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**COMPOSITION AND METHOD FOR BRIGHTENING
CADMIUM AND ZINC**

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The present invention relates to the chemical brightening of metals, and more particularly to a powder composition for preparing a bath to chemically brighten cadmium, zinc and alloys thereof.

This application is a continuation-in-part of application Serial Number 228,253, filed October 4, 1962, now abandoned.

The term "cadmium surfaces" as used hereinafter refers to surfaces of cadmium and cadmium-base alloy articles and other metallic articles having a coating of cadmium or cadmium-base alloy such as produced by electroplating.

The term "zinc surfaces" as used hereinafter refers to surfaces of zinc and zinc-base alloy articles and other metallic articles having a coating of zinc or zinc-base alloy such as produced by hot-dipping or electroplating.

Heretofore, the most widely used baths for brightening cadmium have been prepared by the addition of various components to solutions of nitric and/or sulfuric acids so as to provide an aqueous acid solution containing chromate, fluoride and/or sulfate and nitrate ions. Such baths are used extensively throughout the metal-fabricating industry in large volumes.

More recently, in our copending application Serial Number 97,164, filed March 21, 1961, and entitled Solution and Method for Brightening Cadmium, now United States Patent Number 3,072,516, granted January 8, 1963, we have disclosed and claimed a novel bath and method for brightening cadmium surfaces using trivalent chromium ions in combination with nitrate ions and sulfate and/or fluoride ions. In this patent, we disclose the conventional principle of adding other components to an aqueous solution of nitric acid.

The use of liquid acids in making up such bright-dipping baths is subject to a number of objections—not the least of which is the fact that the proportion or relationship of the ingredients is oftentimes critical for optimum operation as in automatic apparatus, and the measuring of the acid and other components is often relegated to unskilled workers. This problem becomes particularly acute when periodic make-up additions are necessary during use of the bath. Additionally, the use of liquid acids requires expensive containers for shipment thereof and upon which deposits are oftentimes charged so that the containers must be returned and records must be kept. Clearly, freight costs for the water content of liquid acids can be quite substantial. Moreover, safety factors in handling and storing liquid acids often present a considerable problem.

It is an object of the present invention to provide a self-contained dry powder formulation for addition to water to provide a highly effective bath for the chemical treatment of cadmium surfaces and zinc surfaces and which is convenient and safe to ship and handle, relatively economical in operation and precontrollable in the optimum proportion of essential ingredients so as to provide a balanced bath composition.

Another object is to provide such a self-contained dry powder formulation wherein the speed of the bath action upon the metal workpieces may be varied readily by varying the amount of powder formulation added to water.

A specific object is to provide such a self-contained dry

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powder formulation for addition to water to provide a highly effective brightening bath for cadmium surfaces.

A further specific object is to provide such a self-contained dry powder formulation for addition to water to provide a highly effective bath which may produce a bright, cadmium-like finish upon zinc surfaces.

It has now been found that the foregoing and related objects can be readily attained by use of a dry powder formulation consisting essentially of a water-soluble trivalent chromium compound; a water-soluble activating salt selected from the group consisting of fluorides, sulfates, and the combination thereof; and a water-soluble acid-nitrate component selected from the group consisting of urea nitrate, urea nitrate and nitrate salts of inorganic bases, urea nitrate and sulfamic acid, and sulfamic acid and nitrate salts of inorganic bases, said acid-nitrate component being of sufficient acidity to provide a pH of about 0.2 to 3.5 upon addition of the dry powder formulation in an amount sufficient to provide about 0.08 to 5.0 grams per liter of trivalent chromium ion.

As pointed out in our aforementioned patent, the baths for brightening cadmium contain about 0.08 to 1.0 gram per liter of trivalent chromium ion. However, in the present invention, it has been found that the powder formulation may be used to provide up to about 5.0 grams per liter of trivalent chromium ion for greatly enhanced corrosion protection without loss in brightening action for cadmium surfaces and for zinc surfaces as will be explained more fully hereinafter.

In addition to the foregoing essential components, zinc or cadmium ions may be desirably incorporated in the composition as the nitrate, sulfate or fluoride salt to provide an initial concentration of one or both of these ions in the bath. Particularly during the initial period of bath usage following formulation, they have proven desirable in controlling the action upon the cadmium or zinc surfaces and in providing uniform brightness.

As pointed out in our aforementioned patent, hexavalent chromium ions (CrO_4^{2-}) have been found to produce a dulling effect upon the cadmium surfaces so that the presence of hexavalent chromium in the powder formulation is to be avoided when brightening action is desired. The bath produced by the powder composition of the present invention is itself non-oxidizing with respect to the trivalent chromium so that only impurities in the components or impurities carried into the bath upon the workpieces need be considered. In the dilute brightening baths at a pH of 1.0 to 2.0, as little as 0.020 gram per liter produces a dulling effect; and even at the higher pH range of 2.0 to 3.5, the tolerable amount is small and below 0.3 gram per liter. Consequently, the powder formulations of the present invention are substantially free from hexavalent chromium compounds.

To avoid introduction of interfering ions, the essential ions are preferably added in combination with each other to the greatest possible degree. Thus, the trivalent chromium ion is added as the fluoride, sulfate or nitrate salt since chromic sesquioxide (Cr_2O_3) is essentially insoluble in an acid solution and not suitable for the dry powder composition. Of the several chromium salts, chromium fluoride is preferable because it may be readily attained as an anhydrous salt. The fluoride and sulfate ions may also be added as the salts of the alkali metals of ammonia, and the acid salts thereof ($NaHF_2$, KHF_2 , NH_4HF_2 , $NaHSO_4$, etc.) have proven particularly advantageous both in being readily soluble and in providing additional means of controlling the pH of the bath provided upon addition of the composition to water. Zinc and cadmium may be added as the sulfates, nitrates and fluorides. Similarly, the nitrate salts of inorganic bases may be those of the desired cations (chromium and cadmium or zinc) within the desired compositional limits and/or of those

bases having non-interfering cations such as the salts of the alkali metals and ammonia which have proven particularly advantageous.

Of the various acid-nitrate components, urea nitrate and the combination of urea nitrate and the nitrate salts of inorganic bases have proven particularly advantageous, both in providing a desirable pH for the bath upon addition to water and in providing the effective optimum weight ratio of nitrate to chromium ions. Moreover, it has been found that when the acid-nitrate component is entirely or substantially comprised of urea nitrate within optimum compositional ranges, the resultant bath may be operated at higher concentrations of trivalent chromium ion of about 1.0 to 5.0 grams per liter and at a lower pH of about 0.2 to 1.0 to provide not only excellent brightening action but also greatly enhanced corrosion protection for both cadmium and zinc surfaces. This is in contrast with the baths of the aforementioned patent which required a pH of above about 1.0 and a concentration of less than 1.0 gram per liter of trivalent chromium ions when liquid nitric acid was employed as the source of acidity and nitrate ion for the treatment of cadmium surfaces. By use of chromium ion concentration of about 1.5 to 5.0 grams per liter, and preferably about 1.8 to 4.5 grams per liter, at the lower pH range, an increase in protection on the order of ten to fifty times may be obtained. For optimum operation, the urea nitrate should comprise 75 to 90 percent of the powder formulation or the salts in the bath.

Since the activating ion may be provided in part by adding it as the salt of the essential trivalent chromium in chromium fluoride (CrF_3) and chromium sulfate [$\text{Cr}_2(\text{SO}_4)_3$], and the trivalent chromium ion may also be provided as a nitrate salt [$\text{Cr}(\text{NO}_3)_3$] to comprise a portion of the acid nitrate component, the actual weight percentage of the dry powder components may vary over a wide range. Generally, however, the powder composition will contain, on a dry weight basis, 1.0 to 25.0 percent by weight of a trivalent chromium compound, up to 50.0 percent by weight of a soluble activating salt selected from the group consisting of sulfates, fluorides and the combination thereof, and 25.0 to 95.0 percent by weight of acid-nitrate component, and will provide the essential trivalent chromium, nitrate, fluoride and/or sulfate ions, and the necessary hydrogen ions or acidity upon addition to water to provide the desired pH of about 0.2 to 3.5. Preferably, the activating salt comprises less than about 20 percent by weight, and the trivalent chromium compound comprises less than 10 percent by weight, and the acid-nitrate component comprises 75 to 90 percent by weight.

The preferred powder compositions additionally contain zinc or cadmium ions as the cations in the activating salt or in the inorganic nitrates in the acid-nitrate component. The preferred activating salts are the combination of sulfates and fluorides to provide a most appreciable degree of protection from corrosion by fume and moisture. When the two ions are used in combination, the total fluoride ion concentration should be about one-third that of the total sulfate ion for optimum results.

The dry powder compositions of the present invention formulated for brightening cadmium are proportioned so as to provide a bath containing essentially trivalent chromium ions in the range of about 0.08 to 5.0 grams per liter, nitrate ions in the range of about 1.0 to 90.0 grams per liter and ions selected from the group consisting of fluoride, sulfate and the combination thereof in the range of about 0.4 to 26.0 grams per liter. Cadmium and/or zinc ions may also be provided in the amount of about 0.1 to 15.0 grams per liter.

As indicated in our aforementioned patent, an effective and economical highly dilute bath composition for cadmium contains essentially about 0.2 to 0.3 gram per liter of trivalent chromium ions, 3.75 to 5.0 grams per liter of nitrate ions, 0.2 to 0.4 gram per liter of fluoride ions and 0.75 to 1.5 grams per liter of sulfate ions. Additionally,

0.5 to 1.0 gram per liter of zinc and or cadmium ions oftentimes is desirable for optimum control. This dilute bath composition may be provided readily by addition of the dry powder composition of the present application and has been found to produce a highly desirable lustre and mild protection upon both cadmium and zinc surfaces at ambient temperatures in immersion periods of five to forty-five seconds. However, it has been found that greatly enhanced corrosion protection as well as extremely desirable lustre can be obtained by use of more concentrated baths containing 1.5 to 5.0 grams per liter of trivalent chromium ions at a pH of about 0.2 to 1.0, and preferably 1.8 to 4.5 grams per liter of trivalent chromium ions. As in the case of the more dilute baths, the nitrate ion and activating ion must also be present, preferably in substantially the same weight ratio.

The baths of the present invention have proven highly effective in developing a cadmium-like clear finish upon zinc surfaces so as to simulate the appearance of cadmium which is oftentimes desirable where the cost or supply of cadmium is prohibitive of its use.

The pH of the bath should be between about 0.2 to 3.5 and preferably in the range of 0.2 to 2.0 for short dips of up to about ten seconds and in the range of 1.8 to 3.5 for dips up to one minute or longer. Where a pH below about 1.0 is desired or to be obtained, the acid-nitrate component should be substantially or entirely comprised of urea nitrate, the urea nitrate constituting at least about 75 percent by weight thereof. The baths produced by the composition of the present invention are preferably utilized at ambient temperatures on the order of 60 to 90° Fahrenheit for optimum operation. However, temperatures of 45 to 150° Fahrenheit may be employed depending upon the concentration of the bath and the time of treatment. Generally, the more dilute the bath, the higher the temperature that may be employed so as to provide a satisfactory treatment time and brightening action.

The time of treatment will vary with the temperature, pH and concentration of the bath. Generally, the period of immersion will vary between about two seconds and ten minutes, depending upon these three factors. The optimum time of treatment for a given bath concentration, temperature and pH is best determined by visual observation of a specimen workpiece. Generally, the baths produced according to the preferred aspect of the present invention operate at ambient temperatures requiring an immersion period of only about five to forty-five seconds. Subsequent to immersion in the bath, the workpieces are rinsed in cold and then in hot water to facilitate drying.

A general dry powder composition in accordance with the present invention which has been found highly desirable for the production of baths for brightening cadmium and zinc is one containing the following salts in the indicated proportions:

| | Percent by weight |
|---|-------------------|
| Trivalent chromium salt (chromium fluoride, chromium sulfate and combinations thereof) | 2.0-5.0 |
| Activating salt (zinc sulfate, cadmium sulfate, zinc fluoride, cadmium fluoride and combinations thereof) | 8.0-16.0 |
| Auxiliary activating salt (bifluorides and bisulfates of alkali metals and ammonia) | Up to 4.0 |
| Urea nitrate | 75.0-90.0 |

A specific example of a preferred formulation within the above-designated composition for use in treatment of cadmium surfaces is as follows:

| | Percent by weight |
|-------------------------|-------------------|
| Chromium fluoride | 3.7 |
| Zinc sulfate | 12.0 |
| Sodium bifluoride | 1.8 |
| Urea nitrate | 82.5 |

A specific example of a preferred formulation within

the above designated general dry powder composition for use in treatment of zinc surfaces is as follows:

| | Percent by weight |
|-------------------------|-------------------|
| Chromium fluoride ----- | 2.0 |
| Zinc sulfate ----- | 8.0 |
| Sodium bifluoride ----- | 1.0 |
| Urea nitrate ----- | 89.0 |

These compositions are added to water in amounts of from 6.0 to 250.0 grams per liter and utilized conveniently at ambient temperatures with dip times of five to twenty seconds. For economical, highly dilute baths, the rate of addition is about 6.0 to 30.0 grams per liter; for high corrosion protection, the rate of addition is about 100 to 250 grams per liter, and preferably about 150 to 250 grams per liter.

Because of the acidity and corrosive nature of the baths of the present invention, suitable tanks should be employed to avoid contamination such as rigid polyvinyl chloride, steel lined with polyvinyl chloride or resin-bonded glass fibers or polyethylene.

Illustrative of the efficacy of the present invention are the following examples wherein steel specimens electroplated with cadmium or zinc were treated in baths provided by dry powder formulations.

Example 1

To 1.0 liter of water was added 20.0 grams of a dry powder formulation containing 5.0 percent by weight chromium fluoride, 5.0 percent by weight sodium bifluoride, 50.0 percent by weight urea nitrate and 40.0 percent by weight sodium nitrate. The resultant bath had a pH of 2.1.

Upon immersion therein at room temperature for a period of about ten seconds, a clear bright finish was developed upon 2 inch x 3 inch cadmium-plated steel test panels. A drop of a 1.0 percent aqueous solution of lead acetate did not turn the surface black until thirty seconds had elapsed, indicating a desirable degree of protection.

Adding 10.0 grams per liter of the dry powder composition produced a bath having a pH of 2.1 which produced a clear bright finish on similar test panels during a dip of ten seconds. The resulting surface finish gave protection for twenty-five seconds in the lead acetate test.

Example 2

To 1.0 liter of water was added 20.0 grams of a dry powder formulation containing 5.0 percent by weight chromium fluoride, 5.0 percent by weight sodium bifluoride and 90.0 percent by weight urea nitrate. The resulting bath had a pH of 1.3 and gave a clear bright finish to a 2 inch x 3 inch cadmium-plated steel test panel after immersion therein for ten seconds. The finish gave protection for eight seconds in the lead acetate test.

A second bath was prepared by adding 10.0 grams of the above formulation to 1.0 liter which gave a bath having a pH of 1.5. Upon immersion therein for ten seconds, a cadmium-plated steel test panel developed a clear bright finish which gave a value of eight seconds in the lead acetate test.

A third bath was provided by adding 5.0 grams per liter of the above dry powder formulation and the pH was determined at 1.7. A cadmium-plated steel panel developed a clear bright finish after immersion therein for ten seconds and gave a value of six seconds in the lead acetate test.

Example 3

To 1.0 liter of water was added 14.4 grams of a dry powder composition containing 82.5 percent by weight urea nitrate, 3.7 percent by weight chromium fluoride, 12.0 percent by weight zinc sulfate and 1.8 percent by weight sodium bifluoride. The resultant bath had a pH of 1.4 and immersion of a 2 inch x 3 inch cadmium-plated steel test panel therein for a period of ten seconds pro-

duced a clear bright finish which gave a value of ten seconds in the lead acetate test.

Example 4

To 1.0 liter of water was added 20.0 grams of a dry powder composition containing 1.0 percent by weight sodium bifluoride, 2.5 percent by weight chromium fluoride, 8.5 percent by weight zinc sulfate, 44.0 percent by weight sulfamic acid and 44.0 percent by weight sodium nitrate. The resulting bath had a pH of 1.4 and produced a clear bright finish upon a cadmium-plated steel test panel immersed therein for ten seconds. This surface gave a value of three seconds in the lead acetate test.

To another liter of water was added 10.0 grams of this dry powder formulation to provide a bath having a pH of 1.6. Upon immersion therein for ten seconds, a cadmium-plated steel test panel developed a clear bright finish which gave a value of two seconds in the lead acetate test.

A bath containing 40.0 grams per liter of the dry powder formulation had a pH of 1.1 and produced a bright finish with a slight fog upon a cadmium-plated steel test panel. This finish gave a value of five seconds in the lead acetate test.

Example 5

To 1.0 liter of water was added 8.2 grams of a dry powder formulation containing 55.0 percent by weight urea nitrate, 30.6 percent by weight sulfamic acid, 2.8 percent by weight chromium fluoride, 10.5 percent by weight zinc sulfate and 1.1 percent by weight sodium bifluoride. The resultant bath had a pH of 1.5 and produced a semi-bright finish on a cadmium-plated steel test panel having a white fog therein.

Example 6

To 1.0 liter of water was added 3.0 grams of chromium fluoride, 3.0 grams of sodium bifluoride, 30.0 grams urea nitrate, and 24.0 grams of sodium nitrate. The resultant bath had a pH of 2.1. A cadmium-plated steel test panel immersed therein developed a bright finish which gave a value of five seconds in the lead acetate test.

Example 7

A dry powder formulation was prepared containing 2.0 percent by weight chromium fluoride, 8.0 percent by weight zinc sulfate, 1.0 percent by weight sodium bifluoride and 89.0 percent by weight urea nitrate. This dry powder formulation was dissolved in water in the amount of 15 grams per liter. A zinc-plated steel panel was immersed therein at ambient temperature for a period of five seconds and was found to develop a clear bright cadmium-like finish and to withstand discoloration by a 1.0 percent lead acetate solution for a period of twenty-two seconds, indicating a desirable degree of mild protection.

Example 8

A dry powder formulation was prepared containing 3.0 percent by weight chromium fluoride, 11.0 percent by weight zinc sulfate, 1.0 percent by weight sodium bifluoride and 85.0 percent by weight urea nitrate. Several baths were prepared by adding this formulation to water in amounts of 3.75 grams per liter, 30.0 grams per liter and 60.0 grams per liter.

A zinc test panel immersed in the first solution for a period of five seconds at ambient temperature exhibited a dull finish and gave a value of only two seconds upon exposure to a 1.0 percent lead acetate solution.

A panel immersed in the second formulation under similar conditions developed a clear cadmium-like finish and gave a value of thirty seconds with a 1.0 percent by weight lead acetate solution.

A panel immersed in the third solution containing 60.0 grams per liter developed a clear bright finish slightly superior to that of the second bath and gave a value of twenty-seven seconds upon testing with the 1.0 percent lead acetate solution.

Example 9

A dry powder composition was prepared containing 3.0 percent by weight chromium fluoride, 11.0 percent by weight zinc sulfate, 1.0 percent by weight sodium bifluoride and 85.0 percent by weight urea nitrate. Baths were prepared containing 100, 150 and 200 grams per liter, respectively, of the dry powder formulation. Both zinc and cadmium-plated test panels were immersed for periods of five seconds at ambient temperatures in each of the respective baths.

The third bath was found to have a pH of about 0.2. A zinc test panel immersed therein developed a clear bright finish and was found to resist discoloration by a 5.0 percent by weight lead acetate solution for a period of thirty-six seconds, indicating a very high degree of corrosion protection. A cadmium-plated test panel immersed in this same bath was found to develop a clear bright finish and to resist discoloration by a 5 percent lead acetate solution for a period of seventeen seconds, similarly indicating a high degree of corrosion protection.

The second bath containing 150 grams per liter was also found to have a pH of about 0.2. A zinc test panel immersed therein developed a clear bright finish with a trace of iridescence and was found to resist discoloration by a 5.0 percent lead acetate solution for a period of forty-five seconds. A cadmium test panel immersed therein developed a clear bright finish and resisted discoloration by a 5.0 percent lead acetate solution for a period of nineteen seconds.

The first bath containing 100 grams per liter was found to have a pH of 0.3. A zinc panel immersed therein developed a clear bright finish with a slight trace of iridescence and resisted discoloration by a 5.0 percent lead acetate solution for a period of three seconds, indicating a considerably reduced corrosion protection from that provided by the more concentrated baths. The cadmium-plated test panel developed a clear bright finish and resisted discoloration by a 5.0 percent lead acetate solution for a period of three seconds, indicating a reduced protection from that provided by the more concentrated baths.

Three hundred grams per liter of the dry powder formulation was found not to be fully soluble and to provide a pH of about 0.2. A zinc-plated test panel immersed therein for a period of five seconds developed an extremely clear bright finish. Upon exposure to a 1.0 percent lead acetate solution, it was found to resist discoloration for a period of five minutes. Upon exposure to a 5.0 percent by weight lead acetate solution, it was found to resist discoloration for a period of forty-five seconds, indicating a highly desirable degree of corrosion protection. A cadmium-plated test panel immersed therein for a similar period was found to exhibit evidence of attack by the bath upon the cadmium-plate, thus indicating that lesser concentrations should be employed for treatment of cadmium plate.

As will be readily seen from the foregoing detailed specification and specific examples, the present invention provides a self-contained dry powder formulation for addition to water to provide a highly effective bath for the chemical treatment of cadmium surfaces and zinc surfaces. This formulation can be readily shipped and handled conveniently and safely and provides a bath which is relatively economical in operation and pre-controllable in the optimum proportion of essential ingredients added thereto so as to provide a balanced bath composition. In accordance with the preferred aspects of the present invention, the dry powder formulation produces a bath which is highly effective in brightening cadmium and zinc surfaces and providing mild corrosion protection thereto in highly dilute concentration and a high degree of corrosion protection in more concentrated baths.

Having thus described the invention, we claim:

1. A self-contained dry powder composition for addition to water to provide an acid bath for treating cadmium surfaces and zinc surfaces consisting essentially of, on a dry weight basis, 1.0 to 25.0 percent by weight of a water-soluble trivalent chromium compound, up to 50.0 percent by weight of a water-soluble activating salt selected from the group consisting of sulfates, fluorides and the combination thereof, and 25.0 to 95.0 percent by weight of a water-soluble acid-nitrate component selected from the group consisting of urea nitrate, urea nitrate and the nitrate salts of inorganic bases, urea nitrate and sulfamic acid and sulfamic acid and the nitrate salts of inorganic bases, said acid-nitrate component being of sufficient acidity to provide a pH of 0.2 to 3.5 upon addition of the dry powder composition to water in an amount sufficient to provide about 0.08 to 5.0 grams per liter of the trivalent chromium ion, said dry powder composition additionally providing as essential ions nitrate ion and an activating ion selected from the group consisting of sulfates, fluorides and the combination thereof.
2. The composition in accordance with claim 1 wherein said acid-nitrate component is substantially urea nitrate.
3. The composition in accordance with claim 2 wherein said urea nitrate constitutes 75.0 to 90.0 percent by weight of said dry powder composition.
4. The composition in accordance with claim 1 wherein said acid-nitrate component is substantially urea nitrate and the nitrate salt of an inorganic base.
5. The composition in accordance with claim 1 wherein said acid-nitrate component is of sufficient acidity to provide a pH of 1.0 to 3.5 upon addition of the dry powder composition to water in an amount sufficient to provide 0.08 to 1.0 gram per liter of trivalent chromium ion.
6. The composition in accordance with claim 1 wherein said activating salt includes both sulfate and fluoride ions.
7. The composition in accordance with claim 1 wherein said activating salt includes a cation selected from the group consisting of zinc, cadmium and the combination thereof.
8. A self-contained dry powder composition for addition to water to provide an acid bath for treating cadmium surfaces and zinc surfaces consisting essentially of 2.0 to 5.0 percent by weight of a water-soluble trivalent chromium salt selected from the group consisting of chromium fluoride, chromium sulfate and the combination thereof, 8.0 to 16.0 percent by weight of a water-soluble salt selected from the group consisting of zinc sulfate, cadmium sulfate, zinc fluoride, cadmium fluoride and the combination thereof, up to 4.0 percent by weight of a water-soluble salt selected from the group consisting of bifluorides and bisulfates of the alkali metals and ammonia, and 75.0 to 90.0 percent by weight of urea nitrate.
9. The powder composition of claim 8 containing both sulfate and fluoride salts.
10. The method of brightening metallic surfaces selected from the group consisting of cadmium and zinc comprising dissolving in water a self-contained dry powder composition consisting essentially of 1.0 to 25.0 percent by weight of a water-soluble trivalent chromium compound, up to 50.0 percent by weight of a water-soluble activating salt selected from the group consisting of fluorides, sulfates and the combination thereof, and 25.0 to 95.0 percent by weight of a water-soluble acid-nitrate component selected from the group consisting of urea nitrate, urea nitrate and the nitrate salts of inorganic bases, urea nitrate and sulfamic acid, and sulfamic acid and the nitrate salts of inorganic bases, said dry powder composition being added in sufficient quantity to provide 0.08 to 5.0 grams per liter of trivalent chromium ion and a pH of 0.2 to 3.5 in the resultant bath and additionally providing nitrate ion and an activating ion selected from the group consisting of fluorides, sulfates and the combination thereof; maintaining said

bath at a temperature of about 45 to 150 degrees Fahrenheit; immersing a workpiece having a metallic surface selected from the group consisting of cadmium surfaces and zinc surfaces in said bath for a period of time sufficient to brighten the surface thereof; and rinsing said workpiece in cold water.

11. The method of claim 10 wherein said dry powder composition provides 1.5 to 5.0 grams per liter of trivalent chromium ion and a pH of about 0.2 to 1.0 and wherein said acid-nitrate component is comprised substantially of urea nitrate.

12. The method of claim 11 wherein said dry powder composition includes both fluoride and sulfate ions.

13. The method of claim 10 wherein said dry powder composition contains a water-soluble salt of a metal selected from the group consisting of zinc, cadmium and the combination thereof.

14. The method of brightening metallic surfaces selected from the group consisting of cadmium and zinc comprising dissolving in water a self-contained dry powder composition consisting essentially of 1.0 to 10.0 percent by weight of a water-soluble trivalent chromium compound selected from the group consisting of chromium fluoride, chromium sulfate, and the combination thereof, up to 20.0 percent by weight of a water-soluble activating salt selected from the group consisting of bifluorides and bisulfates of the alkali metals and ammonia, and 75.0 to 90.0 percent by weight of a water-soluble acid-nitrate component comprised substantially of urea nitrate, said dry powder composition providing a bath containing essentially about 0.08 to 5.0 grams per liter trivalent chromium ions and 0.4 to 26.0 grams per liter of activating ions selected from the group consisting of fluoride, sulfate and the combination thereof, said dry powder composition additionally providing a pH of 0.2 to 3.5 in the resultant bath; maintaining said bath at a temperature of about 45 to 150 degrees Fahrenheit; immersing a workpiece having a metallic surface selected from the group consisting of cadmium surfaces and zinc surfaces in said solution for a period of time sufficient to brighten the surface thereof; and rinsing said workpiece in cold water.

15. The method of claim 14 wherein said composition

provides a bath containing 1.5-5.0 grams per liter of trivalent chromium ion and a pH of about 0.2-1.0.

16. The method of claim 14 wherein said bath contains 1.8 to 4.5 grams per liter of trivalent chromium ions.

17. The method of brightening metallic surfaces selected from the group consisting of cadmium and zinc comprising dissolving in water a self-contained dry powder composition consisting essentially of 2.0 to 5.0 percent by weight of a water-soluble trivalent chromium salt selected from the group consisting of chromium fluoride, chromium sulfate and the combination thereof, 8.0 to 16.0 percent by weight of a water-soluble salt selected from the group consisting of zinc sulfate, cadmium sulfate, zinc fluoride, cadmium fluoride and the combination thereof, up to 4.0 percent by weight of a water-soluble salt selected from the group consisting of bifluorides and bisulfates of the alkali metals and ammonia, and 75.0 to 90.0 percent by weight of urea nitrate, said dry powder composition providing a bath containing essentially about 1.5 to 5.0 grams per liter trivalent chromium ions and additionally providing a pH of 0.2 to 1.0 in the resultant bath; maintaining said bath at a temperature of about 45 to 150 degrees Fahrenheit; immersing a workpiece having a metallic surface selected from the group consisting of cadmium surfaces and zinc surfaces in said solution for a period of time sufficient to brighten the surface thereof; and rinsing said workpiece in cold water.

18. The method of claim 17 wherein said bath contains the combination of fluoride and sulfate ions.

19. The method of claim 17 wherein said bath contains 1.8 to 4.5 grams per liter of trivalent chromium ions.

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