hydrofluoric acid etch is effective, however, I prefer to use a sequence of etching steps rather than just one. Hence, I prefer to first etch the part in a nitric-hydrofluoric acid solution and, secondly, into a nitric-sulfuric-hydrofluoric acid solution. In this connection I prefer that the first nitric-hydrofluoric acid etching solution contain about 10% by weight nitric acid, about 11% by weight of ammonium bifluoride based additives and the balance water. For the ammonium bifluoride based additive, I prefer to use the Alumetex etch salts. However, any equivalent salts, may be substituted. I prefer to perform this first etch at room temperature for approximately one minute. For the second etch I prefer to use a nitric-sulfuric-hydrofluoric acid solution. In this connection a by weight solution comprising about 20% nitric acid, 43% sulfuric acid, 6% ammonium bifluoride based additives and the balance water, is preferred. As in the first etching step, Alumetex etch salts are preferred as the ammonium bifluoride source material. This second etching is performed at room temperature for about 30 seconds. For aluminum parts other than castings, i.e., wrought or extruded, etching can be eliminated.

The part is then immersed into a zincate bath. The zincate bath comprises about 3½–6 lbs./gal. of a zinc oxide and caustic soda mixture and water. In this connection the mixture can vary from a 1:4 to 1:6 zinc oxide to caustic soda ratio. I prefer to use about a 5 lbs./gal. solution of Almate. However, any equivalent composition may be substituted. Though I prefer to operate the zincate bath at about room temperature, the bath can satisfactorily be operated at temperatures in the order of 60–90° F. Generally a minimum of about 15 sec. immersion time is required. The maximum immersion time is dependent upon factors which may vary with each operation. These may include bath temperature, bath concentration, the nature of the alloy to be treated, and the nature and thickness of the coating desired. Generally, the immersion should produce a continuous film of zinc on the aluminum surface. The film preferably should not be appreciably in excess of about 1.0 mil. The minimum thickness of the film is not particularly significant. Continuity of the film is.

After the zinc immersion step, the part is anodized in a phosphoric acid bath. I have found that the phosphoric acid bath must be used if one is to obtain the benefits of this process. Conventional anodizing baths, such as chromic acid, sulfuric acid, and phosphoric-sulfuric acid baths which are commonly used today for other anodizing processes, are inoperative in my process. Phosphoric acid baths for my process may advantageously be made up with about 8–20% by volume in water of 85% by weight phosphoric acid. I prefer to use about a 15% by volume solution. While I prefer to operate the bath at room temperature, or about 72° F., anodizing can satisfactorily be effected at temperatures of 60–100° F. The

applied voltage may vary from about 9–24 volts. Current densities of about 5–25 ASF during most of the anodizing step are effective in producing a desirable coating. The preferred anodizing current density varies with the alloy composition. The duration of anodizing is dependent on the current density, and therefore indirectly dependent on the alloy composition. For aluminum parts such as die-cast alloy A–13, wrought alloys 3003, 5252, 5457 and extrusion alloy 6063 anodizing for about 3 min. at current densities of about 10 ASF are preferred. The anodized coating formed is a dull, soft film having relatively large pores, in contradistinction to the dense, hard, gray coatings characteristic of the chromic acid baths and the more decorative coatings characteristic of the sulfuric acid baths.

The part is subsequently directly nickel plated. A nickel strike is preferred. Any acceptable nickel bath may be used, but the higher current densities generally characteristic of strike plating are still preferably initially employed. Hence, any of the conventional sulfamate, borate, sulfate or chloride acid nickel baths are acceptable. I prefer to use a bath comprising about 16 oz. per gal. of nickel chloride and having about 6% by weight of hydrochloric acid, the balance being water. With such a bath at about 72° F., I prefer to strike the part for about 3 min. at a current density of about 100 ASF. The nickel plating, like the zincate-anodizing sequence of steps, is important if strongly adherent corrosion resistant parts are to be produced. A copper layer, for example, cannot be substituted for the nickel and still produce the same quality part. The copper will not adhere to the substrate.

Appropriately, the part should be rinsed after each immersion to preclude the possibility of contaminating a subsequent bath with carry-over ingredients from a previous bath.

After the nickel strike any of a variety of plating sequences may be followed, depending on the desired product. For applications such as automobile trim and the like where exposure to highly corrosive environments is a particular threat to the durability of the part, I prefer to complement my improved sub-coating with a conventional dual nickel and dual chrome sequence such as the following procedure which also serves as a specific example of my invention. A die cast aluminum wheel cover having a total surface area of about 5 square feet is cleaned free of oil, grease, loose metal and buffing compounds. Any acceptable cleaning cycle may be employed for this step. In the case where heavy oils or grease films are present, vapor degreasing is followed by treatment in a hot etched-type alkaline cleaner. The part is subsequently rinsed and dipped into a deoxidizer solution such as a 50–50% by volume nitric acid and water solution. The part is rinsed. The part is then etched in a nitric-hydrofluoric acid solution comprising about 16 gal. of a 36° Bé. nitric acid, 74 gal. of water, and 100 lbs. of Alumetex etch salts. The part is thus treated for about 1 min. at about 72° F. The part is rinsed in cold water. The part is again etched, but now in a nitric-sulfuric-hydrofluoric acid solution comprising 183 lbs. of water (made up with ice), 37 gal. of 36° Bé. sulfuric acid, and 72 lbs. of Alumetex etch salts. The part is thus treated for about 30 sec. at about 72° F. The part is rinsed with cold water. The part is next coated with zinc by immersion into a zincate bath comprising a 5 lbs. per gal. solution of Almate mixture. It is thus treated for about 35 sec. at about 72° F. Upon removal from the zincate tank the part is held in position over the tank for about 30 sec. to permit all excess solution to drain back into the tank. The part is rinsed with cold water. The part is then anodized in a 15% by volume phosphoric acid solution of the type previously discussed. The part is anodized for 2 min. with 16 volts at a temperature of 72° F. The initial current density of 75 ASF rapidly falls off to a low of 10 ASF during the course of the anodizing. The part is rinsed with cold water. A nickel strike is then deposited on the thus anodized part. The part is immersed into a bath comprising 16 oz. per gal. of nickel chloride with about 6% by weight of hydrochloric acid and treated therein with about 10 volts for about 3 min. at a current density of 80 ASF and a temperature of 72° F. The part is subsequently rinsed with cold water. The part is next plated with a layer of leveling semi-bright nickel such as from a bath comprising 32 oz. per gal. nickel sulfate, 12 oz. per gal. nickel chloride, 4.5 oz. per gal. of boric acid and appropriate proprietary primary and secondary addition agents. Perglow baths serve equally well here. An equivalent of 2000 amp-min./ft.^{2} of plate is deposited at a current density of 60 amps/ft.^{2} and a temperature of 130° F. The part is rinsed with cold water. A layer of bright nickel is deposited on the layer of leveling semi-bright nickel. A Perglow bath is used and an equivalent of about 1000 amp-min./ft.^{2} of nickel is applied at a current density of 60 amps/ft.^{2} and a temperature of 130° F. The part is rinsed with cold water. The remaining steps are substantially disclosed in U.S. patent to Durham 3,188,186 dated June 8, 1965, for the production of a decorative corrosion resistant cracked chrome deposit. A variety of different plating baths and sequences have been effectively used with my process. The only apparent requirement for producing strongly adherent durably corrosion resistant parts is that the part be sequentially zinc coated, anodized in phosphoric acid and plated with nickel before beginning the finished plating sequence.

Cass tests were conducted on buffed wrought aluminum samples which had been plated in accordance with my invention. The samples were plated to a code Z–150 specification which calls for a total plate thickness of at least 0.0015 inch and having a nickel plate of at least 0.0008 inch thick. Cracked chrome having from 900 to 1275 cracks per linear inch constituted the final layer. Four out of 7 samples withstood 22 hours of Cass test requirements. The remaining 3 showed corrosion ratings from 96.0 to 97.7. 92.0 is an acceptable corrosion rating. For some specific test results, see Table I.

TABLE I

Part	Chromium crack pattern, cracks/lin. inch	Defects	Corrosion rating No.*
Rocker panel molding	1,275	3	96
Outside panel molding	1,275	0	100
Do	1,275	0	100
Fender molding	900	2	97.2
Headlamp molding	900	0	100
Wheel opening	1,275	0	100
Do	1,275	1	97.7

*Sukes, G., "Metal Finishing," Vol. 57, No. 12, p. 59, December 1959.

Adhesion tests were also conducted. The samples were heated to 300° F. for 24 minutes, then quenched in water. The samples were cut with a power saw in the direction of the plating. The plate at the saw cut was next peeled by prying with a blade to separate the plate from the base metal. Another test comprised the twisting of a sector of each sample until the plate cracked. Still another test comprised the heating of sectors of each sample to 300° F. for one hour and then quenching in water to see if the plate would blister. A peel or blister in excess of ⅛" resulting from any of the aforementioned tests was considered to be indicative of poor adhesion. Generally, the samples showed excellent adhesion under the saw cut, peel, twist, and blister tests. For some specific test results, see Table II.

TABLE II

Sample	Peel Tests	Blister tests
1	Less than ⅛" for all tests	Not tested.
2	Less than ⅛" for all tests	No blisters.

Field or in-service corrosion tests were additionally conducted. A variety of parts were selected for placement on test vehicles which were used regularly in the course of everyday driving. The choice of parts to be

tested was guided by the relative position of the part on the vehicle in order to evaluate the influence of location and road splash effects. All of these parts were plated to a code 200 thickness which requires a total plate of at least 0.002 inch with a minimum nickel thickness of at least 0.001 inch. The parts were then nicked to the base metal with a file to provide an intentional break for plating loss observation. Table III shows some of these test results.

TABLE III

Part	Miles driven	Remarks
Wheel opening molding	12,856	Severe dents, but showed no corrosion or loss of plating adhesion.
Radiator grille	20,581	Six pits formed.
Extruded rocker panel	12,856	Pits in the low thickness, high impact area of the panel.

Although this invention has been described in connection with certain specific examples thereof, no limitation is intended thereby except as defined in the appended claims.

I claim:

1. A process for producing an adherent durable electrodeposited coating on aluminum and alloys thereof, comprising the successive steps of immersing said aluminum in a chemical zinc deposition bath comprising an aqueous solution of zinc oxide and caustic soda to produce a continuous film of zinc on said aluminum, immersing said aluminum in an anodizing bath consisting essentially of an aqueous solution of phosphoric acid, anodizing said aluminum for at least about two minutes at a current density of at least about 5 amps/ft.^{2} to consume said zinc film and to oxidize said aluminum, and electrodepositing at least one coating of nickel on said oxidized aluminum.

2. A process as described in claim **1** wherein said zinc deposition bath is an aqueous solution containing about 3.5–6 lbs./gal. of a zinc oxide-caustic soda mixture with the zinc oxide to caustic soda ratio in said mixture being about 1:4–1:6, and said aqueous phosphoric acid anodizing bath comprises the equivalent of about 8–20% by volume of 85% by weight phosphoric acid.

3. A process as described in claim **2** plus the additional step of electrodepositing a coating of chromium on said nickel coated surface.

4. A process as described in claim **3** wherein the electrodepositing of said nickel comprises the successive steps of nickel striking the anodized surface and subsequently applying a dual nickel coating on said nickel strike.

5. A process as described in claim **4** wherein the electrodepositing of said chromium is accomplished using a dual chromium plating sequence.

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