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METAL TREATING

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ABSTRACT OF THE DISCLOSURE

A method of plating a zinc surface by anodizing, then pickling the anodized surface in a solution of an alkali metal bisulfate, an inorganic ferric salt and an alkali metal bifluoride, then electroplating the pickled surface.

This invention relates to the conditioning of surfaces 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 zinc surfaces which usually are subjected to plating an electrodeposit over them, and includes also the baths and compositions used to provide such conditioning. 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% of copper and is widely used for preparing die castings.

A very extensive number of such zinc alloy die castings is given electrodeposits, 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 the surfaces of such die castings to take on satisfactory electrodeposits, that still remains 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 zinc die castings.

While the invention is applicable to various types of 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 the method of the invention employing the baths and compositions embraced as parts of it.

An important aspect of the invention is an initial treatment wherein the zinc die casting is anodized in the stable, specific aqueous alkaline bath, resulting in providing 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. The resulting film is in addition lustrous over any initially buffed areas.

A feature of this initial stage of the invention is the stability, easy control, quick-action, and long life of the anodizing bath.

Another feature of the anodizing stage of the invention is its effective treatment of the pores in the zinc surface to minimize the possibility of their being a source for defects, whereby 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.

In its broadest aspect, the invention involves immersing the preferably initially precleaned zinc surface in an aqueous anodizing bath containing a sufficient concentration, beneficially from about 5.5 to about nine ounces per gallon of water, of a water-soluble alkaline anodizing mixture to provide a pH greater than 11 and under 14, and beneficially from about 12.8 to about 13.6, to enable producing a substantially uniform, adherent from overall gray to black surface color change on the zinc surface on passing a current from the zinc surface as an anode to a cathode for a period of from about 40 to about 90 seconds at a current density of from about 25 to 100 amperes per square foot at a voltage of from about 2 to about 8 volts and with the bath at a temperature from about 140 to 180° F.

The water-soluble alkaline anodizing mixture comprises as its essential alkali-providing constituents from about one to about six parts of an alkali metal hydroxide (preferably sodium hydroxide) to from about six to about one part of either one or both together of a water-soluble alkali metal silicate (also preferably sodium) and a hydrated alkali metal orthophosphate (preferably trisodium phosphate). This hydrated orthophosphate can be replaced in whole or in part by the equivalent quantity of a corresponding anhydrous orthophosphate or the dialkali metal hydrogen phosphate together with alkali metal hydroxide at least stoichiometrically equivalent to the hydrogen of that phosphate.

Sodium metasilicate is the preferred alkali metal silicate, but can be replaced in part or as a whole by the alkali equivalent of any other water-soluble alkali metal silicate such as its orthosilicate or sequisilicate or pentasilicate. Because of its lower cost sodium is the preferred alkali metal cation for these several alkali-providing constituents. However, any other alkali metal cation, such as potassium, can be the cation of any of these alkali-providing constituents when difference in cost does not matter or in those areas where a cost differential does not occur.

The mixture of alkali-providing constituents is prepared as a dry mix by using the anhydrous form of the respective alkalis. In such mixes, an anhydrous alkali metal carbonate, preferably sodium carbonate, can be admixed up to about 5% of the total mixture, to enhance avoiding caking. Such dry mix can include a small percentage of from about one to about a few percent of a suitable compatible finely divided solid wetting agent. The latter may even be of liquid form for inclusion with the alkali-providing constituents when they are prepared as an aqueous concentrate.

In the greater number of cases, about 7.25 ounces (by weight of solids) of the alkali-providing constituents per gallon of water (providing a pH of about 13) and with voltage at about 6 volts and current density of about 60 amperes/square foot (i.e., a.s.f.) produce within about a minute at about 160° F. an overall gray to black colored, satisfactory anodized coating over the zinc surface. It is possible to operate also at lower current density even as low as 10 a.s.f., but desirably no lower because of danger of alkaline etch, and up to about 130 a.s.f., and generally at about 70 a.s.f.

Operation also is possible at lower or even at higher temperature but preferably below boiling, and perhaps better not over 190° or 180° F., but better still around 160°, although operation is satisfactory at about 120° F. The lower the temperature and/or current density, obviously the longer time is required. Thus, if lower current density may be desirable in some cases, it may be helpful to increase the temperature within practical operating limits.

The just earlier noted concentration of 7.25 ounces (by weight on solid basis) and also up to at least about 8 ounces by weight of those solids per gallon of water provide good practical operating conductivity. Concentrations up to about 10 ounces per gallon can be used, but at higher concentration it is advisable to work at lower voltage. It is also possible to obtain good results at a lower concentration such as down to about 6 ounces by weight of alkali solids per gallon of water.

For the most part, satisfactory solutions can give the desired uniform gray through brown to black anodized coatings in the average time of a minute. The more conductive solutions may provide such visibly observable coatings even in about a half minute, and a less active composition may require up to possible a minute and a half to provide the desired result, all depending on the overall conditions.

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 50 seconds to the action of an aqueous acid pickling bath containing a sufficient concentration, of more generally from about one and one-half to about three and one-half ounces by weight of a water-soluble acid pickling mixture, per gallon of water, to provide a pH from about 1.2 to about 2, to enable substantially complete removal of the anodized film with the natural film in the indicated time at ambient temperature.

The essential pickling constituents of the 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 preferably ferric sulfate, or ferric chloride, and also ferric nitrate; and advantageously along with an alkali metal (preferably sodium) acid fluoride.

The alkali metal, preferably 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 may be included with them generally about one part of the alkali metal bifluoride, preferably sodium acid fluoride (i.e., $NaHF_2$).

For the most part, that single part of sodium acid fluoride is adequate with the sodium bisulfate and the ferric salt within the just above recited ranges for them. However, it is possible to include even up to 10 parts of the sodium bifluoride with the noted 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.

After the sufficiently short time to complete the pickling, the thus pickled zinc articles are removed from the pickling bath and subjected to a running water rinse sufficient to remove entrained pickling solutions 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 clean and so allow a completely uniformly continuous electrodeposit to be plated over the entire surface without entrapping any liquid.

A feature of this pickling treatment portion of the invention is such complete removal of both the anodized and natural films to expose the clean fresh zinc metal surface 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 anodizing procedure, aqueous alkali baths used for it, and mixtures of alkali-providing constituents for use in such baths, are illustrated by, but not restricted to, the following examples:

Example 1—Sodium hydroxide and sodium metasilicate mixes.—Three separate mixes were prepared containing (a) equal parts of sodium hydroxide and sodium metasilicate, (b) three parts of the hydroxide to one of the metasilicate, (c) six parts of the hydroxide to one part of the silicate, (d) one part of the hydroxide to three parts of the silicate, and (e) one part of the hydroxide to six parts of the silicate.

In any of these five mixes of this Example 1, namely, (a), (b), (c), (d), and (e), the sodium metasilicate can be replaced by the alkali equivalent of any of the other sodium silicates such as sodium orthosilicate, sodium sesquisilicate, or sodium pentasilicate; or any of these sodium silicates can be replaced by the alkali equivalent of any other alkali metal silicate such as the corresponding potassium silicate.

Example 2—Sodium hydroxide and trisodium phosphate mixes.—Mixes were prepared from (a) equal parts of sodium hydroxide and hydrated trisodium phosphate, (b) three parts of the hydroxide to one part of that phosphate, (c) six parts of the hydroxide to one part of that phosphate, (d) one part of the hydroxide to three parts of that phosphate, and (e) one part of the hydroxide to six parts of the phosphate.

The hydrated trisodium phosphate in any of the mixes of Example 2(a) through (e) can be replaced by the equivalent amount of anhydrous trisodium phosphate and similarly with the equivalent amount of anhydrous disodium hydrogen phosphate together with the stoichiometrically equivalent amount of sodium hydroxide to neutralize the hydrogen ion of the disodium hydrogen phosphate. Any of these ten different anhydrous mixes containing anhydrous trisodium phosphate or disodium hydrogen phosphate can be admixed further with sodium carbonate to the extent of 5% of the total of each such mixture to enhance avoiding caking. In any event, the specific sodium phosphate or sodium carbonate can be replaced by the equivalent alkali amount of the corresponding alkali metal phosphate or carbonate respectively such as tripotassium phosphate or dipotassium hydrogen phosphate respectively.

So also, the sodium hydroxide in any of the five subdivisions of each Examples 1 and 2 can be replaced by the equivalent quantity of potassium hydroxide.

Example 3—Mixes of sodium hydroxide, trisodium phosphate, and sodium silicate.—The anhydrous trisodium phosphate replacing all of the hydrated trisodium phosphate in the 5 subdivisions of Example 2 is replaced respecively to the extent of from about 1 to about 99% respectively by anhydrous sodium metasilicate, thereby yielding corresponding mixes containing the same percentage of sodium hydroxide without change in each of the subdivisions of Example 2 but with from 1 to 99% of the anhydrous trisodium phosphate replaced by anhydrous sodium metasilicate. That provides the corresponding mixes containing sodium hydroxide, anhydrous trisodium phosphate, and anhydrous sodium metasilicate. In each of these different mixes of each of those three different alkali-providing constituents, there can be added up to 5% by weight of the total mix of sodium carbonate to enhance their free flowing character.

Example 4—Mixtures of sodium hydroxide, trisodium phosphate, and sodium metasilicate.—(a) Thirty-one parts of finely divided sodium hydroxide are admixed with 41.6 parts of anhydrous sodium metasilicate and 18 parts of anhydrous trisodium phosphate. (b) 95.5 parts of the mixture of this Example 4(a) are admixed with 4.5 parts of anhydrous sodium carbonate.

Example 5—Mixtures of caustic soda, anhydrous disodium hydrogen phosphate, sodium metasilicate, and sodium carbonate.—(a) 33.8 parts of finely divided caustic soda are admixed with 17.8 parts of anhydrous disodium hydrogen phosphate and 38.2 parts of anhydrous sodium metasilicate. (b) 95 parts of the mixture of the Example 5(a) are admixed with 5 parts of anhydrous sodium carbonate.

Example 6—Anodizing method.—Into a steel (anodizing) tank there was charged an aqueous alkaline solution containing seven and three-quarters ounces of the anodizing mixture of Example 5(b) dissolved per gallon of water, to the level of the top of steel cathodes suspended at one end of the tank. The solution had been preheated so that its temperature in the tank was 160° F. Precleaned and buffed (automobile door handle) zinc die castings, suspended from a suitable rack, then were immersed in the solution as the anodes.

The system was set up so that after the die castings were immersed with the solution covering their entire surfaces to be anodized, the current was turned on at 6 volts to furnish 60 amperes per square foot of area to be anodized. The current was kept on for 60 seconds when the castings appeared to have taken on a very dark brown to black color over their entire immersed surfaces. The current then was turned off and the thus anodized door handle zinc die castings were removed from the anodizing bath and rinsed with cold running water.

Operating the foregoing procedure at 160° F. (71° C.) satisfactory anodic films were formed on buffed Zamak-3 zinc die castings in one minute by separate use of each of the following aqueous alkaline anodizing baths at their respectively below noted concentrations and current density ranges:

Equal parts of the sodium silicate and sodium hydroxide as in Example 1(a) at 40 grams per liter from 10 through 120 a.s.f., at 70 grams per liter from 10 through 50 a.s.f., and at 20 grams per liter at 10 to 20 a.s.f.;

The mix of Example 1(b) at 20 grams per liter from 10 through 110 a.s.f., at 40 grams per liter from 10 to 30 a.s.f., and at 70 grams per liter from 10 through 40 a.s.f.;

The mix of Example 1(c) at 20 grams per liter from 10 through 120 a.s.f., at 40 and also at 70 grams per liter from 10 to 20 a.s.f.;

The mix of Example 1(d) at 70 grams per liter from 10 through 110 a.s.f., at 40 grams per liter from 10 through 120 a.s.f., and at 20 grams per liter from 10 to 20 a.s.f.; and

The mix of Example 1(e) at 70 grams per liter from 10 through 100 a.s.f., at 40 grams per liter from 10 through 50 a.s.f., and at 20 grams per liter from 10 to 30 a.s.f.

Such satisfactory films also were obtained with the mixes of Example 2, with that of Example 2(a) at 20 grams per liter from 10 through 110 a.s.f., at 40 grams per liter from 10 to 100 a.s.f., and at 70 grams per liter from 10 to 20 a.s.f.

The mix of Example 2(b) at 20 grams per liter from 10 through 60 a.s.f., at 40 grams per liter from 10 to 30 a.s.f., and at 70 grams per liter from 10 to 20 a.s.f.;

The mix of Example 2(c) at 20 grams per liter from 10 to 40 a.s.f., and at 40 and 70 grams per liter each from 10 to 20 a.s.f.;

The mix of Example 2(d) at 70 grams per liter from 10 through 120 a.s.f., at 40 grams per liter from 10 through 80 a.s.f., and at 20 grams per liter from 10 to 50 a.s.f.; and

With the mix of Example 2(e) at 70 grams per liter from 10 through 120 a.s.f., with 40 grams per liter from 10 through 70 a.s.f., and at 20 grams per liter from 10 to 40 a.s.f.

Illustrations of the colors of satisfactory anodic films obtained on buffed Zamak-3 zinc die castings in one minute runs at 160° F. with mixes containing different ratios and concentrations of hydrated trisodium phosphate (i.e., $Na_3PO_4 \cdot 10H_2O$) and sodium hydroxide at various current densities are respectively as follows:

With the mix of Example 2(a) at 20 grams per liter was brown at 10 to 40 a.s.f., and black at 50 to 80 a.s.f.; at 40 grams per liter was brown at 10 a.s.f., and black at 20 through 80 a.s.f.; and at 70 grams per liter was gray at 10 a.s.f.;

With the mix of Example 2(b) at 20 grams per liter was brown at 10 to 20 a.s.f. and black at 30 to 50 a.s.f., at 40 grams per liter was gray at 10 to 20 a.s.f. and black at 30 a.s.f., and at 70 grams per liter was gray at 10 a.s.f.;

With the mix of Example 2(c) at 20 grams per liter was brown at 10 to 20 a.s.f. and black at 30 to 40 a.s.f., and at 40 and also 70 grams per liter was gray at 10 a.s.f.;

With the mix of Example 2(d) at 70 grams per liter was brown at 10 to 20 a.s.f., and black at 20 through 80 a.s.f.; at 40 grams per liter was brown at 10 and at 40 a.s.f., gray at 20, 30, 50 and 60 a.s.f., and black at 70 and 80 a.s.f.; and

With the mix of Example 2(e) at 120 grams per liter was brown at 10 a.s.f., and black at 20 through 80 a.s.f.; at 70 grams per liter was brown at 10 through 60 a.s.f., and black at 70–80 a.s.f.; at 40 grams per liter was brown at 10 to 20 a.s.f., and gray at 30 through 70 a.s.f.; and at 20 grams per liter was gray at from 10 to 40 a.s.f.

The results indicate that these highly alkaline anodizing solutions apparently take no zinc metal into solution but merely oxidize the surface metals without any indicated solution of any of the oxide film produced by the anodization.

The pickling solutions of the invention and the method of pickling with them are illustrated by, but not restricted to, the following examples:

Example 7—Acid pickling mix.—250 parts of ferric sulfate (with $9H_2O$ water of crystallization) are admixed with 730 parts of anhydrous sodium acid sulfate and 15 parts of sodium acid fluoride (i.e., $NaHF_2$), all being finely divided and technical grade. 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 8.—40 parts of ferric sulfate, 50 parts of sodium bisulfate, and 10 parts of sodium bifluoride (i.e., $NaHF_2$), as used in Example 7, are homogeneously mixed and similarly packaged in the same size drums.

Example 9.—200 parts of the ferric sulfate, 790 parts of sodium bisulfate, and 10 parts of sodium bifluoride, as used in Example 7, are homogeneously mixed and similarly packed in the same size drums.

Example 10.—100 parts of ferric sulfate, 890 parts of sodium bisulfate and 10 parts of sodium bifluoride, as used in Example 7, are homogeneously mixed and similarly packaged in the same size drums.

Other acid pickling mixes having various other proportions of the three ingredients of the preceding Examples 7 through 10 can be prepared within the ranges recited above column—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 these mixes the sodium bifluoride can be replaced by its fluoride ion equivalent of sodium fluoborate. Likewise, any of these three sodium salts used in any of them 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.

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

Example 11—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 pickling solu-

tion of the acid pickling mix of Example 7 to provide in the tank a dilute pickling bath having dissolved therein two ounces of that pickling mix per gallon of water at ambient temperature. The pH of the dilute bath was 1.5. The racked, cold water rinsed anodized door handle zinc die castings, the anodized product of Example 6, then were completely immersed in that 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 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 appearance and adhesion of the electrodeposits particularly on the unbuffed areas of the castings.

The procedure of Example 11 can be repeated in the same way by using in place of the acid pickling mix of Example 6 the acid pickling mix of any of the other Examples 8, 9 and 10 separately respectively also at a concentration of 2 ounces per gallon and likewise for 30 seconds.

Tests with acid pickling baths prepared separately from the acid pickling mix of each of the Examples 7 through 10 showed satisfactory removal of similarly prepared anodic films together with the underlying natural film from other Zamak-3 zinc surfaces, at the same two ounce per gallon concentration in as little as 15 seconds and also that they can be retained in the pickling bath even for 60 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 to 60 seconds. Alternatively, such heavier coating can be removed by increasing the concentration of the pickling mix in the bath, say, to 2.5 or 3 or 3.5 or up to 4 ounces per gallon, or any suitable concentration within that range 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 column—above. For example, an aqueous acid pickling bath prepared from the acid pickling mix of Example 7 shows satisfactory effectiveness when used in a concentration even as low as one ounce, as well as between one and two ounces, per gallon.

Then also, an aqueous acid pickling bath prepared from one ounce per gallon of the acid pickling mix of Example 10 shows satisfactory effectiveness in a full minute, whereas at a cencentration of two ounces per gallon the separate different acid pickling bath from the pickling mix of each of the Examples 7 through 10 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 7, 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 8 in an immersion time of as little as 15 seconds.

Both the anodizing and the pickling mixes and their respective anodizing and pickling baths are easily prepared. Their effectiveness is readily tested by easy electrodeposition 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.

Both the anodizing bath and the pickling bath, 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. For example, the anodizing bath at eight ounces of the mix of Example 4 per gallon thus far has been found to last for at least six weeks and with as little maintenance addition as one-half ounce per gallon per week.

Also, the anodizing bath, as well as the pickling bath, 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 each of the baths, for example, (a) watching for the development of the overall gray to brown or black appearance of the anodized film in that operation, and (b) only for 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 operation of the invention is effective even on surface areas showing a high degree of irregularity. The anodized films produced are fully continuous, adherent and cannot be wiped off. In many cases it may be possible to avoid the preliminary buffing or at least to reduce its extent, before the anodizing step.

The anodizing step and subsequent pickling conditions the basis fresh zinc surface for the subsequent preliminary copper plating deemed necessary before nickel 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 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 anoxide 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 11 above by (a) aluminum parts coated with a natural aluminum oxide film, and alternatively by (b) anodized aluminum parts.

In the anodizing treatment of the invention, when the pH of the anodizing electrolyte bath is low, e.g., possibly at about 12 and lower, it may be found to be desirable to operate within the lower part of the current density range disclosed hereinabove as effective.

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 embodiments within the scope of the appended claims which are intended also to cover equivalents of the specific embodiments.

The contents of the foregoing Examples 7 to 11 and the

related disclosure concerning pickling compositions, mixes, aqueous pickling baths and the pickling method are included in applicant's copending application Ser. No. 787,589, filed Dec. 27, 1968, wherein the subject matter of those compositions, mixes, baths and method are described and claimed in broader scope.

What is claimed is:

1. In the method of reducing the tendency to blistering and related adverse effects on the adhesion of protective coatings to be applied over zinc surfaces having a composition to which electrodeposits can be applied, the combination of steps which comprises

(a) subjecting said zinc surfaces to any of the customary preliminary liquid solution and detergent precleaning steps indicated to be needed;

(b) connecting said zinc surfaces so as to be the anode immersed in an alkaline electrolyte in an electrolytic cell, which electrolyte is an aqueous alkaline anodizing bath having dissolved in its water a quantity sufficient to provide therein a pH in excess of 11 and under 14 of a mixture of cooperating water-soluble alkaline anodizing agents comprising (i) from about one to about six parts of an alkali metal hydroxide to (ii) from about six to about one part of at least one member of the class consisting of a water-soluble alkali metal silicate and an alkali metal orthophosphate with the latter calculated as if having ten molecules of water of crystallization; said electrolyte being maintained at a temperature from about 120° to about 190° F.; the cathode of said electrolytic cell being substantially nonreactive chemically with the electrolyte under the operating conditions; and

(c) passing an electric current through said cell with said immersed zinc surfaces as the anode, before significant chemical reaction of the alkaline electrolyte can occur on them and at an anode current density from in the neighborhood of about ten amperes per square foot and at least sufficient for anodic reaction to occur in preference to chemical attack on the anode and up to about 130 amperes per square foot and for a time sufficient to form on said zinc surfaces to be treated a substantially overall continuous anodic film which is colored in the range of from gray to brown to black; and using a voltage sufficient to provide the aforesaid current density.

2. The method as claimed in claim 1, wherein the alkali metal hydroxide used in it consists essentially of sodium hydroxide, and any water-soluble alkali metal silicate present consists essentially of the corresponding sodium silicate; and any alkali metal orthophosphate present consists essentially of corresponding sodium orthophosphate.

3. The method as claimed in claim 2, which along with its sodium hydroxide anodizing agent includes an alkali metal silicate consisting essentially of sodium metasilicate and also an alkali metal orthophosphate consisting essentially of trisodium phosphate.

4. The method as claimed in claim 3, wherein the alkaline anodizing agents are present in the ratio of roughly about 31 parts of sodium hydroxide, roughly about 41.6 parts of anhydrous sodium metasilicate, and roughly about 18 parts of anhydrous trisodium phosphate.

5. The method as claimed in claim 1, wherein the pH of the electrolyte is from about 12.8 to about 13.6.

6. The method as claimed in claim 1, wherein the electrolyte bath temperature is from about 140 to about 180° F.

7. The method as claimed in claim 1, wherein the copper content of the zinc surface is from about 0.1 to 1 percent.

8. The process as claimed in claim 1, wherein the average current density is from about 60 to about 90 amperes per square foot.

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