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PROCESS OF TREATING ZINC CASTINGS

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This invention relates to an improved acidic chromate solution for providing chemical polishing of zinc die cast surfaces with the additional advantages of forming a film which will protect against corrosion.

A primary object of this invention is to produce a bright corrosion-resistant surface on zinc casings by a simple chemical treatment, such as by dipping or immersion.

Another object of this invention is to provide a bright surface on zinc castings and then plating over such surface with copper or nickel or chromium, thus eliminating the cost of buffing, burnishing, etc.

An equally important object of this invention is to provide an aqueous acidic chromate solution for obtaining a bright chemically polished surface on zinc castings such as sand and die castings, and provide the same with a clear, corrosion-protective, chromate conversion coating. Such coating is also useful as a final finish or as a base for paint and the usual electroplated deposits, such as copper, nickel or chromium. The bright surface coating, with or without the subsequent electroplated coatings, will preclude the need for hand buffing or substantially lessen the necessity for conventional finishing treatments.

All previous solutions and compounds suitable for producing chromate surface conversion coating on zinc plate, galvanized metal, etc. have one of two effects on zinc die castings. In one case, the bath has an almost negligible attack on the metal and a protective film is deposited without the occurrence of any chemical polishing or brightening. On the other hand, if the attack is appreciable, the aluminum and other alloying constituents are dissolved more slowly than the zinc and the surfaces are etched and left with a dark gray smut of undissolved material.

The solutions of this invention attack the metal sufficiently to produce chemical polishing without leaving a smut. A chromate surface conversion coating is deposited on the metal at the same time. This coating varies from an extremely thin type which is practically invisible to a thicker coating having a pronounced yellow color. The coatings of this invention have a generally higher degree of corrosion protection than similar coatings from solutions formulated for use on pure zinc only.

In the three tables which follow, examples useful in carrying out the aims of this invention are shown. The materials used are as follows: CrO_3, chromic acid anhydride, NH_4HF_2, ammonium acid fluoride, for which the

acid fluorides of metals may be substituted in quantities to provide an equivalent fluoride concentration, e.g., KF, potassium fluoride, for which sodium or ammonium fluorides may be substituted as above, HF, hydrofluoric acid concentration 30% to 60% by weight, preferably 60% by weight, sp. gr. 1.24, but commercial grades of hydrofluoric acid, namely, 48% to 52% have been successfuly used in the various examples, HNO_3, nitric acid, preferably 61.4% by weight, sp. gr. 1.38, but commercial concentrations of from 58% to 72% have been used in the various examples successfully, H_2SO_4, sulfuric acid, preferably 93.5% by weight, sp. gr. 1.84 but commercial grades from 60% to 93.5% have been successfully used in the various examples, HAc, acetic acid, glacial, 99.5%, sp gr. 1.05, but 80% to 99.5% have been successfully used in various examples, and HCl, hydrochloric acid, sp. gr. 1.16, 31.5%, but concentrations of 24.6% to 35.2% have been successfully used in the various examples. The concentrations are, of course, expressed in aqueous solution.

The values for all dry materials, namely, CrO_3, NH_4HF_2, NaF and KF in the tables represent grams of compound per liter of aqueous solution, while the values of hydrofluoric acid, nitric acid, sulfuric acid, hydrochloric acid and acetic acid, namely, liquid materials, are represented in the various tables as milliliters of liquid per liter of aqueous solution.

TABLE 1

General Formulas

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
CrO_3	40.8	120–160	120–160	120–160	110–180	40–90	40–160
NH_4HF_2		20–40	20–40		40–65	10–40	
NaF	5–20						
KF							5–50
HF				15–40			
HNO_3	10–50	10–80	40–80	10–80	50–00	20–50	10–80
H_2SO_4	2–8		4–8				
HCl	3–10	3–10		3–10			
HAc	0–45	0–100	0–45	0–100			

Examples 1 through 7 illustrate ranges of concentrations based on the use of chromic acid anhydride with a fluoride and a high concentration of hydrogen ion furnished by a mineral acid, for example, nitric acid. Sulfate ions from sulfuric acid and/or chloride ions from hydrochloric acid are used in some solutions for their catalytic effect in speeding the reaction. Acetic acid is used where necessary for control of the thickness of the coatings, particularly when the time between removal of the work from the chemical polishing bath and its immersion in the succeeding water rinse is greater than 15 seconds. The upper and lower limits of the ranges recited in the foregoing Examples 1 to 7, as well as intermediate amounts of the constituents, have been successfully used.

In the various examples recited throughout this specification, the zinc casting treated is first cleaned in the usual manner with a conventional alkaline cleaner for zinc die castings, preferably by dipping in the cleaning bath, the immersion time being about 10 to 30 seconds and the solution preferably being at elevated temperature; then the cleaned castings are hot or cold rinsed in water thoroughly and introduced into one of the dips of this invention, the temperature of the dips being between 110° F. and 160° F., preferably about 140° F. and the immersion time being from about 5 seconds to 2 minutes, preferably about 30 seconds; then the treated castings are hot or cold water rinsed and dried in a conventional manner as by blowing warm air over the same or passing the castings through a drying chamber.

The compositions and treatment of this invention, as

stated, are primarily useful in connection with imparting a brightness to zinc die castings, notably, for such products as are known in the trade as "Zamac #3 Alloys" composed of zinc about 96% and aluminum 4%, and "Zamac #5 Alloys" composed approximately of zinc 96%, aluminum 3.8% and copper 2%.

TABLE 2

Formulas for Zamac #3

	Example 8	Example 9	Example 10	Example 11	Example 12
CrO_3	120	100	60	30	150
NH_4HF_2	20	13.2	8	4	150
HNO_3	20	25	16	8	40
H_2SO_4	10	6.6	4	2	5
HCl					
HAc	15	42	45	[1] 45	15

[1] In example 11, 25 milliliters of acetic acid were successfully used as were amounts intermediate the range between 25 and 45 milliliters of acetic acid.

Examples 8, 9 and 10 are solutions which may be safely used to produce a bright surface on Zamac #3 die castings. The treatment is followed by water rinsing and a conventional bleaching dip in a dilute solution of sodium hydroxide to remove the yellow constituents in the coating and leave a clear bright surface as a final finish. The work in this condition may be re-cleaned and then electroplated with other metals, for example, copper, nickel, and chromium. Example 11 is a solution suitable for producing a bright yellow finish which may be used as a final finish. Example 12 is a solution which contains the constituents in the proportions in which they are depleted in normal operation. It is intended for use in replenishing solutions such as Example 8 and is not itself suitable for use alone in performing the functions of this invention.

TABLE 3

Formulas for Zamac #5

	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20
CrO_3	120	60	30	150	6.0	3.0	120	120
NH_4HF_2	20	8	4	40	0.8	0.4	20	30
HNO_3	50	40	20	160	8.0	4.0	40	40
H_2SO_4	10	4	2	5	0.4	0.2	10	10
HCl	40	15	7.5	35	2.0	1.0	10	10
HAc	15	45	25	30			15	15

Examples 13, 14 and 15 perform the same functions for Zamac #5 as is performed for Zamac #3 by Examples 8, 9 and 10, namely, chemical polishing for a clear bright final finish or in preparation for subsequent plating. If the sodium hydroxide or other bleaching dip is omitted, Example 15 may be used for a yellow final finish. Example 16 is a solution for maintaining the solutions of Examples 13, 14 and 15 in operating condition and corresponds to Example 12.

Examples 17 and 18 are for applying a thin, light yellow coating on die castings with a minimum of attack on the metal and, therefore, a minimum consumption of chemicals.

Examples 19 and 20 are adapted for use with either Zamac #3 or Zamac #5.

All of the foregoing examples, namely, those as set forth in Tables 1, 2 and 3 above, were operated with the bath at a temperature of about 140° F. for an immersion time of about 30 seconds, except Example 20, which is formulated to operate at about 80° F. The higher concentration of the fluoride salt in this example makes this possible. The concentration of hydrofluoric acid was 60% by weight, with a sp. gr. of 1.24, the concentration of the nitric acid was 61.4% by weight, with a sp. gr. of 1.38, the sp. gr. of sulfuric acid was 93.5% by weight, with a sp. gr. of 1.84, the sp. gr. of acetic acid was 1.05 and the concentration 99.5% by weight, and the concentration of hydrochloric acid was 31.5% by weight, with a sp. gr. of 1.16, the concentrations being recited in terms of aqueous solution.

The ranges recited above relative to temperature of the bath and time of immersion or treatment were successfully used and the amounts of these acids with the ranges of concentrations recited were also used successfully. The examples recite the preferable results.

In addition to the foregoing examples, the following were also carried out successfully:

EXAMPLE 21

This example was the same as Example 1 but instead of sodium fluoride, there was used ammonium fluoride. This example illustrates the use of a compound of equivalent or greater solubility than sodium fluoride.

EXAMPLE 22

This example was like Example 2 except that it was carried out with 40 milliliters of nitric acid instead of 80 milliliters, as recited in Example 2.

EXAMPLE 23

This example was like Example 3 except that hydrochloric acid was used instead of sulfuric acid, and the example was satisfactorily carried out using a lower limit of 3 milliliters of hydrochloric acid, an upper limit of 10 milliliters of hydrochloric acid, and intermediate amounts.

EXAMPLE 24

110–180 g./l. CrO_3 } powder
40–65 g./l. NH_4HF_2 }
User will add:
50–90 ml./l. HNO_3

EXAMPLE 25

40–90 g./l. CrO_3 } powder
10–40 g./l. NH_4HF_2 }
User will add:
20–50 ml./l. HNO_3

Formulas 24 and 25 may be sold as a powder and the user will add the required amount of HNO_3.

EXAMPLE 26

160 g./l. CrO_3
65 ml./l. HNO_3
55 g./l. NH_4HF_2

Example 26 will be sold either with or without the HNO_3.

The following formulation was used on Zamac #3 castings which were then given conventional electroplating coatings of copper, chromium and nickel, respectively:

EXAMPLE 27

99 g./l. CrO_3
25 ml./l. HNO_3
6.6 ml./l. H_2SO_4
13.2 g./l. NH_4HF_2
42 ml./l. HAc

The dip temperature, as with the other examples recited above, was 140° F. and the immersion time was 30 seconds.

Examples 10 or 27, preferably Example 27, is used prior to conventional electroplating with copper, chromium or nickel and the castings, both before and after electroplating, have an appearance of being hand buffed or polished, more so, however, when electroplated.

EXAMPLE 28

This formulation was used on a Zamac #5 casting (96% zinc, 3.8% aluminum and 2% copper) to give a semi-polish or bright yellow finish:

30 g./l. CrO_3
20 ml./l. HNO_3
2 ml./l. H_2SO_4
4 g./l. NH_4HF_2
25 ml./l. HAc
7.5 ml./l. HCl

Likewise, the temperature of the coating bath was 140° F. and immersion time 30 seconds.

EXAMPLE 29

In addition to the replenishing baths referred to above, Example 8 for illustration, as well as Examples 10 and 11 and other of the examples, was fortified or replenished, i.e., maintained, from time to time to economically increase its operating life by adding to it and preferably to the baths for Zamac castings of Examples 1 to 27, notably Examples 6, 10 and 27, the following formulations:

150 g./l. CrO_3
150 ml./l. HNO_3
5 ml./l. H_2SO_4
15 ml./l. HAc
40 g./l. NH_4HF_2

The bath temperature was continuously 140° F. and the immersion time the same as described, i.e., 30 seconds.

Another example of a replenishing composition useful in connection with various of the examples described above, and particularly with Examples 14 and 28, is the following:

EXAMPLE 30

150 g./l. CrO_3
150 ml./l. HNO_3
5 ml./l. H_2SO_4
30 ml. /l. HAc
40 g./l. NH_4HF_2
30 ml./l. HCl

This replenishing or maintaining solution added to Examples 14 and 28, which are preferably used on Zamac castings, economically improves the operating life of the solutions of these examples, the temperature of the bath and immersion time being the same as described above, namely, about 140° F. for about 30 seconds.

EXAMPLE 31

From the foregoing it will be noted that one basic formula for a bright protective finish comprises about:

120 g./l. CrO_3
40 g./l. NH_4HF_2
50 ml./l. HNO_3

The addition of HCl and H_2SO_4 act as catalysts to reduce the required fluoride. The salt spray test results, applied to all examples, were usually favorably improved by the addition of these mineral acids.

EXAMPLE 32

A formula for Zamac #5 casting is as follows:

120 g./l. CrO_3
20 g./l. NH_4HF_2
50 ml./l. HNO_3
40 ml./l. HCl
10 ml./l. H_2SO_4

When HAc in amount of about 15 ml./l. is added, as in Example 13, this improved the bleaching characteristics of the film produced on the zinc castings, enabling the obtaining of a clear film. In adding the HAc, in some cases, no HCl is needed with Zamac #3 castings which do not include copper.

EXAMPLE 33

A preferred formulation for Zamac #3 castings comprises:

100 g./l. CrO_3
25 ml./l. HNO_3
30 ml./l. HAc
10 ml./l. H_2SO_4
40 g./l. NH_4HF_2

EXAMPLE 34

For a Zamac #5 casting (zinc, aluminum and copper) a preferred formulation is:

100 g./l. CrO_3
60 ml./l. HNO_3
10 ml./l. H_2SO_4
20 g./l. NH_4HF_2
40 g./l. HCl
30 ml./l. HAc

With all of the formulations described herein replenishing or maintenance solutions, as described above, are used.

For the preferred formulations I find that with the CrO_3 in varying amounts, as indicated above, about

5 to 30 ml./l. HNO_3
15 to 45 ml./l. HAc
5 to 10 ml./l. H_2SO_4
10 to 25 g./l. NH_4HF_2 and
3 to 40 ml./l. HNO_3

produce useful coating and treating compositions. The CrO_3 content is varied as indicated from about 30 g./l. upward.

In the broad range, and as explained, the concentration of the acetic acid will vary between 0 to 100 ml./l., preferably 15 to 50 ml./l.; of the nitric acid between about 4 and 80 ml./l., preferably 4 to 60 ml./l.; of the sulfuric acid between about 0.1 to 10 ml./l., preferably 2 to 8 ml./l.; and of the hydrochloric acid between about 0 to 50 ml./l., preferably about 3 to 40 ml./l.

Conventional bleaching with NaOH of the coatings in the various treatments described herein is unnecessary if a yellow finish is desired, and, likewise, such bleaching may be eliminated because the formulations mentioned, of themselves, produce either a clear or yellow finish, which is bright, in any case.

Where the amount of HNO_3 is high, the use of other of the mineral and organic acids may be reduced. The same is true when the HCl is increased, i.e., reduction in the amount of such other acids is possible.

The bath temperatures succesfully used with the formulations of this application vary between 110° F. and 160° F. but preferably 140° F. is used. Also, I have used time periods of treatment from 5 seconds to 2 minutes with the various formulations but prefer a treatment of about 30 seconds.

While ammonium bifluoride is preferred, sodium fluoride and other fluorides of equivalent or greater solubility may be used as indicated in the foregoing examples.

Referring to Examples 12, 16, 29 and 30, and the other replenishing and maintenance solutions, these contain the same constituents as the baths they are used to maintain, and it is critical that the CrO_3 and HNO_3 are present in such replenishing solutions in substantial excess over the other constituents of these maintenance solutions.

I claim:

1. The process of treating zinc castings comprising immersing the same in an aqeueous acidic chromate bath containing CrO_3, at least about 30 g./l., and about 5 to 60 ml./l. HNO_3, 0 to 100 ml./l HAc, 2 to 10 ml./l. H_2SO_4

and 4 to 50 g./l. of a soluble fluoride, for from 5 seconds to 2 minutes with the bath at a temperature between 80° F. and 160° F.

2. The process according to claim 1 wherein the bath contains 3 to 40 ml./l. HCl.

3. The process according to claim 1 wherein the temperature of the bath is between about 110° F. and 160° F.

4. The process of treating zinc castings comprising immersing the same in an aqueous acidic chromate bath containing CrO_3, about 60 g./l., and about 5 to 60 ml./l. HNO_3, 0 to 100 ml./l. HAc, 2 to 10 ml./l. H_2SO_4 and 4 to 50 g./l. of a soluble fluoride, for from 5 seconds to 2 minutes with the bath at a temperature between about 110° F. and 160° F.

5. The process of treating zinc castings comprising immersing the same in an aqueous acidic chromate bath containing CrO_3, about 99 g./l., and about 5 to 60 ml./l. HNO_3, 0 to 100 ml./l. HAc, 2 to 10 ml./l. H_2SO_4 and 4 to 50 g./l. of a soluble fluoride, for from 5 seconds to 2 minutes with the bath at a temperature between about 110° F. and 160° F.

6. The process of treating zinc castings comprising immersing the same in an aqueous acidic chromate bath containing CrO_3, about 120 g./l., and about 5 to 60 ml./l. HNO_3, 0 to 100 ml./l. HAc, 2 to 10 ml./l. H_2SO_4 and 4 to 50 g./l. of a soluble fluoride, for from 5 seconds to 2 minutes with the bath at a temperature between about 110° F. and 160° F.

7. The process of treating zinc castings comprising immersing the same in an aqueous acidic chromate bath containing CrO_3, about 100 g./l., and about 5 to 60 ml./l. HNO_3, 0 to 100 ml./l. HAc, 2 to 10 ml./l. H_2SO_4 and 4 to 50 g./l. of a soluble fluoride, for from 5 seconds to 2 minutes with the bath at a temperature between about 110° F. and 160° F.

8. The process of treating zinc castings comprising immersing the same in an aqueous acidic chromate bath containing CrO_3, at least about 30 g./l., and about 5 to 60 ml./l. HNO_3, 0 to 100 ml./l. HAc, 2 to 10 ml./l. H_2SO_4 and 4 to 50 g./l. of a soluble fluoride, for from 5 seconds to 2 minutes with the bath at a temperature between about 110° F. and 160° F. and HCl, about 3 to 40 ml./l.

9. The process of treating zinc castings comprising immersing the same in an aqueous acidic chromate bath containing CrO_3, about 120 g./l., and about 40 ml./l HNO_3, about 15 ml./l. HAc, about 10 ml./l. H_2SO_4, about 10 ml./l. HCl and about 30 g./l. NH_4HF_2, for from 5 seconds to 2 minutes with the bath at a temperature of about 80° F.

References Cited in the file of this patent

UNITED STATES PATENTS

2,186,579	Dubpernell	Jan. 9, 1940
2,613,165	Fischer	Oct. 7, 1952
2,614,913	Reindl et al.	Oct. 21, 1952
2,796,372	Chester	June 18, 1957
2,904,413	Hampel	Sept. 15, 1959
2,955,027	Newell et al.	Oct. 4, 1960