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COMPOSITION AND METHOD FOR BLACKENING THE SURFACES OF CADMIUM AND ZINC

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The present invention relates to metal-treating compositions, and more particularly to a composition and method for imparting a black appearance to the surface of cadmium and zinc and alloys thereof.

Heretofore, it has been proposed in United States Patent No. 2,483,510 and United States Patent No. 2,524,577 to blacken the surface of zinc and cadmium, respectively, in a bath containing essentially hexavalent chromium ions, soluble silver ions and an activating acid radical selected from the group consisting of sulfate and fluoride. As exploited commercially by the assignee of the patents, the aforementioned bath has been provided by two separate aqueous solutions, one containing a soluble silver salt (silver nitrate) and the other containing hexavalent chromium, sulfuric acid and an aliphatic acid. The two solutions then are mixed and heated to a temperature of about 140 degrees Fahrenheit to obtain optimum homogeneity. The baths of the above patents have enjoyed substantial success and have been widely utilized despite the facts that the components are sold and transported in two-part, liquid form which are admixed at elevated temperatures, and that the film is very readily subject to abrasion or scuffing in the wet state.

Since the basket and other bulk-finishing operations are prevalently utilized for economy in treating small workpieces, it is highly desirable that the wet film developed by surface-treating baths be of sufficient hardness to withstand the scuffing and abrasion normally occurring during further processing of the workpieces.

It is an aim of the present invention to provide a novel and highly effective composition for developing a black film of increased toughness in the wet state upon surfaces of cadmium and zinc, and alloys thereof.

Another aim is to provide a self-contained dry powder composition which upon addition to water will provide per se a highly effective bath for developing a black film upon surfaces of cadmium zinc, and alloys thereof.

It is also an aim to provide a method for developing a black-appearing film upon the surface of zinc, cadmium, and alloys thereof, which film is characterized by relative resistance to abrasion and scuffing in the wet state.

An additional aim is to provide such a method and composition which is relatively economical, easy to operate and which can produce a uniform black appearance of relatively high gloss.

Other objects and advantages will be readily apparent to those skilled in the art from a reading of the following detailed specification and claims.

We have now found that the foregoing and related objects can be readily attained by use of a dry chemical formulation containing a water-soluble hexavalent chromium compound, a water-soluble sulfate compound, a water-soluble phosphate compound, and a water-soluble silver compound, one or more of said compounds being sufficiently acid in nature to provide a pH for the bath formed upon addition to water of about 0.5 to 3.0. The preferred formulations additionally contain a soluble nitrate compound in excess of the molar equivalent of silver. This dry powder formulation is added to water, most conveniently of ambient temperatures, and mixed therewith to dissolve the sulfate, phosphate, nitrate and hexavalent chromium and to attain a solution to equilibrium concentration of the soluble silver ion. Although some of the silver will precipate as the chromate salt, the relative solubility of silver in the aqueous acid bath of the above anions will ensure continuing solution of silver from the precipate to maintain an equilibrium and effective concentration.

More particularly, the powder composition should contain essentially about 40 to 55 percent by weight of hexavalent chromium compound (calculated as CrO_3), 35 to 55 percent by weight of soluble sulfate compound (calculated as $NaHSO_4$), 3.0 to 11.0 percent by weight of soluble phosphate compound (calculated as NaH_2PO_4), and 0.5 to 2.5 percent by weight of soluble silver compound. The preferred powder compositions preferably contain 43.0 to 50.0 percent by weight of hexavalent chromium compound, 38.0 to 45.0 percent by weight of soluble sulfate compound, 5.0 to 9.0 percent by weight of soluble phosphate compound, and 0.8 to 1.5 percent by weight of soluble silver compound. As previously indicated, a soluble nitrate compound is most desirably included in amounts of about 1.0 to 6.0 percent by weight, and preferably about 2.5 to 4.5 percent by weight. One or more of the multivalent compounds is acidic in nature to provide the desired acid pH, conveniently by use of chromic acid anhydride and alkali metal hydrogen sulfate, and alkali metal dihydrogen phosphate may also be employed for this purpose.

As will be readily appreciated, the sulfate, nitrate and phosphate radicals are most desirably provided as their alkali metal salts, and particularly sodium salts, because of solubility, cost and the desire for avoiding introduction of interfering cations. Although silver may be added as the fluoride or soluble complex salts, the nitrate salt is most desirable because of its solubility, cost and ease of handling as well as the need for avoiding introduction of interfering anions.

Although the hexavalent chromium may be introduced as the chromate or dichromate salt, the basicity of these salts may create difficulty in attaining the desired pH with the powder composition per se. Accordingly, chromic acid anhydride (CrO_3) is most desirably employed.

The powder composition is added to water in amounts of 20.0 to 450.0 grams per liter, and preferably about 30.0 to 100.0 grams per liter. A particularly advantageous feature of the present invention is that the bath is highly effective at low concentrations for optimum economy in operation. Accordingly, the dry powder composition is most desirably employed in amounts of 30.0 to 50.0 grams per liter. The formulation is stirred for sufficient time to ensure optimum solution of the soluble components and homogeneity, and the precipitate of silver should be agitated into the body of the bath to obtain equilibrium concentration thereof.

Although higher concentrations of the components may be employed while maintaining the same molar relationship of components, the preferred baths of the present invention essentially contain about 8.0 to 25.0 grams per liter of hexavalent chromium (calculated as CrO_3), 8.0 to 25.0 grams per liter of sulfate radical, 0.5 to 7.5 grams per liter of phosphate radical, and 0.1 to 0.8 gram per liter of silver ion, together with a sufficient concentration of hydronium ion to produce a pH of 0.5 to 3.0. The optimum bath concentration of these ions and radicals is about 12.0 to 20.0 grams per liter of hexavalent chromium, 12.0 to 18.0 grams per liter of sulfate radical, 1.0 to 4.0 grams per liter of phosphate radical, and 0.3 to 0.5 gram per liter of silver ion. The nitrate ion is desirably present in an amount of about 0.4 to 4.0 grams per liter, and preferably 0.7 to 2.0 grams per liter.

The pH of the bath may vary within the range of 0.5 to 3.0 with satisfactory results. Generally, however, zinc requires a somewhat more acidic bath, and the pH of zinc baths is desirably maintained below 2.5. The bath preferably has a pH of about 0.6 to 1.3 for use with both cadmium and zinc, and alloys thereof, although with cadmium, a second optimum range occurs at a pH of 2.25 to 3.0.

Although the bath may be employed at elevated temperatures, it is generally preferable to utilize ambient temperatures, i.e., 65 to 95 degrees Fahrenheit, for optimum control. As will be readily appreciated, the time necessary for developing the black film will decrease with increase in temperature and is considerably shorter for cadmium than upon zinc, but generally will fall within the range of 5 to 90 seconds, although longer periods may be employed for thicker films when a deep plate or solid zinc or cadmium workpiece is treated. With the preferred bath compositions at a temperature of about 80 to 90 degrees Fahrenheit, immersion times of about 20 to 40 seconds for zinc and about 10 to 25 seconds for cadmium are sufficient.

Although the theory of operation of the above formulation is not completely understood, it is believed that the phosphate radical reacts with trivalent chromium produced by the oxidation-reduction reaction at the surface of the metal to deposit fine crystals of chromium phosphate throughout the film produced by the chromate and silver, which film is considered to be formed principally of spongy, amorphous chromium chromate and dispersed silver chromate. These crystals of chromium phosphate are believed to harden or toughen the film in the wet state and impart greatly improved resistance to abrasion or scuffing during processing. The black color of the film produced by the present invention appears richer and deeper in thinner depths, which improvement is considered to result from the blending of the green and violet colors of the various phosphate hydrate forms with the crystals of the silver chromate and in combination with the blackish chromium chromate yields a rich, deep black film of greater masking power.

Although the function of the nitrate ion is not fully understood, it is believed that nitrate ion in excess of the molar equivalency of the silver ion enhances the solubility of the silver ion and aids in dissolving the powder formulation in water at ambient temperatures to obtain an effective solution. It has been noted that the addition of nitrate imparts a desirable glossiness or richness to the film to enhance its aesthetic properties.

Periodically, the bath should be agitated sufficiently to bring the silver precipitate into full contact with the solution so as to ensure dissolving sufficient silver to reach equilibrium concentration in the bath. This may be done mechanically on an intermittent basis or conveniently by a continuous flow mechanism in the treating tank. As will be readily appreciated, the bath will become replenished in operating ion concentration, and additional dry powder composition may be added to replenish the bath and raise the concentration to optimum working limits.

The following is a specific example of a composition which has proven highly effective in the practice of the present invention:

Compound:	Percent by weight
Chromic acid	46.60
Sodium bisulfate	42.10
Monosodium phosphate	6.80
Silver nitrate	1.09
Sodium nitrate	3.41

This dry powder composition is added to water in amounts of about 4 to 6 ounces per gallon (30 to 45 grams per liter) and stirred for a sufficient length of time to dissolve the soluble components and obtain optimum solution of the silver. The bath is preferably maintained at a temperature of about 80 to 90 degrees Fahrenheit, and the cadmium workpieces are immersed therein for periods of about 5 to 20 seconds and the zinc for about 20 to 40 seconds. Subsequent to immersion in the bath of the present invention, the workpieces are rinsed in water and dried.

Illustrative of the efficacy of the present invention are the following examples.

Example 1

To water having a temperature of about 80 degrees Fahrenheit was added the dry powder composition of the present invention set forth in the specific formulation. The dry powder formulation was added in an amount equal to 5 ounces per gallon, and the solution was agitated for ten minutes to ensure full solution of the soluble components and equilibrium solution of the silver ion. The pH of the bath was determined to be 0.8.

Workpieces of steel alloy electroplated with cadmium to a thickness of 0.0003 inch were racked and immersed in the bath for a period of about thirty seconds with the bath temperature being maintained at a temperature of about 85 degrees Fahrenheit. The workpieces were rinsed in water and dried.

Prior to drying, rubbing of the black surface with the index finger failed to dislodge the film and established its adherency.

The resultant workpieces were found to have a glossy, adherent black finish which was free from irridescence and any tendency to powder.

Example 2

In a bath similar to that in Example 1 were immersed 1 inch x 4 inch steel panels having an electroplated zinc coating of approximately 0.0003 inch thickness for a period of about fifty seconds with the bath being maintained at a temperature of approximately 83 degrees Fahrenheit. The steel panels were then rinsed and dried.

Prior to drying, rubbing of the black film with the index finger failed to disrupt the film and remove any color, indicating the tenacity and adherence of the film in the wet state. After drying, the panels were found to have a glossy black coating which was highly adherent and free from irridescence and powdering.

As will be readily appreciated from the foregoing specific examples and specification, the present invention provides a dry powder composition and bath for the treatment of cadmium, zinc and alloys thereof which will produce a tenacious hard black film of desirable aesthetic properties. A particular advantage of the present invention is that the film is resistant to scuffing or abrasion in the wet state so as to enable basket handling of large numbers of small parts. Additionally, the baths of the present invention are effective in low concentrations and may be prepared by dissolving the dry powder composition in water of ambient temperature rather than requiring the use of elevated temperatures for obtaining solution of the components.

As will be readily appreciated, various modifications may be made without departing from the scope and spirit of the invention.

Having thus described the invention, we claim:

1. A dry powder composition for addition to water to provide a black film upon the surface of zinc, cadmium and alloys thereof, containing essentially about 40.0 to 55.0 percent by weight of a water-soluble hexavalent chromium compound, 3.0 to 11.0 percent by weight of a water-soluble phosphate compound, 0.5 to 2.5 percent by weight of a water-soluble silver compound, and 30.0 to 55.0 percent by weight of a water-soluble sulfate compound, at least one of said compounds being sufficiently acidic in nature to provide a pH of about 0.5 to 3.0 for the bath formed upon addition of the dry powder composition to water.

2. The composition of claim 1 containing a water-soluble nitrate compound in an amount sufficient to provide nitrate radical in excess of the molar equivalent of the silver content thereof.

3. The composition of claim 1 wherein said water-soluble hexavalent chromium compound is chromic acid anhydride (chromium trioxide).

4. The composition of claim 1 wherein said water-soluble phosphate compound is a dihydric alkali metal phosphate.

5. A dry powder composition for addition to water to provide a bath for developing a black film upon the surface of zinc, cadmium and alloys thereof, containing essentially about 40.0 to 55.0 percent by weight of a water-soluble hexavalent chromium compound (calculated as CrO_3), 3.0 to 11.0 percent by weight of a water-soluble phosphate compound (calculated as NaH_2PO_4), 30.0 to 55.0 percent by weight of a water-soluble sulfate compound (calculated as $NaHSO_4$), and 0.5 to 2.5 percent by weight of a water-soluble silver compound, at least one of said compounds being sufficiently acidic in nature to provide a pH of about 0.5 to 3.0 for the bath formed upon addition of the dry powder composition to water.

6. The composition of claim 5 additionally containing 1.0 to 6.0 percent by weight of a water-soluble nitrate compound.

7. A dry powder composition for addition to water to provide a bath for developing a black film upon the surface of zinc, cadmium and alloys thereof, containing essentially about 40.0 to 55.0 percent by weight of chromic acid anhydride, 3.0 to 11.0 percent by weight of dihydric alkali metal phosphate, 30.0 to 55.0 percent by weight of alkali metal acid sulfate, and 0.5 to 2.5 percent by weight of silver nitrate, at least one of said compounds being sufficiently acidic in nature to provide a pH of about 0.5 to 3.0 for the bath formed by addition of the dry powder composition to water.

8. A dry powder composition for addition to water to provide a bath for developing a black film upon the surface of zinc, cadmium and alloys thereof, containing essentially about 40.0 to 55.0 percent by weight of chromic acid anhydride, 3.0 to 11.0 percent by weight of monosodium phosphate, 30.0 to 55.0 percent by weight of sodium acid sulfate, 1.0 to 6.0 percent by weight of sodium nitrate and 0.8 to 1.5 percent by weight of silver nitrate.

9. A bath for imparting a black surface coating to workpieces of zinc, cadmium and alloys thereof comprising an aqueous solution of a dry powder composition containing essentially about 40.0 to 55.0 percent by weight of a water-soluble hexavalent chromium compound (calculated as CrO_3), 3.0 to 11.0 percent by weight of a water-soluble phosphate compound

(calculated as NaH_2PO_4)

30.0 to 55.0 percent by weight of a water-soluble sulfate compound (calculated as $NaHSO_4$), and 0.5 to 2.5 percent by weight of a water-soluble silver compound, said dry powder composition providing about 0.1 to 0.8 gram per liter of silver ion and at least one of said compounds being sufficiently acidic in nature to provide a pH of about 0.5 to 3.0 for said bath.

10. The bath of claim 9 wherein said dry powder composition additionally contains 1.0 to 6.0 percent by weight of water-soluble nitrate compound.

11. A bath for imparting a black surface coating to workpieces of zinc, cadmium and alloys thereof comprising an aqueous solution of a dry powder composition, said bath containing essentially about 8.0 to 25.0 grams per liter of hexavalent chromium ion (calculated as CrO_3), 8.0 to 25.0 grams per liter of sulfate radical, 0.5 to 7.5 grams per liter of phosphate radical, and 0.1 to 0.8 gram per liter of silver ion, said bath having a pH of 0.5 to 3.0.

12. The bath of claim 11 additionally containing 0.4 to 4.0 grams per liter of nitrate ion.

13. The method for imparting a black surface finish to cadmium, zinc and alloys thereof, comprising dissolving in water reagents to form a bath containing essentially 8.0 to 25.0 grams per liter of hexavalent chromium ion, 0.5 to 7.5 grams per liter of phosphate radical, 8.0 to 25.0 grams per liter of sulfate radical, and 0.1 to 0.8 gram per liter of silver ion, said bath having a pH of about 0.5 to 3.0; and immersing in said bath workpieces having a surface of a metal selected from the group consisting of cadmium, zinc and alloys thereof for a period of time sufficient to develop a black finish thereon.

14. The method in accordance with claim 13 wherein said bath additionally contains nitrate ion in excess of the molar equivalent of silver ion.

15. The method for imparting a black surface finish to cadmium, zinc and alloys thereof, comprising dissolving in water reagents to form a bath containing essentially 8.0 to 25.0 grams per liter of hexavalent chromium ion (calculated as CrO_3), 8.0 to 25.0 grams per liter of sulfate radical, 0.5 to 7.5 grams per liter of phosphate radical, 0.1 to 0.8 gram per liter of silver ion, and 0.4 to 4.0 grams per liter of nitrate ion, said bath having a pH of 0.5 to 3.0; and immersing in said bath workpieces having a surface of a metal selected from the group consisting of cadmium, zinc and alloys thereof for a period of time sufficient to develop a black finish thereon.

References Cited by the Examiner

UNITED STATES PATENTS

1,826,866	10/1931	Cole	148—6.16
2,296,884	9/1942	Thompson	148—6.16 XR
2,298,418	10/1942	Roesner et al.	148—6.16
2,303,242	11/1942	Tanner et al.	148—6.16
2,329,065	9/1943	Lum et al.	148—6.15
2,437,441	3/1948	Rogers	148—6.15
2,483,510	10/1949	Stareck	148—6.21
2,494,908	1/1950	Spruance et al.	148—6.16
2,497,905	2/1950	Ostrander	148—6.21 XR
2,524,577	10/1950	Stareck	148—6.21
2,813,815	11/1957	Miles	148—6.16
2,970,935	2/1961	Cavanaugh	148—6.16

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