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CORROSION PROTECTING METAL FINISHING COMPOSITION

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This invention relates to corrosion protecting metal finishing compositions and more particularly metal finishing compositions which are prepared in a dry or powdered form and can be used to produce various types of finishes by dissolving them in various types of aqueous acidic media. The invention is especially concerned with the provision of compositions which are adapted to be used to provide corrosion protection for zinc surfaced articles or cadmium surfaced articles or zinc-copper alloy surfaced articles.

It has heretofore been proposed to protect zinc surfaces against corrosion by applying thereto aqueous chromic acid solutions followed by rinsing with water and leaching with an aqueous alkaline solution. The chromic acid solutions in some manner form a coating containing hexavalent and trivalent chromium compounds. This coating normally appears on a zinc surface as a yellow brown iridescent stain. A bright surface is obtained upon subsequent leaching with an alkali apparently due to the fact that the more highly colored hexavalent chromium compounds are leached from the protective film.

In the past it has been customary for the manufacturer of these corrosion protecting compositions to prepare them in the form of aqueous solutions which are sold as liquid concentrates in carboys and then diluted to the proper concentrate by the user. These materials could be prepared directly by the user but the handling of chromic acid involves some hazards.

One of the objects of the present invention is to provide a corrosion protecting finishing composition especially suitable for zinc surfaces or cadmium surfaces or zinc-copper alloy surfaces which is initially prepared, stored and transported in a powdered form and requires only the addition of water and an acid in order to make it suitable for use in treating metal surfaces to enhance the corrosion resistance of such surfaces.

Another object of the invention is to provide a relatively simple composition of the type described which will produce different color effects in the finishing of metal surfaces, especially zinc and cadmium, depending upon the specific type of acidic reagent added to the dry composition and the pH of the resultant bath employed for the treatment of the metal article.

A further object of the invention is to provide a method of producing bright, olive drab or bronze finishes on zinc surfaced articles from the same initial dry composition merely by varying the type of acid which is added thereto and, in the case of the bright phase, supplying a secondary leaching treatment.

An additional object of the invention is to provide a new and improved method of providing olive drab, dark gold, light gold, and bright uniform finishes on cadmium surfaced articles by using as the initial material the same dry composition, dissolving said composition in different acids and concentrations of acids and applying the resultant solution to cadmium surfaced articles with a secondary leaching treatment in the case of the bright phase.

Another object of the invention is to provide a dry composition of the type described which will remain stable during storage and transportation. Other objects will appear hereinafter.

In accordance with the invention it has been found that a composition which remains stable during storage and transportation can be prepared by intimately mixing together or blending a finely divided water soluble dichromate, either in crystallized or powdered form, and a water soluble, non-acidic, non-hygroscopic sulfate, preferably with the addition of a non-acidic, non-hygroscopic water soluble reducing agent and a non-acidic, non-hygroscopic water soluble salt of a lower aliphatic carboxylic acid. The resultant composition can be dissolved in water and an acid to produce finishing compositions suitable for providing various types of finishes depending upon the acid used and the concentration thereof. These finishing compositions are especially useful for providing olive drab, bronze and bright finishes on zinc plated surfaces and for providing olive drab, dark gold, light gold and bright finishes on cadmium plated surfaces. In addition to the color effects obtained and the uniformity of the color the resultant articles which have been treated with the aforesaid finishing compositions are provided with enhanced corrosion resistance.

The following composition illustrates a preferred type of dry composition for the practice of the invention:

Ingredients	Parts by Weight
Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)	90
Sodium sulfate (Na_2SO_4)	3–10
Sodium sulfite (Na_2SO_3)	0.5–5
Sodium acetate (CH_3OONa)	0–25

In preparing this composition the sodium dichromate is preferably ground in a hammer mill or other device which will reduce the size of the crystals or powder to a substantially uniform fine particle size free from lumps. The other ingredients are then blended with the sodium dichromate. Alternatively, all of the ingredients can be blended together and mixed in a suitable blending apparatus which will simultaneously reduce the size and break up any lumps so that the resultant product is a blend of relatively fine particles which will also readily dissolve in aqueous acidic solutions.

In order to provide a bright lustrous coating having a high specular reflectivity on a zinc surfaced article the foregoing dry composition is mixed with water and nitric acid to form a treating solution. The article is immersed in or otherwise treated with said solution preferably at a temperature of 70° to 90° F. for a relatively short period of time preferably 5 to 30 seconds. It is then rinsed with water and given a secondary treatment with an alkaline aqueous solution to remove hexavalent chromium salts.

In order to produce an olive drab color on a zinc surfaced article the aforementioned dry composition is mixed with water and sulfuric acid to form a solution. The zinc surfaced article is then immersed in or otherwise treated with this solution preferably at a temperature of 70° to 90° F. for a period of 5 to 30 seconds after which it is rinsed with water. No secondary treatment is required.

To produce a bronze color on a zinc surfaced article the aforementioned dry composition is dissolved in an aqueous solution of hydrochloric acid and the zinc surfaced article is immersed therein preferably at a temperature of 70° to 90° F. for a period of 5 to 30 seconds. Thereafter the article is rinsed with water. No secondary treatment with an alkaline solution is required.

To produced a bright lustrous cadmium surfaced article the aforementioned dry composition is dissolved in an aqueous solution of nitric acid and the cadmium surfaced article is immersed therein for a period of 5 to 30 seconds preferably at a temperature of 70° to 90° F. after which it is removed from the solution, rinsed with water and given a secondary treatment with an alkaline aqueous solution in order to leach out the hexavalent chromium salts. The procedure is generally the same as that employed for treating zinc surfaced articles except that the optimum results can be obtained with about half as much of the dry composition and nitric acid.

To produce an olive drab surface on cadmium good results are obtained by employing substantially the same composition which is used for the same purpose to produce an olive drab surface on zinc. The time of immersion, however, should preferably be about 1 minute at a temperature of 70° to 90° F.

To produce a dark gold surface on cadmium the aforementioned dry composition is dissolved in an aqueous solution of hydrochloric acid and a cadmium surfaced article is immersed therein preferably for a period of 5 to 30 seconds at a temperature of 70° to 90° F. after which it is removed and rinsed with water. No secondary treatment is required.

A light gold color on a cadmium surface can be produced by dissolving the aforementioned dry composition in a mixture of an aqueous solution of hydrochloric acid and sulfuric acid and immersing the cadmium surfaced article therein preferably for a period of 5 to 30 seconds at a temperature of 70° to 90° F. The article is then removed from the solution, rinsed with water and dried. No secondary treatment is required.

The invention will be further illustrated but is not limited by the following examples in which the quantities are stated in parts by weight unless otherwise indicated.

Example I

A dry composition was prepared by mixing together the following ingredients:

Ingredients	Parts by Weight
Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)	90
Sodium sulfate (Na_2SO_4)	5
Sodium sulfite (Na_2SO_3)	2.5
Sodium acetate (CH_3COONa)	2.5

In preparing this composition the sodium dichromate was reduced to fine particle size in a hammer mill and the other ingredients were mixed therewith.

Example II

The composition of Example I was made up into a treating solution by mixing it with water and nitric acid in the proportion of 21.5 ounces per gallon of the composition of Example I and 225 cc. per gallon of nitric acid, the remainder being water. A zinc plated article was immersed in the resultant solution for a period of approximately 15 seconds at a temperature of 70° to 90° F. and then removed and rinsed with water. The resultant article was given a secondary treatment by immersing it in a solution containing 2 ounces per gallon of sodium metasilicate for a period of 5 to 30 seconds at a temperature of 120° to 140° F. The article was removed from the second bath, rinsed and dried. An extremely bright zinc surfaced article having a high resistance to corrosion was obtained by this method.

Example III

The dry composition of Example I was dissolved in a mixture of water and sulfuric acid in proportions of 8 ounces per gallon of the dry composition and 44.5 cc. of sulfuric acid, the remainder being water.

Zinc surfaced articles when immersed in the resultant treating solution for a period of 5 to 30 seconds at a temperature of 70° to 90° F. were given a uniform olive drab coating. The articles were removed from the solution, rinsed with water and dried. No secondary treatment was required.

Example IV

A treating solution was prepared by mixing together 5.35 ounces per gallon of the dry composition of Example I and 75 cc. per gallon of hydrochloric acid, the remainder being water.

Excellent uniform bronze colors on zinc surfaced articles were obtained by immersing such articles in the resultant solution for a period of 5 to 30 seconds at a temperature of 70° to 90° F., then removing the articles from the solution, rinsing with water and drying. No secondary treatment was required.

Example V

A treating composition was prepared by mixing together 11 ounces per gallon of the dry composition of Example I and 113 cc. per gallon of nitric acid, the remainder being water.

A cadmium plated article was immersed in this treating composition for a period of 15 seconds, then removed, rinsed with water and immersed in a solution containing 4 to 6 ounces per gallon of equal parts by weight of sodium hydroxide and sodium sulfate at a temperature of 70° to 90° F. for about 15 seconds. Thereafter the article was removed from the second solution, rinsed with water and dried. The resultant article exhibited excellent specular reflectivity and high corrosion resistance.

Example VI

The dry composition of Example I was mixed with water and sulfuric acid in the proportion of 8 ounces per gallon of the dry composition and 45 cc. per gallon of sulfuric acid, the remainder being water.

Cadmium plated articles were immersed in the resultant treating solution for 1 minute at temperatures of 70° to 90° F., then removed, rinsed with water and dried. The resultant articles had a uniform olive drab color.

Example VII

The dry composition of Example I was dissolved in water and hydrochloric acid in the proportion of 5.35 ounces per gallon of the dry composition and 75 cc. per gallon of HCl, the remainder being water.

Cadmium plated articles were immersed in the resultant solution for a period of about 15 seconds at a temperature of 70° to 90° F., then removed from the solution, rinsed with water and dried. The resultant articles had a uniform dark gold appearance.

Example VIII

The dry composition of Example I was dissolved in an aqueous solution of hydrochloric acid and sulfuric acid in the proportion of 5.35 ounces per gallon of the dry composition, 57 cc. per gallon of HCl and 7.5 cc. of H_2SO_4, the remainder being water.

Cadmium plated articles were immersed in the resultant solution for a period of about 15 seconds at a temperature of 70° to 90° F., then removed from the solution, rinsed with water and dried. A beautiful light gold color was developed on the surface of the articles.

Where articles are being plated continuously the optimum concentrations of the ingredients of the treating solutions can be maintained by adding the various ingredients intermittently or continuously. Where articles having a bright surface are desired as in Examples II and V the additions to the treating solution are the dry composition of Example I and nitric acid. In the processes for producing olive drab colors as in Examples III and VI color control is maintained by the addition

of the dry composition of Example I and sulfuric acid. In processes for producing bronze colors as in Example IV, or dark gold colors as in Example VII, color control in continuous operations is maintained by the addition of the dry composition of Example I and hydrochloric acid. In processes where the final article has a light gold color on a cadmium plate, color control in continuous operations is maintained by adding the dry composition of Example I, hydrochloric acid and sulfuric acid.

In the compositions of the invention the sodium sulfate acts as a catalyst and also as a buffer. The sodium sulfite serves as a reducing agent when the mixture is subsequently added to an aqueous acid solution to reduce a part of the chromium from the hexavalent to the trivalent state. The sodium acetate acts as a buffer and also to increase rinsability of the treated article.

It is important for the purpose of the invention that the various ingredients of the dry composition be substantially non-acidic because acid salts or other acidic materials tend to react with the water soluble dichromate to form chromic acid, which is undesirable in the dry product on account of its hygroscopicity.

Instead of the sodium sulfite other reducing agents can be used which are capable of reducing hexavalent chromium compounds to trivalent chromium compounds in acidic solutions, but it is desirable to employ reducing agents which do not form insoluble byproducts with the acid of the acidic aqueous solution subsequently used to dissolve the dry composition. Other examples of preferred reducing agents are sodium thiosulfate, sodium hydrosulfite, potassium sulfite, potassium thiosulfate, potassium hydrosulfite, ammonium sulfite, ammonium thiosulfate, and ammonium hydrosulfite. The hydrosulfites are also commonly referred to as hyposulfites. Other reducing agents which reduce chromic acid in acid solution can be used. Reducing agents such as calcium sulfite are undesirable because of the formation of insoluble calcium sulfate. Organic reducing agents can be used but are generally less desirable because of possible violent reaction in the presence of chromium compounds.

The reduction reaction between the dichromate radical and the sulfite radical which occurs when the dry composition previously described is mixed with an acid and employed in treating a metal surface such as a zinc surface can be expressed by the following equation:

$$Cr_2O_7^{--} + 3SO_3^{--} + 8H^{+} \longrightarrow 2Cr^{+++} + 3SO_4^{--} + 4H_2O$$

In the treatment of zinc surfaced articles reduction takes place at the surface of the zinc with an increase in pH and hexavalent and trivalent chromium chromates are deposited. A similar phenomenon occurs with cadmium plated articles. For the purpose of the invention it is preferable that the finishing composition contain enough reducing agent to reduce at least 0.5% of the chromium to a trivalent state. The optimum result is obtained by employing enough of the reducing agent, e. g., sodium sulfite, to reduce about 2% of the chromium in the treating solution to the trivalent state. If the amount of trivalent chromium formed in the treating solution is too high the resultant product does not have the optimum brightness. While the invention is not limited to any theory, it is believed that when the trivalent chromium builds up too much it causes iridescence or variation in brightness in the bright phase. For this reason it is preferable to use a quantity of a reducing agent which will not reduce more than about 5% of the hexavalent chromium to the trivalent state.

The minimum amount of sulfate in the dry composition, calculated as Na_2SO_4, is preferably at least 3%, and the maximum amount is preferably around 10%, the optimum amount being around 5%. As the quantity of sulfate is decreased from the optimum the brightness is decreased in the bright phase, and as the quantity of sulfate is increased there is a tendency, particularly in the bright phase, to produce bluer shades which are usually less desirable for commercial purposes. The sulfate radical may also be supplied in the form of other water soluble non-acidic, non-hygroscopic salts such as potassium sulfate and magnesium sulfate. The ratio of sulfate, calculated as Na_2SO_4, to dichromate, calculated as $Na_2Cr_2O_7.2H_2O$, is preferably within the range of 1:30 to 1:9.

The sodium acetate is an optional ingredient which increases the rinsability of the article and acts as a buffer. It has very little effect, however, in altering the color of the surface of the article and hence the amounts can be varied over relatively wide limits. Instead of sodium acetate other water soluble lower aliphatic carboxylic acid salts can be used including, for example, sodium propionate, sodium butyrate and salts of lower aliphatic carboxylic acids containing not more than 6 carbon atoms and metals which do not precipitate insoluble sulfates in the acidic treating solutions.

In the practice of the invention potassium dichromate can be used to replace a part or all of the sodium dichromate, but is less desirable, particularly in the bright phase procedures, because of its lower solubility and tendency to crystallize from the treating solution at lower temperatures.

The color obtained depends to a large extent upon the acids used and the pH. Where the article is to have a high specular reflectivity, that is, where the bright phase procedures are used, the best results have been obtained by employing nitric acid and a pH of around 0.1 to 1.0, or even less than 0.1 (below the values measurable electrometrically) for treating either zinc or cadmium surfaces. If the pH is over 1 some effect is still obtained in the bright phase but the chromium compounds which are formed in the conversion coating are difficult to leach.

In the olive drab phase procedure on zinc the optimum pH of the treating solution is around 0.8 to 0.9 and the preferred pH range is 0.5 to 1.25. If the pH becomes too high, the desired uniform conversion coating does not form.

In the bronze phase procedure on zinc the optimum pH of the treating solution is around 0.8 to 0.9 and the preferred pH range is 0.4 to 1.75. If the pH becomes too high the desired uniform conversion coating does not form.

In the dark gold phase procedure on cadmium the optimum pH of the treating solution lies within a range of 0.4 to 2.0.

In the light olive drab phase procedure on cadmium the optimum pH of the treating solution is within the range of 0.5 to 1.25.

As previously indicated, the secondary treatment to leach out hexavalent chromium salts which would otherwise tend to discolor the conversion coating is essential only in the bright phase procedures. This secondary treatment may be carried out with a caustic alkali such as sodium hydroxide which should preferably be used in a concentration of at least two ounces of NaOH per gallon of aqueous solution. Lower concentrations can be used but tend to produce articles having a bluish tint. Other alkaline substances such as sodium carbonate or soda ash can be used in the secondary treating bath. Especially good results have been obtained by employing as the secondary bath aqueous solutions of alkali metal silicates which are preferably used hot, i. e. 120° to 140° F. The secondary treating baths described in U. S. Patents 2,548,419 and 2,548,420 can be employed in the practice of the invention.

Unusual and surprising results with respect to enhanced corrosion protection have been obtained by employing as the secondary treating bath an alkaline aqueous solution containing a sulfate, e. g., sodium sulfate, potassium sulfate, magnesium sulfate and/or ammonium sulfate with

or without 5% to 30% dextrose. The leaching effect of the bath is about the same as that of the alkali alone but the corrosion protection is much better and ordinary temperatures (70° F. to 90° F.) can be used. While the reason for this phenomenon is not definitely known, it is believed that the alkali removes part of the protecting film and the presence of the sulfate in some manner prevents this removal. This invention is described and claimed in copending application Serial No. 359,217, filed by one of the joint inventors herein June 2, 1953.

The amount of chromium present in the treating solution can be varied depending upon the color effect desired and the type of metal treated. For bright phase procedures on zinc surfaced articles in order to obtain the optimum results the quantity of hexavalent chromium compounds (calculated as Cr) in the treating solution is within the range of 11.5 to 80 grams per liter. This corresponds to approximately 40 grams to 250 grams per liter of treating solution of the composition of Example I.

For bright phase procedures on cadmium surfaced articles in order to obtain optimum results the quantity of hexavalent chromium compounds (calculated as Cr) should be within the range of 5.5 to 63 grams per liter of treating solution.

For optimum results in the olive drab phase on zinc surfaced articles the treating solution should preferably contain hexavalent chromium compounds (calculated as Cr) within the range of 9.5 to 28.5 grams per liter of treating solution. This corresponds to approximately 30 to 90 grams per liter of the composition of Example I.

In order to produce a light olive drab color on cadmium surfaced articles the hexavalent chromium content of the bath (calculated as Cr) is preferably within the range of 9 grams to 63 grams per liter of treating solution. This corresponds to approximately 30 to 200 grams per liter of the composition of Example I.

For optimum results in the bronze phase on zinc or the dark gold phase on cadmium the treating solution preferably contains hexavalent chromium compounds (calculated as Cr) within the range of 1.5 to 63 grams per liter of treating solution. This corresponds to approximately 5 to 200 grams of the composition of Example I per liter of treating solution.

Where nitric acid is used in preparing the acid treating solution different results are obtained on zinc and cadmium depending upon the relative concentrations of nitric acid and chromium compounds present in the treating solution. Also, there appears to be a relationship between the pH and chromium concentration on zinc which does not apply to cadmium and vice versa. Thus it is possible to obtain a golden color on cadmium at a pH within the range of 0.4 to 2.0 with a chromium content of 1.5 grams to 63 grams per liter of treating solution (5 grams to 200 grams of the composition of Example I), but on zinc the golden yellow color is obtained only in the upper part of this range around pH 2.0. As the pH is decreased in nitric acid solutions used for treating zinc the color becomes lighter and in the lower part of the range is extremely light.

As an example of some of the variations that occur with varying concentrations of nitric acid in the preparation of treating solutions for zinc it was noted that a solution made from 10 grams per liter of the composition of Example I and 20 cc. per liter of HNO_3 when used to treat zinc in the manner previously described resulted in an article having a gray appearance either leached or unleached. With 40 grams per liter of the composition of Example I and 20 cc. of HNO_3 per liter of treating solution the resultant article had a yellow appearance without any secondary leaching treatment and a bright appearance when subjected to a secondary leaching treatment. These relative concentrations appear to be about the minimum at which a desired bright appearance can be obtained with a secondary leaching. With 40 grams per liter of the composition of Example I and 30 cc. per liter of nitric acid in the treating solution zinc surfaced articles present a very weak yellow appearance unleached and a bright appearance when leached by a secondary treatment as previously described. With 10 grams per liter of the composition of Example I and 10 cc. per liter of HNO_3 the treating solution gives a satisfactory yellow color on zinc surfaced articles when the articles are not subjected to a secondary leaching treatment. However, if the articles are leached the resultant surface is mottled. For bright phase procedures on cadmium surfaced articles excellent results are obtained with about half of the quantities of chromium compounds and nitric acid normally employed in treating solutions for zinc surfaced articles.

The products which have been treated with acidic solutions prepared in accordance with the invention show a high resistance to the formation of white corrosion products in the case of zinc surfaced articles and to cadmium "whiskers" in the case of cadmium surfaced articles. The invention is especially advantageous in that the dry composition is stable on storage, easy to handle, occupies a very small amount of storage space and can be shipped at much lower costs than has previously been possible with the so-called liquid chromates. At the same time a wide variety of color effects can be obtained on various types of metal articles merely by varying the concentrations of the dry composition and the types of acid used to prepare the treating solutions. Although the treating solutions are primarily useful for treating zinc and cadmium they can also be employed in treating white or yellow alloys of zinc and copper. The resultant products are characterized by enhanced corrosion resistance which may be varied within relatively wide limits depending upon the specific type of treatment.

The expression "zinc surfaced article" is employed herein to cover any article having an exterior surface of zinc regardless of whether the article itself is made of zinc, a ferrous metal or some other metal capable of being coated with zinc. The expression "zinc plated article" is employed herein to describe a zinc coated article in which the zinc coating has been applied by an electroplating process. The expression "white alloys of zinc and copper" is employed herein to describe alloys of zinc and copper which have a white or silvery apperance, as distinguished from alloys of zinc and copper which are yellow in appearance. The alloys of zinc and copper which have a white or silvery appearance preferably contain about 5% to about 30% by weight copper, the remainder being zinc. The expression "cadmium surfaced articles" is employed herein to cover any article having an exterior surface of cadmium regardless of whether the article itself is made of cadmium, a ferrous metal or some other metal capable of being coated with cadmium. The expression "cadmium plated article" is employed herein to describe a cadmium coated article in which the cadmium coating has been applied by an electroplating process.

The invention is hereby claimed as follows:

1. An aqueous acidic metal treating solution consisting essentially of 1.5 to 80 grams per liter, calculated as Cr, of dichromate dissolved in an aqueous solution of an acid from the group consisting of hydrochloric acid and nitric acid having a pH not greater than 2.0, a quantity of non-acidic sulfate, calculated as Na_2SO_4, to dichromate, calculated as $Na_2Cr_2O_7.2H_2O$, within the range of 1:30 and 1:9 dissolved in said solution, from 2.5 to 25 parts by weight, calculated as sodium acetate, of a lower aliphatic carboxylic acid salt per 90 parts by weight of $Na_2Cr_2O_7.2H_2O$, and a quantity of an inorganic reducing agent which does not form insoluble sulfates in said solution dissolved in said solution in an amount sufficient to reduce at least 0.5% and not more than 5% of the

hexavalent chromium in said solution to the trivalent state.

2. An aqueous acidic metal treating solution consisting essentially of 1.5 to 63 grams per liter, calculated as Cr, of dichromate dissolved in an aqueous solution of hydrochloric acid containing sufficient hydrochloric acid to produce a pH within the range of 0.4 to 1.75, a quantity of non-acidic sulfate, calculated as Na_2SO_4, to dichromate, calculated as $Na_2Cr_2O_7.2H_2O$, within the range of 1:30 to 1:9 dissolved in said solution, from 2.5 to 25 parts by weight of sodium acetate per 90 parts by weight of $Na_2Cr_2O_7.2H_2O$, and a quantity of an inorganic reducing agent which does not form insoluble sulfates dissolved in said solution and sufficient to reduce at least 0.5% and not more than 5% of the hexavalent chromium in said solution to the trivalent state.

3. An aqueous acidic metal treating solution consisting essentially of 5.5 to 63 grams per liter, calculated as Cr, of dichromate dissolved in an aqueous solution of nitric acid containing sufficient nitric acid to produce a pH below about 1.0, a quantity of non-acidic sulfate, calculated as Na_2SO_4, to dichromate, caluculated as

$$Na_2Cr_2O_7.2H_2O$$

within the range of 1:30 to 1:9 dissolved in said solution, from 2.5 to 25 parts by weight of sodium acetate per 90 parts by weight of $Na_2Cr_2O_7.2H_2O$, and a quantity of an inorganic reducing agent which does not form insoluble sulfates dissolved in said solution and sufficient to reduce at least 0.5% and not more than 5% of the hexavalent chromium in said solution to the trivalent state.

4. A method of finishing articles from the class consisting of cadmium surfaced articles, zinc-copper surfaced articles and zinc surfaced articles which comprises treating them with an acidic aqueous solution of an acid from the group consisting of nitric acid and hydrochloric acid having a pH not substantially greater than 1.75 having dissolved therein a dichromate in the proportion of about 1.5 to about 80 grams per liter, calculated as Cr, from 2.5 to 25 parts by weight, calculated as sodium acetate, of a lower aliphatic carboxylic acid salt per 90 parts by weight of $Na_2Cr_2O_7.2H_2O$, and an inorganic non-acidic sulfate in a weight ratio of said sulfate, calculated as Na_2SO_4, to said dichromate, calculated as

$$Na_2Cr_2O_7.2H_2O$$

within the range of 1:30 to 1:9 together with an amount of an inorganic reducing agent incapable of forming insoluble sulfates in said acidic solution sufficient to reduce 0.5% to 5% of the hexavalent chromium to trivalent chromium in said solution.

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