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DIP PROCESS FOR FORMING TRANSPARENT SURFACE CONVERSION COATINGS ON ZINC, AND COMPOSITIONS FOR DIP SOLUTIONS

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This invention relates to a dip process for forming a surface conversion coating on zinc and high zinc alloys, to a dip solution for use in the process, and to a composition for making the dip solution. More particularly, the invention provides a one-step dip process for forming a bright, colorless, transparent, protective surface conversion coating on zinc and is further characterized as follows:

(1) The solution does not etch or dull zinc.

(2) Brightening of the ztnc is accomplished in a short time, from a few seconds up to two minutes.

(3) The basic metal under zinc coatings is not exposed by stripping of zinc in the time required for brightening.

(4) The conversion coating will stand hot water treatment without disintegrating or cracking.

(5) The coating which is formed is uniform from a practical standpoint.

(6) The article with the surface conversion coating formed thereon has good salt spray resistance.

(7) Fingermarks which occur on bright zinc when handled are not observable when bright zinc covered with the transparent surface conversion coating is handled.

(8) The surface coating is transparent, exhibiting the underlying zinc as bright metallic zinc.

(9) the dip solution has a reasonably long useful life, being buffered to provide a retarded rise of the pH.

(10) Surface conversion coatings having the foregoing characteristics are formed in both still and agitated immersion.

The aqueous dip solution has the following composition, expressed in terms of the essential substances, for which a preferred concentration and an over-all or range of concentrations are given along with conditions of pH and temperature of the solution:

	Preferred	Range
Hexavalent chromium, Cr^{VI} ____ g./l.	100	25 to 150
Sulfate, SO_4 ____ g./l.	20	5 to 60
Nitrate, NO_3 ____ g./l.	10	2 to 40
Acetate, CH_3COO ____ g./l.	40	up to 80
pH	−0.2 to +0.3	−0.3 to +1.0
Temperature ____ ° F.	60 to 90	60 to 130

The designation "hexavalent chromium, Cr^{VI}," is to be understood as representing chromium in a form combined with at least one other element, the quantity however being based on the designation "Cr"; hexavalent chromium, Cr^{VI}, may alternatively be expressed in terms of CrO_3, the preferred concentration of which is 192.3 g./l. and the over-all concentration of which is 48.1 to 288.5 g./l. The designation "up to 80" for acetate represents that some acetate is always present, usually at least 1 g./l. of acetate. The source of each of the foregoing substances is variable provided that the resulting solution has a pH between −0.3 and +1.0. Examples of source materials are chromic acid, sodium bichromate and its dihydrate, sodium trichromate, sodium tetrachromate and its tetrahydrate, potassium bichromate,

potassium trichromate, potassium tetrachromate, ammonium bichromate, ammonium trichromate, ammonium tetrachromate, zinc bichromate trihydrate, zinc trichromate trihydrate, sodium chromate and the tetra-, hexa-, and decahydrates of the same, potassium chromate, lithium chromate, zinc chromate, ammonium chromate, ammonium lithium chromate, ammonium potassium chromate, ammonium sodium chromate, potassium sodium chromate, tripotassium monosodium bichromate, potassium calcium chromate, potassium magnesium chromate and its di- and hexahydrates, potassium zinc chromate dihydrate, magnesium chromate, rubidium chromate, cesium chromate, sulfuric acid, sodium bisulfate, potassium bisulfate, lithium bisulfate, rubidium bisulfate, cesium bisulfate, sodium sulfate, potassium sulfate, lithium sulfate, zinc sulfate, magnesium sulfate, rubidium sulfate, cesium sulfate, nitric acid, potassium hydrogen nitrate, rubidium hydrogen nitrate, cesium hydrogen nitrate, sodium nitrate, potassium nitrate, lithium nitrate, zinc nitrate, calcium nitrate, ammonium nitrate, magnesium nitrate, rubidium nitrate, cesium nitrate, acetic acid, sodium hydrogen acetate, potassium hydrogen acetate, sodium acetate, potassium acetate, lithium acetate, zinc acetate, calcium acetate, ammonium acetate, magnesium acetate, rubidium acetate, and cesium acetate.

The amount of a source material will, of course, be equivalent to the amount of substance required. All four substances may be supplied in the form of acid source materials as in Example 3 below, or in the form of mixed acid and salt source materials as in Examples 1 and 2, or in the form of acid salt source materials: provided always that the pH of the resulting solution is between −0.3 and +1.0.

Specifice examples of the qualitative and quantitative composition of some dip solutions are as follows:

Example 1

	G./l.
Chromic acid, CrO_3	200
Sodium sulfate, Na_2SO_4	6
Sodium bisulfate, $NaHSO_4$	24
Sodium nitrate, $NaNO_3$	15
Sodium acetate, $NaC_2H_3O_2$	55

Example 2

Chromic acid, CrO_3	150
Sodium bichromate dihydrate, $Na_2Cr_2O_7 \cdot 2H_2O$	50
Sodium bisulfate, $NaHSO_4$	30
Sodium nitrate, $NaNO_3$	15
Sodium hydrogen acetate, $NaH(C_2H_3O_2)_2$	55

Example 3

Chromic acid, CrO_3	65
Sulfuric acid, H_2SO_4	8
Nitric acid, HNO_3	3.5
Acetic acid, $HC_2H_3O_2$	13

Generally, the nitrate concentration varies inversely with the hexavalent chromium concentration, and the sulfate and acetate concentration vary directly with the hexavalent chromium concentration.

The use of lower temperatures within the above ranges is advantageous.

The time of immersion in the dip solution is from about 5 seconds to 2 minutes, and is usually from 10 to 20 seconds. The time of immersion is longer with higher pH, lower temperature, and lower concentration; and the time is shorter for lower pH, higher temperature, and higher concentration.

The action of the solution on the zinc is to form a surface conversion coating of definite thickness, i. e. on the order of about two to five millionths of an inch. With prolonged immersion, the action of the solution on the

zinc continues but the coating does not get appreciably thicker.

With an ordinary solution of a chromate or chromic acid, and a sulphate, the zinc acts to reduce the chromate or chromic acid, and a brown coating is formed. Nothing desirable in the way of brightening the zinc is obtained, and the tendency is toward the formation of rough coatings. In a solution made up according to the invention, the nitrate counteracts the formation of the brown color of the coating. Being a smaller ion than the chromate ion, the nitrate ion more readily penetrates to the zinc, and the zinc reduces it rather than the chromate. With increasing amounts of nitrate up to the preferred amount, the surface conversion coatings which are formed become increasingly lighter in color, until a transparent coating without any apparent brown coloration is obtained. The nitrate also acts to widen the pH range at which the dip solution has a brightening action on the zinc.

A chief function of the acetate radical is to limit the thickness of the surface conversion coating; if the coating is too thick, it will either crack or form a powder when treated with hot water. The acetate also enables the pH range to be wider; one can go higher in the pH range when acetate is present, and this in turn prolongs the useful life of the dip solution, which becomes less and less acid with use. The acetate appears to buffer the hydrogen ion concentration. Chromic acid in the solution also acts to buffer the hydrogen ion concentration. Another function of the acetate radical appears to be to increase the solubility of trivalent chromium compounds which may be found in the dip solution and thereby keeps them from precipitating in the coating. The acetate has a further effect of increasing the smoothness of the coating.

A composition useful for making up or maintaining dip solutions may be broadly defined as consisting essentially of the following substances in the following amounts:

	Parts by weight
Cr^{VI}	25 to 150
SO_4	5 to 60
NO_3	2 to 40
$C_2H_3O_2$	Up to 80

at least one-half of the composition being in the form of the acid or acid salt (equivalent in acidity to the acid) of one or more of the substances. In other words, at least 50% by weight of the total amount of substances listed is made up of one or more substances whose source materials are acids and/or acid salts, and the balance comprises one or more substances whose source materials are acids, acid salts, and/or normal salts. As before, the Cr^{VI} may be alternatively expressed as CrO_3, the amount of which varies from 48.1 to 288.5 parts by weight. The composition is essentially characterized by the fact that it produces a solution having a pH between −0.3 and +1.0 when the source materials comprising the composition are dissolved in water to provide concentrations of the dissolved substances which are within the concentration ranges defined above in connection with the dip solutions. Illustrative source materials are those already noted, some of which are normally solid and some of which are normally liquid, and as will be apparent, the resulting composition may be either in the solid or the liquid state depending on the source materials of which it is composed. Solid and liquid compositions each possess certain advantages over the other. Thus, solid compositions are easier to package and transport, and some users prefer them to handle and to store; by contrast, liquid compositions are put up in glass carboys which are less convenient to ship and are subject to breakage, in the latter event a highly corrosive liquid being set loose, and also liquid compositions involve higher freight expenses because of the water present in them, in other words shipping water is not economical. On the other hand, a liquid composition can be dissolved in the bath in which it is to be used more quickly than a solid composition, and, if desired, may be initially made up to a concentration suitable for immediate use; also, it contains in a single mixture all of the ingredients, whereas in the case of a solid composition a single mixture constitutes a fire hazard due to the presence of the acetate- and CrO_3-containing source materials, and it is preferred to make two packages to keep these materials separate.

Specific examples of the composition of matter are as follows:

Example 4

	Parts by weight
Chromic acid, CrO_3	200
Sodium sulfate, Na_2SO_4	6
Sodium bisulfate, $NaHSO_4$	24
Sodium nitrate, $NaNO_3$	15
Sodium acetate, $NaC_2H_3O_2$	55

Example 5

Chromic acid, CrO_3	150
Sodium bichromate dihydrate, $Na_2Cr_2O_7.2H_2O$	50
Sodium bisulfate, $NaHSO_4$	30
Sodium nitrate, $NaNO_3$	15
Sodium hydrogen acetate, $NaH(C_2H_3O_2)_2$	55

Example 6

Chromic acid, CrO_3	65
Sulfuric acid, H_2SO_4	8
Nitric acid, HNO_3	3.5
Acetic acid, $HC_2H_3O_2$	13

In carrying out the process, a zinc or zinc-surfaced article is dipped or immersed in an aqueous solution of the kind described, kept immersed for about five seconds to two minutes, usually from 10 to 20 seconds, depending on the specific characteristics of the solution as explained above, and then removed. The article is rinsed as by dipping in hot water. After the immersion treatment the article has the appearance of bright metallic zinc and is protected against corrosion, hot water, fingermarking, etc. by the transparent surface conversion coating.

The following examples illustrate the formation of coatings on zinc-surfaced articles, using various dip solutions.

Examples 7 to 14

A number of aqueous dip solutions were made up, their compositions being set forth in the table below, wherein the numerical quantities are in terms of grams per liter. The symbol "Ac" represents acetate,

$CH_3.COO$

The solutions of Examples 7 to 11 were made by dissolving in water chromic acid, sulfuric acid, sodium nitrate, and glacial acetic acid in amounts equivalent to the substances listed. Similarly, the solution of Example 12 was made from chromic acid, sodium bisulfate, sodium nitrate, and acetic acid; that of Example 13 was made from chromic acid, sulfuric acid, nitric acid, and acetic acid; and that of Example 14 was made from chromic acid, sulfuric acid, sodium bisulfate, sodium nitrate, acetic acid and sodium hydrogen acetate. The pH values shown were obtained by adjustment of the original solutions by additions of sodium hydroxide; in the case of Example 13, no adjustment of the original solution was made.

Example No.	7	8	9	10	11	12	13	14
Solution No.	34-11	34-14	38-33	38-34	38-37	39-1	43-50	53-1
Solution Compn.:								
CrO_3	200	100	100	300	200	100	100	150
SO_4	15	60	7.5	22.5	30	15	15	16.6
NO_3	10	20	5	15	40	20	20	7.5
Ac	40	40	20	60	80	40	80	30.4
pH	0.2	0.2	0.2	0.2	0.2	0.09	0.2	0.06

Pieces of zinc-coated steel of uniform size, having a zinc coating thickness of about 0.0004 inch, were dipped in the solutions of Examples 7 to 11 for a period of 30 seconds, rinsed in water, then dipped in an aqueous solution containing 4 oz. per gallon of sodium hydroxide to help neutralize traces of adhering dip solution, and rinsed in warm water at a temperature of about 150° F.; in Example 12, two pieces were dipped, one for 10 seconds and the other for 30 seconds, and both were rinsed in hot water; and in Example 13 the dip was for 10 seconds and the piece was rinsed in boiling water. Dipping was carried out at room temperature in 400 cc. of each solution. The coatings produced in Examples 8, 9, 10, 11, and 13 were carefully examined and found to be bright, transparent, protective coatings. When the coatings were viewed at a right angle, i. e., looked at perpendicularly, a faint bluish color was apparent; the coatings were visible as iridescent coatings when viewed at an acute angle. These coatings did not crack on contact with hot water and were resistant to fingermarking. The pieces from Examples 7 and 12, which had coatings like the preceding pieces, were immediately subjected to standard salt spray tests; after 16 hours the piece from Example 7 had white corrosion products at its edge portions; the two pieces from Example 12 resisted the salt spray for 46 hours, when small black spots were apparent on them, and after 70 hours white corrosion products were present. As is known, uncoated zinc corrodes readily when exposed to atmosphere, so that in the foregoing salt spray tests, in which severe accelerated conditions of corrosion obtain, the resistance of the coated zinc for even one hour, or less, shows that the coating would protect the zinc for substantial periods against usual atmospheric conditions.

The solution of Example 14, and also that of Example 12, was made up in quantity: 55 liters and 53 liters, respectively. Two zinc-coated wire refrigerator shelves, 10" x 14", were dipped in the Example 14 solution for 10 seconds, rinsed in hot water, and found to have bright, transparent, protective coatings of the type described above. A shelf was dipped in the solution of Example 12, being given a 10 second dip, water rinse, dipped in an aqueous solution containing 5 g./l. of sodium hydroxide, and rinsed in water. It had a coating of the type described. It was then subjected to a salt spray test, and after 16 hours it showed some white products on the larger wires and some blotches on the smaller wires. Sufficient acetic acid was then added to the Example 12 solution to raise the acetate concentration to 60 g./l., a shelf was dipped in the resulting solution for 10 seconds, rinsed in water, and found to have a bright, clear protective coating.

This application is a continuation-in-part of application Serial No. 641,864, filed January 17, 1946, and of application Serial No. 23,874, filed April 20, 1948, both now abandoned.

In the light of the foregoing description, the following is claimed:

1. A process of coating zinc surfaces which comprises immersing a zinc-surfaced material in an aqueous solution of a plurality of compounds which provide the substances, and the amounts of said substances, hereinafter described, said compounds being selected from the group consisting of salts and acids, the entire amount of one of said substances being provided by at least one salt, said solution consisting essentially of the following said substances dissolved therein in the following amounts:

	Grams per liter
CrO_3	48.1 to 288.5
SO_4	5 to 60
NO_3	2 to 40
$CH_3.COO$	Up to 80

said solution having a temperature from 60° to 130° F. and a pH between −0.3 and +1.0, the immersion of the said material being continued until a bright, colorless transparent protective coating is imparted to the zinc surface, and removing the material from the solution.

2. An aqueous solution for coating zinc surfaces with a bright, colorless transparent protective coating, said solution having dissolved therein a plurality of compounds which provide the substances, and the amounts of said substances, hereinafter described, said compounds being selected from the group consisting of salts and acids, the entire amount of one of said substances being provided by at least one salt, said solution consisting essentially of the following said substances dissolved therein in the following amounts:

	Grams per liter
CrO_3	48.1 to 288.5
SO_4	5 to 60
NO_3	2 to 40
$CH_3.COO$	Up to 80

said solution having a temperature from 60° to 130° F. and a pH between −0.3 and +1.0.

3. A mixture of compounds for making up a solution for coating zinc surfaces with a bright, colorless, transparent, protective coating, said compounds providing said mixture with the substances, and the amounts of said substances, hereinafter described, at least 50% by weight of said substances being provided by at least one compound selected from the group consisting of acids and acid salts, the balance of said substances being provided by at least one compound selected from the group consisting of acids, acid salts, and normal salts, the entire amount of one of said substances being provided by at least one salt, said mixture consisting essentially of the following said substances in the following amounts:

	Parts by weight
CrO_3	48.1 to 288.5
SO_4	5 to 60
NO_3	2 to 40
$CH_3.COO$	Up to 80

said mixture being characterized by dissolving in water to produce a solution having a pH between −0.3 and +1.0 and consisting essentially of the following substances in the following amounts:

	Grams per liter
CrO_3	48.1 to 288.5
SO_4	5 to 60
NO_3	2 to 40
$CH_3.COO$	Up to 80

the quantity of said mixture and of said water being correlated to provide the foregoing amounts of said substances in said solution.

4. The mixture of claim 3 characterized by being normally solid.

5. The mixture of claim 3 characterized by being normally liquid.

6. A process of coating zinc surfaces which comprises immersing a zinc-surfaced material in an aqueous solution of a plurality of compounds which provide the substances, and the amounts of said substances, hereinafter described, said compounds being selected from the group consisting of salts and a mixture of salts and acids, said solution consisting essentially of the following said substances dissolved therein in the following amounts:

	Grams per liter
CrO_3	48.1 to 288.5
SO_4	5 to 60
NO_3	2 to 40
$CH_3.COO$	Up to 80

the solution having a temperature from 60° to 130° F. and a pH between −0.3 and +1.0, the immersion of the said material being continued until a bright, colorless

transparent protective coating is imparted to the zinc surface, and removing the material from the solution.

7. An aqueous solution for coating zinc surfaces with a bright, colorless transparent protective coating, said solution having dissolved therein a plurality of compounds which provide the substances, and the amounts of said substances, hereinafter described, said compounds being selected from the group consisting of salts and a mixture of salts and acids, said solution consisting essentially of the following said substances dissolved therein in the following amounts:

	Grams per liter
CrO_3	48.1 to 288.5
SO_4	5 to 60
NO_3	2 to 40
$CH_3.COO$	Up to 80

the solution having a temperature from 60° to 130° F. and a pH between −0.3 and +1.0.

8. A mixture of compounds for making up a solution for coating zinc surfaces with a bright, colorless, transparent, protective coating, said compounds providing said mixture with the substances, and the amounts of said substances, hereinafter described, said compounds being selected from the group consisting of salts and a mixture of salts and acids, said mixture consisting essentially of the following substances in the following amounts:

	Parts by weight
CrO_3	48.1 to 288.5
SO_4	5 to 60
NO_3	2 to 40
$CH_3.COO$	Up to 80

said mixture being characterized by dissolving in water to produce a solution having a pH between −0.3 and +1.0 and consisting essentially of the following substances in the following amounts:

	Grams per liter
CrO_3	48.1 to 288.5
SO_4	5 to 60
NO_3	2 to 40
$CH_3.COO$	Up to 80

the quantity of said mixture and of said water being correlated to provide the foregoing amounts of said substances in said solution.

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