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# METHOD OF CONDITIONING HIGH ALUMINUM CONTENT ZINC ALLOYS TO RECEIVE ADHERENT ELECTROPLATED METAL COATINGS

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## ABSTRACT OF THE DISCLOSURE

An alkaline soaking method is provided for conditioning the surface of high aluminum content zinc alloys, particularly superplastic zinc alloys containing about 20 to about 22 percent aluminum, so that adherent electroplated coatings can be applied. The method avoids prior art processing steps typically applied to zinc base alloys which have been found, in accordance with the invention, to be detrimental to the subject alloys.

## BACKGROUND OF THE INVENTION

Alloys nominally comprising by weight about 78 percent zinc and about 22 percent aluminum have recently become of increased commercial interest because of their ability to exhibit viscoelasticity, more usually referred to as superplasticity, when conditioned by methods such as that set forth in U.S. Pat. No. 3,420,717 entitled "Metal Softening Process and Product Thereof." In this superplastic state, techniques commonly employed in the polymer and glass industries may be utilized to readily form these alloys into intricately shaped articles for commercial applications. Such articles, particularly those destined for automotive and appliance applications, generally require a surface finish for durability and/or aesthetic appeal. The most universally accepted finish is the so-called chromium plate, actually a plating system comprising copper, nickel and chromium. Other electroplated finishes in common use also include brass, bronze, gold, nickel, silver, and tin.

The techniques employed to electrodeposit the various metals enumerated above are well known to those skilled in the art, and adherent coatings of the desired metals can be readily deposited upon basis metal surfaces, provided that surface has been properly prepared.

One procedure used in the plating of zinc base alloys, and known to afford excellent adhesion, for example, to Zamak-3 (ASTM Alloy AG 40A), a zinc base die casting alloy containing by weight 3.5 to 4.3 percent aluminum and 0.020 to 0.05 percent magnesium, includes the following cleaning and conditioning steps: The alloy is first buffed, and then degreased by immersion in hot liquid trichloroethylene followed by immersion in cool liquid trichloroethylene, and finally suspended in an atmosphere of trichloroethylene vapor. The alloy is then cleaned anodically in a 6 ounce per gallon alkaline solution of Oakite-295 (a proprietary composition offered by Oakite Products, Incorporated, Berkeley Heights, N.J., which is an alkaline, anodic zinc cleaner containing a combination of wetting, buffering, inhibiting, chelating and sequestering agents) at 60–70° C., using a 5-volt applied potential for a period of 30 seconds. The anodic cleaning is followed first by a hot water rinse and then by a cold water rinse. After rinsing the alloy is immersed in a 0.5 percent (by weight) sulfuric acid solution for 5 to 10 seconds at room temperature, followed by a cold water rinse.

The above procedure results in a zinc alloy surface which is free of dirt, grease and oxides, and which exhibits a bright or lightly etched appearance, free of water breaks.

After cleaning and conditioning, the alloy is given a copper strike coating by immersion for one minute in a dilute cyanide copper plating solution, entering with the plating current on. Upon deposition of the copper strike coating, the zinc alloy may be processed in a variety of plating solutions, either alkaline or acid, to produce the metallic coating or combination of coatings desired for appearance, corrosion resistance and/or mechanical properties.

Unfortunately, however, such procedures being presently used for wrought zinc and zinc die casting alloys do not produce the same results in zinc alloys having higher aluminum contents, for example in the order of about 20 to about 22 percent. Electroplated metallic coatings deposited on such high aluminum content alloys which have been cleaned by conventional means are invariably found to be blistered due to lack of adhesion to the basis metal. Baking treatments, which are typically employed when selected areas of such alloys are painted after electroplating, result in still further blistering and exfoliation.

The lack of adhesion exhibited by electroplated finishes on conventionally cleaned and conditioned high aluminum content zinc alloys may be due to the presence of a film of aluminum oxide which is not removed in cleaning, or that reforms before plating, and thus acts as a plating barrier. Alternatively and/or additionally, the alloy may be attacked excessively in the various cleaning solutions. This can result in a dissolution of surface metal leaving a porous surface, or the surface metal may possibly be redeposited and poorly adherent. Finally, an excessively thick and brittle copper-zinc diffusion layer may form on the alloy surface, possibly as a consequence of overcleaning. These theories are set forth only to illustrate possible reasons for poor adherence of electroplated finishes on conventionally cleaned, high aluminum content zinc alloys. It is not intended, therefore, that the invention be limited to or by these possible theories of operation.

Regardless of the mechanism involved, it is believed that plating difficulties result primarily from the substantially higher aluminum content of the subject alloys when compared with the 3.5 to 4.3 percent aluminum content of a typical zinc die casting alloy. A 22 percent aluminum containing zinc alloy is calculated to have a structure that is approximately 43 percent aluminum by volume, and any compositional inhomogeneity may readily result in specific areas being still richer in aluminum.

It is well known that aluminum reacts with air and water to form a very thin, tightly adherent oxide film. It is therefore difficult to deposit another metal directly on aluminum because this oxide film must be removed in order that proper adhesion between the aluminum basis metal and the electrodeposited coating can be achieved. Generally, aluminum is given an intermediate coating, commonly zinc or tin obtained by chemical deposition from zincate or stannate solutions, before final plating is effected. However, even this method does not provide for adhesion on the subject alloys comparable to that obtained on zinc metal by conventional methods.

An evaluation has been made of a number of conventional plating process steps to determine their effect on the adhesion of electroplated metal coatings to the high aluminum content zinc alloys. Anodic electrocleaning causes excessive oxidation of these alloys even though the solutions are inhibited for use on zinc metal. Nascent oxygen formed at the anodic alloy surface reacts with the aluminum phase, preventing the adherence of any electrodeposit on such a surface. Acid dips which are of a strength sufficient to remove the oxide film, also detrimentally attack the basis metal. The zincate procedure typically used to condition aluminum for electroplating generally fails to provide adequate adhesion on the high aluminum content zinc alloys. The chemically deposited zinc coating only loosely adheres to the surface, probably due to the fact that while zinc is the major alloying constituent, the zincate tends to form an immersion deposit only on the aluminum phase. Finally, all conventional cleaning cycles include water rinses. The reactivity of aluminum with air and water to form the thin, tight oxide films believed responsible for poor adhesion, makes it imperative that such rinses be avoided.

Accordingly, representative objects of the present invention are to provide a method for conditioning high aluminum content zinc alloys, particularly superplastic zinc alloys containing by weight about 20 to about 22 percent aluminum, so that adherent electroplated metal coatings can be applied, and to provide such a method which can be effected with relative ease on a commercial scale, which is efficient and economical in operation, and which produces commercially acceptable results with fewer processing steps.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the apparatus embodying features of construction, combinations of elements, and arrangements of parts which are adapted to effect such steps, all as exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

## SUMMARY AND DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention relates to a method of conditioning the surfaces of high aluminum content zinc alloys in order that adherent metallic coatings may be electrodeposited thereon, and more particularly to such a conditioning method which is especially applicable to superplastic zinc alloys containing about 20 to about 22 percent aluminum.

In accordance with the invention, an all-alkaline soaking method is used to clean and prepare high aluminum content zinc alloys, particularly superplastic zinc alloys containing about 20 to about 22 percent aluminum by weight, whether in the superplastic state or not. The method conditions the alloy to receive electrodeposited metal coatings with adhesion characteristics comparable to those obtained on other zinc alloys, for example, zinc die casting alloys. The solutions used to carry out the method of the invention are also formulated to be mutually compatible, making drag-in from one solution to the next of little if any consequence.

To carry out the method the alloy is first conventionally degreased in a chlorinated solvent such as trichloroethylene or perchlorethylene. Following degreasing, the alloy is soaked clean, preferably for about 0.5 to about 2 minutes, and most preferably for about 1 minute in a solution of the following composition:

| | Grams per liter |
|---|---|
| Trisodium phosphate | 2.5 |
| Sodium metasilicate | 1.5 |
| Sodium hydroxide | 0.05 |
| Sodium lauryl sulfate | 0.5 |

The above solution should preferably be adjusted to a pH between 9 and 11 and most preferably about 10 by the addition of phosphoric acid. The preferred temperature for soaking is 140° F. to 175° F., and most preferably about 158° F. After soaking, the alloy is preferably rinsed for about 5 to 30 seconds, most preferably for about 10 seconds, in the following solution:

Sodium bicarbonate—3.3 to 3.5 grams per liter (preferably 3.37 grams per liter).

Sodium hydroxide—1.2 to 1.3 grams per liter (preferably 1.25 grams per liter).

The rinse solution is preferably adjusted to a pH of between 9 and 12, and most preferably between 10 and 11, and rinsing preferably takes place at room temperature. After rinsing the alloy is conditioned preferably for about 1 minute at room temperature in a 25 gram per liter solution of sodium cyanide.

The concentrations, pH's temperature and immersion times given above have been found to result in effective cleaning of the surfaces of articles fabricated of zinc alloys containing about 20 to about 22 percent aluminum, without surface attack thereof. Satisfactory adherence of subsequently electroplated metal coatings has also been found to occur when the conditioning method of the invention is employed.

After thus being conditioned in accordance with the invention, the alloy is ready for plating. Preliminarily, the alloy should be given about a 0.00005 inch coating of copper in a conventional copper strike solution, the alloy entering the solution with the current on. The following is an example of a cyanide copper strike plating solution and typical plating parameters found to give acceptable results in this regard:

| | Grams per liter |
|---|---|
| Copper cyanide | 18.5 |
| Sodium cyanide | 30.0 |
| Sodium carbonate | 15.0 |
| Rochelle salt | 22.5 |

Sodium hydroxide to pH 12.
Temperature, 131° F.
Cathode C.D., 40 a.s.f. (amperes per square foot).

In order to afford protection against chemical attack by the solution employed in subsequent plating operations, it is important that the alloy surface be completely coated with copper upon leaving the strike plating bath.

After copper striking as described, an additional coating or combination of coatings, as desired, can be plated on the alloy using conventional procedures. As with other zinc alloys, it is advisable to plate an additional 0.0003 inch of copper from a high efficiency bath on top of the copper strike coat before applying other coatings. If an acid high efficiency copper bath is employed for this purpose the cyanide copper strike coating should have a minimum thickness of about 0.0001 inch, that is, double that previously described.

Zinc alloys containing about 20 to about 22 percent aluminum which have been electroplated after having been conditioned in accordance with the invention, have been bent around a ¼ inch diameter mandrel without peeling (see ASTM Specification B489–68); they have also been baked for 30 minutes at 302° F. without blistering. It is found in fact that baking usually improves adhesion of electroplated coatings to high aluminum content alloys, whereas it has often had a deleterious effect in the case of conventional zinc alloys because of the formation of a thick, intermediate alloy layer. The high aluminum content of the subject alloys retards the rate of diffusion so that the morphology after baking more resembles that of conventional alloys in the as-plated condition.

A quantitative test for determining the degree of adhesion between a plated metal coating and a substrate is covered by ASTM Specification B533–70. In this test, one measures that tensile load acting at between 85 and 95 degrees to the substrate surface which is required to peel a 1 inch width of metal plating from the substrate at the rate of 0.9 to 1.1 inches per minute. The tensile load so determined is termed the "peel strength."

Using the ASTM test, the peel strengths of electroplated coatings deposited on 3 inch by 5 inch panels of both Zamak-3 alloy and a 22 percent aluminum containing zinc base alloy were determined. The panels of zinc-22 percent aluminum alloy were conditioned by the method of the invention, while the panels of Zamak-3 alloy were conditioned by the previously discussed conventional procedure which includes anodic cleaning in Oakite-295 and a dip in a 0.5 percent by weight solution of sulfuric acid. The electroplated coatings consisted of a 0.0003 inch copper layer covered by a 0.0017 inch layer of nickel, each deposited by conventional procedures.

| Alloy and condition | Peel strength, lbs./in. | |
|---|---|---|
| | As plated | Baked at 302° F., 30 mins. |
| Zinc-22% aluminum (as rolled) | 15 | 16 |
| Zamak-3 (die cast) | 20 | 20 |

With reference to the table, a peel strength of 5 pounds per inch is considered good in the case of plated ABS plastic.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above method and in the constructions set forth without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention, which as a matter of language, might be said to fall therebetween.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

**1.** The method of conditioning high aluminum content zinc alloys to receive adherent electroplated coatings, comprising, in combination, the steps of:

(A) soaking said alloy to clean the surface thereof in a solution having a pH adjusted to between about 9 and 11 by the addition of phosphoric acid and consisting essentially of about 2.5 grams per liter of trisodium phosphate, about 1.5 grams per liter of sodium metasilicate, about 0.05 gram per liter of sodium hydroxide and about 0.5 gram per liter of sodium lauryl sulfate,

(B) rinsing said alloy in a solution having a pH between about 9 and 12 and consisting essentially of between about 3.3 to about 3.5 grams per liter of sodium bicarbonate and between about 1.2 to about 1.3 grams per liter of sodium hydroxide, and

(C) conditioning said alloy in a solution consisting essentially of about 25 grams per liter of sodium cyanide.

**2.** The method of claim **1** including the step of preliminarily degreasing said alloy in a chlorinated solvent.

**3.** The method of claim **1** wherein said zinc alloy contains about 20 percent to about 22 percent aluminum by weight.

**4.** The method of claim **3** wherein said alloy is capable of exhibiting super-plasticity.

**5.** The method of claim **1** wherein said soaking is effected for about 0.5 to about 2.0 minutes.

**6.** The method of claim **5** wherein said soaking is effected for about 1 minute.

**7.** The method of claim **1** wherein said soaking is effected in said solution at a pH adjusted to about 10.

**8.** The method of claim **1** wherein said soaking is effected at a temperature between about 140° F. and about 175° F.

**9.** The method of claim **8** wherein said soaking is effected at a temperature of about 158° F.

**10.** The method of claim **1** wherein said rinsing is effected in a solution consisting essentially of about 3.37 grams per liter of sodium bicarbonate and about 1.25 grams per liter of sodium hydroxide.



**11.** The method of claim **1** wherein said rinsing is effected for about 5 to about 30 seconds.

**12.** The method of claim **11** wherein said rinsing is effected for about 10 seconds.

**13.** The method of claim **1** wherein said rinsing is effected in said solution at a pH between about 10 and 11.

**14.** The method of claim **1** wherein said rinsing is effected at room temperature.

**15.** The method of claim **1** wherein said conditioning is effected for about 1 minute.

**16.** The method of claim **1** wherein said conditioning is effected at room temperature.

**17.** The method of conditioning zinc alloys containing about 20 percent to about 22 percent aluminum by weight, to receive adherent electroplated coatings, comprising, in combination, the steps of:

(A) soaking said alloy for about 0.5 to about 2 minutes at a temperature between about 140° F. to about 175° F., in a solution having a pH adjusted to between about 9 and 11 by the addition of phosphoric acid and consisting essentially of about 2.5 grams per liter of trisodium phosphate, about 1.5 grams per liter of sodium metasilicate, about 0.05 gram per liter of sodium hydroxide and about 0.5 gram per liter of sodium lauryl sulfate,

(B) rinsing said alloy for about 5 to about 30 seconds at room temperature in a solution having a pH between about 9 and 12 and consisting essentially of between about 3.3 to about 3.5 grams per liter of sodium bicarbonate and between about 1.2 to about 1.3 grams per liter of sodium hydroxide, and

(C) conditioning said alloy for about 1 minute at room temperature in a solution consisting essentially of about 25 grams per liter of sodium cyanide.

**18.** The method of conditioning zinc alloys capable of exhibiting superplasticity and containing about 20 percent to about 22 percent aluminum by weight, to receive adherent electroplated coatings, comprising, in combination, the steps of:

(A) soaking said alloy for about 1 minute at a temperature of about 158° F., in a solution having a pH adjusted to about 10 by the addition of phosphoric acid and consisting essentially of about 2.5 grams per liter of trisodium phosphate, about 1.5 grams per liter of sodium metasilicate, about 0.05 gram per liter of sodium hydroxide and about 0.5 gram per liter of sodium lauryl sulfate,

(B) rinsing said alloy for about 10 seconds at room temperature in a solution having a pH between about 10 and 11 and consisting essentially of about 3.37 grams per liter of sodium bicarbonate and about 1.25 grams per liter of sodium hydroxide, and

(C) conditioning said alloy for about 1 minute at room temperature in a solution consisting essentially of about 25 grams per liter of sodium cyanide.

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