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[54] METHOD FOR AVOIDING PITTING IN PLATING OXIDE-FILM-DEVELOPING METALS

[75] Inventor: **Samuel S. Frey,** Elizabeth, N.J.

[73] Assignee: **Oakite Products Inc.,** Berkeley Heights, N.J.

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[60] Division of Ser. No. 787,589, Dec. 27, 1969, Pat. No. 3,684,719, which is a continuation-in-part of Ser. No. 447,089, April 9, 1965, Pat. No. 3,446,715.

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[51] **Int. Cl.** **C23g 1/10**

[58] **Field of Search** ..... 134/3, 27, 28, 29, 134/41; 252/79.3, 147, 148; 204/35 N, 141.5

[56] **References Cited**

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Primary Examiner—Morris O. Wolk
Assistant Examiner—D. G. Millman
Attorney—A. A. Orlinger

[57] **ABSTRACT**

The tendency to blistering and related adverse effects on adhesion of protective coatings to be applied over the surface of a metal oxidizable by anodization and capable of taking an electrodeposit, is reduced by forming an anodic film on the metal surface, and then removing that film with any natural oxide film on which it may have been formed, by immersing the oxidized surface in an aqueous pickling bath containing dissolved inorganic ferric salt, sulfuric acid or a bisulfate, and an inorganic fluoride.

5 Claims, No Drawings

METHOD FOR AVOIDING PITTING IN PLATING OXIDE-FILM-DEVELOPING METALS

This application is a division of copending application Ser. No. 787,589 filed Dec. 27, 1968, and now U.S. Pat. No. 3,684,719, which was a continuation-in-part of applicant's then copending application Ser. No. 447,089 filed Apr. 9, 1965 now U.S. Pat. No. 3,446,715. This invention is that of the conditioning of surfaces of metals and alloys thereof, the oxides of which ordinarily are soluble in sulfuric acid, and especially of zinc and zinc base alloys (jointly called "zinc surfaces") to receive a coating such as a protective coating and especially an electrodeposit. The invention more particularly is that of a method of conditioning such oxidizable metal and especially zinc surfaces, which usually are subjected to plating an electrodeposit over them, for such plating. The invention includes also a pickling process and baths and compositions used in this conditioning method. The method of the invention is applicable especially to conditioning surfaces of such zinc alloys which generally have no more than one percent of copper content, such as the alloy commonly known as Zamak—3 which contains about 0.1 percent of copper and is widely used for preparing die castings.

A very extensive number of metal surfaces composed of at least one metal whereon can be formed a so-called natural oxide film from contact with air, as well as an anodically-formed oxide film, especially such zinc alloy die castings, is given an electrodeposit, such as copper followed by nickel and then usually by chromium, for such use as parts (e.g. door handles, radiator ornaments, light reflector frames) for automobiles, and other products used in large numbers. While a number of attempts have been made to improve the preparation of these metal surfaces, e.g. the surfaces of such die castings, to take on satisfactory electrodeposits, that still remain a serious problem. Extensive improvement still is needed because of the considerable lack of surface uniformity and frequency of blistering which still is experienced with electrodeposits on these metal surfaces, particularly of zinc die castings.

While the invention is applicable to various types of such metal surfaces and zinc products which are to be electroplated, it is particularly applicable to such zinc metal and zinc alloy die castings. Accordingly, the specific nature of the invention will be described in relation to its applicability to those die castings without intent that it be limited merely to use with them.

These and other still existing shortcomings and disadvantages are significantly appreciably diminished, and to an unusual extent practically overcome, by using the method of the invention employing its baths and compositions.

An important part of the method of the invention is an initial stage wherein the zinc die casting is anodized in a stable, specific aqueous alkaline bath which provides a uniform anodized film over and integral with the usual oxide film (which conveniently is called the "natural film") ordinarily existing on the surface of the zinc base die castings.

A feature of this initial anodizing stage of the invention is its effective treatment of porous areas in the zinc surface to minimize possibility of their being a source for defects. Thereby they avoid the heretofore experienced entrapment of solutions used prior to and/or in the plating, which allowed their reacting with the zinc to generate hydrogen and cause blisters and other damage to the electrodeposit.

This stage of the invention involves immersing the preferably initially precleaned zinc surface in an aqueous anodizing bath containing a sufficient concentration of a water-soluble alkaline anodizing mixture as more fully described and exemplified in said U.S. Pat. No. 3,446,715 which issued on applicant's copending application Ser. No. 447,089, to produce a substantially uniform, adherent and from overall gray to black surface color change on the zinc surface by the anodizing procedure more fully described and exemplified in said copending application.

For said anodizing baths and procedure, see, for example column 2 line 6 to column 3 line 17 and column 4 to line 3 to column 6 line 31 of said U.S. Pat. No. 3,446,715 which issued from application Ser. No. 447,089.

A further significant aspect and succeeding stage of the method of the invention, broadly considered, involves subjecting the satisfactorily anodized zinc surface developed in the first stage treatment, desirably after an intermediate water rinse, to a specific pickling treatment by immersing the articles for from about 15 seconds to about 100 seconds, more effectively from about 35 seconds to about 90 seconds, to the action of an aqueous acid pickling bath containing a sufficient concentration of a pickling composition, either as a solid mixture or an aqueous liquid concentrate, having three essential cooperating pickling ingredients (a) a water-soluble inorganic ferric salt, (b) sulfuric acid or an alkali metal bisulfate, and (c) a water-soluble inorganic fluoride-ion-containing compound such as hydrofluoric acid, fluoroboric acid or fluorotitanic acid, or an alkali metal salt of any of those acids, or the ferric salt with a mixture of any of the (b) compounds, and a mixture of any of the (c) compounds, to provide a pH from about 0.8 to about 2.5 to enable substantially complete removal of the anodized film with the natural film in the above indicated time and at ambient temperature.

The essential pickling constituents of the solid pickling mixture include as principal agents an alkali metal (advantageously sodium) acid sulfate (i.e. bisulfate) and a water-soluble, advantageously inorganic ferric salt such as beneficially ferric sulfate, or ferric chloride or also ferric nitrate; and advantageously along with an alkali metal (preferably sodium) acid fluoride, or an alkali metal fluoroborate or fluorotitanate such as the sodium salt of either of the latter two salts, and also their ammonium salts.

The alkali metal, beneficially sodium, bisulfate can range from about 90 to about 9 parts with the water-soluble ferric salt ranging from about 10 to about 90 parts (that is to say, the higher the content of the bisulfate, the lower the ferric salt content), and advantageously there can be included with them generally about one part of the alkali metal bifluoride, preferably sodium acid fluoride (i.e. $NaHF_2$), or the fluoride-ion-containing equivalent amount of an alkali metal, such as the sodium, fluoroborate or fluorotitanate. The various respective parts of these constituents are by weight.

For the most part, that single part of sodium acid fluoride or equivalent amount of other water-soluble fluoride-ion-containing salt is adequate with the just above recited respective range of the sodium bisulfate

and the ferric salt. However, it is possible to include even up to 10 parts of the sodium bifluoride or the equivalent amount of sodium fluoroborate or fluorotitanate or mixtures of any of them with the noted respective ranges of the bisulfate and the ferric salt, and generally without adverse effect where the increased cost does not matter, although ordinarily it is more desirable to use the lower concentrations of the alkali metal bifluoride for generally simpler operation.

The principal or essential pickling constituents of the liquid pickling compositions are (a) the above-noted inorganic ferric salt, (b) an inorganic fluorine-ion-containing acid as hydrofluoric acid, fluoroboric acid, fluorotitanic acid or mixtures of any of them, and sulfuric acid, in solution in an amount of water sufficient to hold the ferric salt in solution.

For the liquid pickling concentrate, it is beneficial to use as the source of the ferric salt the commerically readily available aqueous solution containing 50 percent ferric sulfate and in the range from about 0.9 to 10 parts of that solution, from about 2 to about 4 parts of the 10 percent (as HF) aqueous hydrofluoric acid, and from about 0.5 part to about 8 parts of 66° Baume sulfuric acid, wherein all parts are by weight. The concentrate then can contain by weight from about 13 to about 22.5 percent of ferric sulfate (anhydrous basis), from 6 to about 2 percent of hydrogen fluoride, from about 13.5 to about 35 percent of H_2SO_4, and from about 67.5 to about 41.5 percent of water.

In each of the foregoing concentrates, the ferric sulfate can be replaced by the ferric ion equivalent amount of any other water-soluble inorganic ferric salt; and the hydrofluoric acid by the fluoride-containing equivalent of fluoroboric acid or fluorotitanic acid.

For generally good pickling operation, a pickling bath can be prepared with from about 1.5 to about 3.5 ounces (weight) of the solid mix per gallon of water, although somewhat less or more can be used to provide a pH from about 1.2 to about 2. The pickling bath then can contain, by weight, the inorganic ferric salt to the extent to provide from about 0.06 to about 0.33 percent of the ferric ion, the fluoric-containing compound to provide from about 0.01 to about 0.114 percent of fluoride ion equivalent, sulfuric acid to provide from about 0.52 to about 1.96 percent of sulfate ion (including any from ferric sulfate when it is used as the ferric salt), and from about 0.009 to about 0.190 of hydrogen ion from the acidic ingredients.

After immersion for the sufficiently short time to complete the pickling, the thus pickled zinc articles are removed from the pickling bath and subjected to a running, preferably cold, water rinse sufficient to remove entrained pickling solution and the pickling products. The anodized film and the natural oxide film are seen to be uniformly removed leaving an overall clean, matte, silvery fresh metal zinc surface. That is so also in any pores which thus were completely cleaned and so to allow a completely uniformly continuous electrodeposit to be plated over the entire surface without entrapping any plating solution.

A feature of this pickling treatment stage of the invention is such complete removal of both the anodized and natural films to expose the clean fresh zinc metal surfaces as just described.

A further feature of this aspect of the invention is accomplishment of such maximum removal of the films in a minimum of time, even as little as only 15 seconds in many cases and with such substantially low concentration of the combined acid pickling agents.

The solid pickling mixture compositions of the invention and the method of pickling with pickling baths prepared from them are illustrated by, but not restricted to, the following examples wherein parts are by weight:

Example 1 - Pickling Mix: 250 parts of ferric sulfate (with 9 H_2O water of crystallization) are admixed with 730 parts of anhydrous sodium acid sulfate and 15 parts of sodium acid fluoride (i.e. $NaHF_2$) or sodium bifluoride, all being technical grade and finely divided to permit mixing uniformly. The homogenous mixture is packed in drums of the same sizes as those in which the alkaline anodizing mixes are packed, namely, holding 170 pounds or 380 pounds net each respectively.

Example 2 — 40 parts of ferric sulfate, 50 parts of sodium bisulfate, and 10 parts of sodium bifluoride, and used in Example 1, are homogeneously mixed and similarly packaged in the same size drums.

Example 3 — 200 parts of the ferric sulfate, 790 parts of sodium bisulfate, and 10 parts of sodium bifluoride, as used in Example 1, are homogeneously mixed and similarly packed in the same size drums.

Example 4 — 100 parts of ferric sulfate, 890 parts of sodium bisulfate and 10 parts of sodium bifluoride, as used in Example 1, are homogeneously mixed and similarly packaged in the same size drums.

Other solid pickling mixes having various other proportions of the three ingredients of the preceding Examples 1 through 4 can be prepared within the ranges recited above. The ferric sulfate can be replaced in any of them by substantially equal weights of technical grade of ferric chloride ($6H_2O$ water of crystallization) or the ferric ion equivalent of ferric nitrate.

Similarly, in any of those solid mixes, the sodium bifluoride can be replaced by its fluoride ion equivalent of sodium fluoborate or sodium fluorotitanate. Likewise, any of the sodium salts used in any of these solid mixes can be replaced by any other practical alkali metal salt such as the corresponding potassium salt where the additional cost is not a factor or in an area where the potassium salt is competitively priced.

The sodium bifluoride used, or other alkali metal bifluoride mentioned as applicable, in, any of the foregoing examples or modifications of any of them can be replaced in part or as a whole by an equivalent amount of ammonium bifluoride to provide corresponding additional solid mix examples. Ordinarily, with the then resulting quite low percentage content of ammonium bifluoride in such solids mixes, there should be no concern about the deliquescent property of ammonium bifluoride itself, particularly if the drums in which the mixes are packed are airtight. Because of the closeness in molecular weight between sodium bifluoride and ammonium bifluoride, each of Examples 1–4 can be considered as if prepared with their respective sodium bifluoride content replaced by the same weight of ammonium bifluoride.

The following illustrative only and not restrictive examples illustrate liquid concentrates from which additional pickling baths can be prepared:

Example 5 — 45 parts of a 50 percent aqueous ferric sulfate solution is diluted with 13.6 parts of water. Into the resulting diluted solution are admixed 18 parts of a 10% (as HF) hydrofluoric acid and then 23.4 parts of

66° Baume sulfuric acid. The mixture is stirred to give a uniform pickling concentrate.

Example 6 — 35 parts of the 50 percent ferric sulfate solution are diluted with 23.6 parts of water and into the resulting dilute solution are admixed the same respective number of parts of the same hydrofluoric acid and sulfuric acid as used in Example 5, and the resulting mix agitated to uniformity.

Example 7 — 25 parts of the same 50 percent ferric sulfate solution are diluted with 33.6 parts of water, and into the resulting diluted solution are admixed the same respective number of parts of the same hydrofluoric acid and sulfuric acid as used in Example 5, and the resulting mix agitated to uniformity. Example 8 — Example 5 is repeated by reducing the ferric sulfate solution to 15 parts and increasing to 43.6 parts the water with which it is diluted.

Example 9 — Example 5 is repeated by increasing its ferric sulfate solution to 55 parts and reducing its water added for dilution to 3.6 parts.

Example 10 — 45 parts of the 50 percent aqueous solution of ferric sulfate are diluted with 27.8 parts of water. Into the diluted solution is admixed 3.8 parts of a 50 percent aqueous fluoroboric acid solution and also 23.4 parts of 66° Baume sulfuric acid, and the resulting mix agitated to uniformity.

Example 11 —40 Example 10 is repeated with its fluoroboric acid replaced by 10.2 parts of an aqueous solution containing 25 percent of ammonium bifluoride and its water for dilution reduced to 21.4 parts.

Example 12 — Example 10 is repeated with its water reduced to 27.5 parts and its fluoroboric acid replaced by 4.1 parts of an aqueous solution containing 60 percent of fluorotitantic acid.

In any of the Examples 5 through 12, the ferric sulfate can be replaced in part or as a whole by any other applicable inorganic water-soluble ferric salt; and so also the fluorine-containing acid of any of them can be replaced in part or as a whole by an equivalent amount of any other such acid or of an alkali metal salt of any of them.

Any of the liquid concentrates of any of the foregoing examples and above described modifications of them, and any others prepared by using the different principal pickling ingredients within the earlier above-mentioned respective ranges of content for them, can be used for preparing pickling baths of the invention by dissolving from about two to about four percent by volume of such concentrate per gallon of water, to provide a pickling bath within the earlier above pH range, and beneficially from about pH 0.9 to about 1.5 (electrometric).

A compatible wetting agent, beneficially anionic, can be included where seen to be helpful and generally to the extent of less than one percent.

Example 13 - Method of Pickling the Anodized Die Castings:

Water was run into a rubber-lined tank of 300 gallons capacity to over half of its capacity. There then was admixed a concentrated aqueous acid solution of the solid pickling mix of Example 1 to provide in the tank a dilute solution as a pickling bath having dissolved therein two ounces of that solid pickling mix per gallon of water at ambient temperature. The pH of the resulting pickling bath was 1.5.

Racked, cold water rinsed anodized door handle zinc die castings, e.g. the anodized product of Example 6 of the aforesaid U.S. Pat. No. 3,446,715 issued on application Ser. No. 447,089, then were completely immersed in that (dilute) acid pickling bath for a full half minute of immersion time, after which they were removed and rinsed with sufficient cold running water to remove entrained pickling bath solution. The rinsed castings presented an overall clean, matte, silvery sheen of the fresh metal zinc surface exposed after removal of the dark brown to black anodized film and with it also the natural oxide film that was present on the castings before their surfaces were anodized by the method of said Example 6.

The thus pickled and rinsed zinc die castings then were ready for electroplating, and so were electroplated in the customary manner with a copper strike, then regular copper electroplate, followed by nickel plate and finally chrome plate. The plated castings showed improved luster and overall appearance and enhanced adhesion of the electrodeposits particularly on unbuffed areas of the castings, as well as on the buffed areas.

The procedure of Example 13 can be repeated in the same way by using in place of the solid pickling mix of Example 1 the solid pickling mix of any of Example 2, 3 and 4, or of any of the earlier described possible modifications of them, separately respectively and at the same concentration as in Example 13 or any suitable different concentration within the range disclosed herein and similarly for 30 seconds or more up to 90 seconds as any modification in pickling agents and working concentration may indicate to be necessary.

So also the pickling process of Example 13 can be repeated similarly by using the liquid pickling concentrate of any of the Examples 5 through 12, or of any of the described possible modifications of them, at a concentration disclosed for them and optimally with the pickling bath at a pH of from about 0.9 to about 1.5 and immersion in the bath for from about 45 to about 90 seconds.

Tests with acid pickling baths prepared separately from the solid pickling mix of each of the Examples 1 through 4, as well as from the liquid pickling concentrate of Examples 5 through 12, showed satisfactory removal of similarly prepared anodic films together with the underlying natural film from other Zamak-3 zinc surfaces, at their same respective concentrations in as little as 15 seconds and also that they can be retained in the pickling bath for 45 to 60 seconds and even up to 90 seconds.

Where the anodized film is heavier because of longer application of the current in the anodizing procedure, such heavier anodized coatings can be removed either by extending the immersion in the acid pickling bath up to 60 or 90 seconds. Alternatively, such heavier coating can be removed by increasing the concentration of the pickling mix or liquid concentrate in the bath to any suitable concentration within the disclosed ranges as a quick simple test on one or two castings, or areas of a single casting or panels, of the same zinc alloy might show that immersion of the casting or portion of it or panel in the acid pickling solution at a particular concentration removes fully the colored anodized film with the underlying natural film and exposes the silvery sheen of the freshly exposed zinc.

Obviously, variations in the individual activity of different acid pickling baths will vary with their respective individual compositions within the ranges recited ear-

lier above. For example, an aqueous acid pickling bath prepared from the acid pickling mix of Example 1 shows satisfactory effectiveness when used in a concentration even as low as one ounce, as well as between one and two ounches, per gallon.

Then also, an aqueous acid pickling bath prepared from one ounce per gallon of the acid pickling mix of Example 4 shows satisfactory effectiveness in a full minute, whereas at a concentration of two ounches per gallon the separate different acid pickling bath from the pickling mix of each of the Examples 1 through 4 shows full effectiveness in from as little as 15 seconds to one minute.

Then also, an aqueous acid pickling bath prepared from two ounces per gallon of an acid pickling mix containing 60 parts of the ferric sulfate, 39 parts of the sodium bisulfate, and 1 part of the sodium bifluoride is equal in effectiveness to the aqueous pickling bath of the same concentration of the mix of Example 1, but only in the immersion range of 30 to 60 seconds, and is effective in an immersion time of as little as 15 seconds at a concentration of four ounces per gallon. The aqueous acid pickling bath prepared from one to two ounces of the pickling mix containing ten parts of the ferric sulfate, 80 parts of the sodium bisulfate, and 10 parts of the sodium bifluoride requires an immersion time of more than 30 seconds but up to one minute to be as effective as is the same concentration bath from the mix of Example 2 in an immersion time of as little as 15 seconds.

Both the solid pickling mixes and the liquid pickling concentrates as well as their respective pickling baths are easily prepared. Their effectiveness is readily tested by easy electro-deposition application of ordinary copper plate, followed by nickel plate, and then with the easy test of baking at a reasonably elevated temperature, say, within 275° to 300°F., to see whether blistering or flaking can occur, within an hour.

The pickling baths from both the solid mixes and the liquid concentrates, because of their effective quick action within such short time respectively, and long service life, are compatible with, and readily can be, and have been, included in, the modern automatic rack-holding conveyor continuous systems.

The pickling bath from either a solid mix or a liquid concentrate is quite easily controlled not only as to its maintenance but also as to its continuing effectiveness in operation. In that connection, only visual observation is needed to follow the proper operation of these baths, for example, by watching for the development of the overall matte, silvery sheen of the freshly exposed zinc surfaces when both the anodized film and the natural oxide film are removed in the pickling operation.

The anodizing step followed by the pickling stage conditions the basis fresh zinc surface for the subsequent preliminary copper plating deemed necessary before nickel is to be deposited over zinc.

The pickling treatment of the invention provides for uniform removal of the natural film as well as the particular anodized film in minimum operating time with low and minimum concentrations of pickling agents.

The pickling mixes and also liquid pickling concentrates of the invention are useful also for preparing pickling baths of the compositions described hereinabove for use by the method of the invention also in likewise stripping oxide films from the surfaces of other metals on which a natural oxide film can form during contact with air, for example, as with aluminum, and on which an oxide film can be formed by an anodizing treatment. Such use on such other metals can be illustrated, for example, by replacing the zinc die castings in Example 13 above by (a) aluminum parts coated with a natural aluminum oxide film, and alternatively by (b) anodized aluminum parts.

While the invention has been explained in detail by describing certain specific embodiments of it, it is understood that various modifications and substitutions may be made in any of the specific emodiments within the scope of the appended claims which are intended also to cover equivalents of the specific embodiments.

What is claimed is:

1. The method of reducing the tendency to blistering and related adverse effects on the adhesion of protective coatings to be applied over the surface of a metal oxidizable by anodizing treatment and having a composition to which an electrodeposit can be applied, which method comprises forming on said metal surface an overall oxide film by anodic oxidation, and thereafter removing said resulting anodic film along with any natural oxide film on which said anodic film may have been formed, by immersing the oxide film -coated surface in an aqueous acid pickling bath having a pH of from about 0.8 to about 2.5 and containing dissolved in its water a sufficient amount, to provide said pH, of a mixture composition consisting essentially of the cooperating agents (i) a water-soluble inorganic ferric salt in an amount wherein its iron content is equivalent to from about 10 to about 90 parts of crystalline ferric sulfate, (ii) at least one of the alkali metal bisulfates and sulfuric acid and in an amount equivalent in acidity to form about 90 to about 9 parts of sodium bisulfate, and (iii) at least one water-soluble inorganic fluorine-element-containing compound of the formula M-D wherein M is a cation selected from hydrogen, an alkali metal, and the ammonium group, and D is a fluorine-element-containing anion, said compound being in an amount wherein its fluorine content is equivalent to that of sodium bifluoride present to the extent of from about 0.1 to about one percent by weight of said cooperating agents; and allowing said immersion to continue for a time sufficient for the oxide film to be removed as shown by the appearance of a clean fresh metal sheen over the immersed surface.

2. The method as claimed in claim **15**, wherein said pickling bath contains dissolved in its water from about one to five percent by volume of an aqueous solution containing about 22.5 percent of ferric sulfate, about 23.5 percent of 66° Baume sulfuric acid, and about 1.8 percent of hydrogen fluoride.

3. The method as claimed in claim **2**, wherein said bath contains in percentage by weight thereof, from about 0.06 to about 0.33 of ferric ion, from about 0.01 to about 0.114 of fluoride ion, from about 0.52 to about 1.96 of sulfate ion, and from about 0.009 to about 0.190 of hydrogen ion.

4. The method as claimed in claim **15**, wherein said pickling bath contains by weight from about 0.18 to about 0.54 percent of ferric ion provided by crystalline ferric sulfate, from about 0.59 to about 1.76 percent of sulfate ion provided by sodium bisulfate, and from about 0.006 to about 0.018 percent of fluoride ion provided by sodium bifluoride, and the pH is from about 1.2 to about 2.5.

5. The method of reducing the tendency to blistering and related adverse effects as claimed in claim **4**, wherein the ferric salt is ferric sulfate, the bisulfate is sodium bisulfate, and the fluorine-element-containing compound is sodium bifluoride.

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