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COATING MALLEABLE NON-NOBLE HEAVY METALS

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This invention relates to the coating of malleable, non-noble heavy metals, and has for its object the provision of an improved method of producing a useful coating or film on such metals.

By "malleable, non-noble, heavy metals" I mean ferrous metals or alloys such as iron and steel, zinc and cadmium and alloys composed principally of zinc or cadmium or both, lead, tin and the like.

The invention is particularly concerned with the production of a visible film or coating on malleable, non-noble heavy metals, or on objects having a surface of a malleable, non-noble heavy metal, for the purpose of retarding corrosion and particularly the formation of corrosion products resulting from atmospheric or moisture exposure.

It has been suggested heretofore to treat zinc with chromate or dichromate solutions, or with dilute solutions of chromic acid, to passivate the metal and increase its resistance to corrosion. It has also been suggested to treat zinc or cadmium with a solution containing chromic and sulphuric acids to produce a so-called "bright etch" or bright metallic finish. In treating zinc or cadmium with chromic and sulphuric acids it has been the object to employ a solution having such a ratio of sulphate ions to chromate or dichromate ions that a "bright etch" would result without forming a film or coating on the metal. So far as I am aware, such heretofore suggested immersion methods have not intentionally produced a visible or corrosion-retarding film.

As a result of my investigations I have discovered that a visible, colored, protective or corrosion-retarding film or coating can be formed on a malleable, non-noble heavy metal by immersion of the metal for a relatively short time in an acid aqueous solution containing chromic acid ions and the anions of a mineral acid. The chromic acid ions may result from the solution in water of either chromium trioxide or a water-soluble dichromate and by "mineral acid" I mean sulphuric acid, hydrochloric acid and nitric acid. Based upon these discoveries, my present invention involves producing visible protective or corrosion-retarding coatings on a malleable non-noble heavy metal, or on an object having a surface of such a metal, by subjecting the metal (for example by immersion treatment) to the action of an acid aqueous solution containing chromic acid ions and the anions of a mineral acid. Solutions for practicing the invention may be made up by dissolving in the water appropriate amounts of chromium trioxide or a water-soluble dichromate such as sodium dichromate, and adding to or

otherwise suitably including in the solution a predetermined amount of the mineral acid or a water-soluble salt of the mineral acid such, for example, as the sodium salt sufficient to establish adequate acidity and anion concentration. The acidity of the solution should be at least equivalent to 3 ccs. of sulphuric acid (specific gravity 1.84) per liter of water, as indicated in the specific compositions of solutions given hereinafter.

In carrying out the invention, the article to be coated may be subjected to an immersion treatment in or sprayed with an acid aqueous solution having an appropriate ratio of chromic acid ions to the anions of the mineral acid to form a visible corrosion-retarding coating. The films or coatings formed may vary from pale yellow and light tan through a wide range of colors to black and tend to display iridescence.

A satisfactory solution for the practice of the invention may contain from about 10 grams of chromium trioxide per liter of water up to 300 grams or about the saturation point, but the range from about 25 to 200 grams per liter of water has been found to be highly satisfactory. The relatively dilute solutions usually produce less attractive films and have a lower reserve chromic acid ion content than the solutions of higher concentrations. With relatively highly concentrated solutions the loss by dragout is unnecessarily high. The quantity of mineral acid anion in the solution should be proportional to the amount of chromic acid ion present, and should be greater for coating tin and ferrous metals than when coating zinc, cadmium and lead. Thus, for coating zinc, cadmium and lead by treatment with solutions containing, for example, about 25 grams of chromium trioxide per liter of water, from 1 to 19 cc. of sulphuric acid (specific gravity 1.84) may be added per liter of water, and with a solution containing about 200 grams of chromium trioxide per liter of water, from 6 to 80 cc. of sulphuric acid (specific gravity 1.84) may be added per liter of water. For coating tin and ferrous metals by treatment with a solution containing about 200 grams of chromium trioxide per liter of water, from 140 to 500 cc. of sulphuric acid (specific gravity 1.84) may be added per liter of water. For coating ferrous metals by treatment with a solution containing about 10 grams of chromic acid or water soluble dichromate per liter of water about 10 cc. of sulphuric acid (specific gravity 1.84) per liter of water may be added. The sulphate ion may be added to solutions for coating zinc, cadmium and lead in the form of a salt,

such as sodium sulphate, in amounts equivalent to the above indicated amounts of sulphuric acid.

With solutions containing about 200 grams of chromium trioxide per liter of water, my present preferred range of sulphuric acid concentration (in cc. added per liter of water) is substantially as follows:

Metal	Sulphuric acid (Sp. Gr. 1.84)
Lead.....	10-100
Zinc.....	8- 50
Cadmium.....	8- 50
Ferrous metals.....	140-190
Tin.....	250-310

The films formed on zinc or cadmium base metals when immersed in solutions of the above type possess a golden-brown (bronze or brass) color and tend to display iridescence, especially when the amount of sulphuric acid is low in proportion to the amount of chromic acid. In case the content of sulphuric acid is very low, the amount of sulphate anion being just above the amount at which only etching occurs, the films formed are semi-transparent having a noticeable blue tinge.

The films formed on cold rolled steel when immersed in solutions of the above types possess a pale yellow or light tan to brownish yellow color. The films formed on lead are bluish in color and on tin are faint yellow. In all cases the films tend to display iridescence, especially when the amount of sulphuric acid is low in proportion to the amount of chromic acid.

Hydrochloric acid or nitric acid may be used in lieu of sulphuric acid, although I prefer not to use either hydrochloric acid or nitric acid when coating tin. Similarly, in lieu of sulphuric acid water soluble salts of hydrochloric acid may be used in coating zinc, cadmium, lead and ferrous metals, and water soluble salts of nitric acid may be used in coating zinc, cadmium and lead. In general the coatings produced in solutions containing nitrate ions are less desirable than those produced in solutions containing sulphate or chloride ions.

In coating zinc and cadmium, the amount of chloride ions required to produce a film having a given color or appearance is slightly greater than where the solution contains sulphate ions, and the amount of nitrate ions required to produce a film of about the same color and appearance is very much larger. With solutions containing about 200 grams of chromium trioxide per liter of water, my present preferred range of hydrochloric and nitric acids (in cc. added per liter of water) is indicated by the following table:

Metal	Hydrochloric acid 35% HCl; Sp. Gr. 1.18	Nitric acid 69% HNO ₃ ; Sp. Gr. 1.42
Lead.....	7-45	1-7
Cold rolled steel.....	280-400	310-500

The invention may be carried out by employing a solution containing a dichromate, for example, sodium or potassium dichromate, in which the acid is provided by a mineral acid. If the sodium salt be used, the solution may contain from about 15 to 300 or more grams of sodium dichromate (Na₂Cr₂O₇·2H₂O) per liter of water, the range from about 50 to 300 grams per liter of water being preferred. With solutions containing about 300 grams of sodium dichromate

per liter of water, my present preferred range of mineral acid concentrations (in cc. added per liter of water) is generally indicated by the following table:

Metal	Sulphuric acid Sp. Gr. 1.84	Hydrochloric acid 35% HCl; Sp. Gr. 1.18	Nitric acid 69% HNO ₃ ; Sp. Gr. 1.42
Zinc and cadmium.....	3- 80		
Lead.....	3-220	3- 70	2- 10
Ferrous.....	180-210	380-480	310-550
Tin.....	310-350		

In coating zinc, cadmium and lead, the mineral acid anion may be included in the chromic acid solution by adding a substantially equivalent amount of a water soluble salt of the mineral acid. In coating other metals it will generally be found preferable to use the mineral acid itself as the source of mineral acid anion. However, in the case of ferrous metals very desirable coatings are obtained with solutions containing about 200 grams of chromic acid per liter of water with the addition of about 85 to 300 grams of sodium chloride per liter of water. Desirable coatings may also be obtained on ferrous metals with solutions containing about 10 grams chromic acid and 10 grams or more of sodium chloride per liter of water. Solutions of concentrations between these limits may likewise be used.

Before immersion the metal articles to be treated should be cleansed to remove dirt or grease. This may be done by a cathodic treatment of the article for ½ to 3 minutes in a hot solution of trisodium phosphate, using enough current to causes copious evolution of gas. At the conclusion of the cathodic treatment the article is rinsed in hot and then in cold water to remove any adhering impurities.

The coatings are formed in all modifications of the invention by simply immersing the article in the solution for periods ranging from 2 seconds to 3 minutes, periods of from 2 to 30 seconds being usually of sufficient duration to produce satisfactory results. The immersion time depends somewhat upon the composition of the solution being used, but chiefly upon the character of the metal being treated. The metal and solution may be normal room temperature when carrying out the immersion treatment.

The immersion solutions gradually become spent, mainly because of the exhaustion of ions containing hexavalent chromium in the production of the coating, which latter appears to contain a substantial amount of trivalent chromium along with some hexavalent chromium. After the immersion treatment, the article is cleansed of adhering solution and then dried by any appropriate means as for example in an air blast. The coating is fragile immediately after its formation and must be aged for a short time before being subjected to abrasion.

The principal disadvantage in commercial practice of using relatively dilute solutions of chromic acid or water soluble dichromate is that such solutions have a short operating life, because of the low reserve chromic acid ion content. Solutions with a low chromic acid ion content also have a narrower range of mineral acid concentration within which the usual preferred colored coatings can be obtained and for this reason are somewhat more difficult to control. These disadvantages become less important, when the volume of the solution used is relatively large in comparison to the amount of metal treated by it.

For example, zinc base die-castings may advantageously be coated by a short immersion in a fairly concentrated chromic acid ion solution contained in a relatively small tank. On the other hand, in coating steel where it is often necessary to treat large unwieldy pieces such as automobile fenders on a production basis, it may be desirable to treat them on conveyors by passing them through a chamber in which the coating solution is sprayed on them, and since the time of treatment would generally be somewhat longer (than by direct immersion) a solution relatively dilute in chromic acid ions might be advantageously employed, and a large volume of solution might well be required for circulation through the system.

The films or coatings produced in accordance with the invention not only retard corrosion of the metal but are also useful for decorative purposes. Protection of the metal from corrosion may in some cases be enhanced by applying a finishing coat of paint or enamel, for example a paint film of conventional rust protective character, to the film or coating produced in accordance with the invention.

This application is a continuation in part of my copending application Serial No. 670,992, filed May 13, 1933, issued March 24, 1936 as U. S. Patent No. 2,035,380.

I claim:

1. The method of coating a malleable non-noble heavy metal which comprises subjecting the surface of the metal to the action of an acid solution containing a reagent selected from the group consisting of chromic acid and water soluble dichromates, the acidity of said solution being at least equivalent to 3 ccs. per liter of water of sulphuric acid having a specific gravity of 1.84, said solution also containing the anions of a mineral acid of the group consisting of sulfuric acid, hydrochloric acid and nitric acid, regulating the ratio between the concentration of said reagent and the concentration of mineral acid anions in said solution within limits at which a colored coating is formed, and leaving the surface of the metal in contact with the solution until a visible colored protective coating appears on said surface.

2. The method of producing a visible colored protective coating on a malleable non-noble heavy metal which comprises subjecting the surface of the metal to the action of an aqueous solution having an acidity equivalent to at least 3 ccs. per liter of water of sulphuric acid having a specific gravity of 1.84 and containing from 25 to 300 grams per liter of water of a reagent selected from the group consisting of chromic acid and water soluble dichromates, said solution also containing the anions of a mineral acid of the group consisting of sulfuric acid, hydrochloric acid and nitric acid, regulating the ratio between the concentration of said reagent and the concentration of the mineral acid anions

in said solution within limits at which a colored coating is formed and leaving the surface of the metal in contact with the solution until a visible colored protective coating appears on said surface.

3. The method of producing a visible colored protective coating on a malleable non-noble heavy metal which comprises subjecting the surface of the metal to the action of an aqueous solution containing about 200 grams of chromium trioxide per liter of water and a mineral acid of the group consisting of sulfuric acid, hydrochloric acid and nitric acid, the acidity of said solution being at least equivalent to 3 ccs. per liter of water of sulphuric acid having a specific gravity of 1.84, regulating the ratio between the concentration of chromium trioxide and the concentration of the mineral acid in said solution within limits at which a colored coating is formed and leaving the surface of the metal in contact with the solution until a visible colored protective coating appears on said surface.

4. The method of producing a visible colored protective coating on a malleable non-noble heavy metal which comprises subjecting the surface of the metal to the action of an acid aqueous solution containing about 300 grams per liter of a water soluble dichromate and the anions of a mineral acid of the group consisting of sulfuric acid, hydrochloric acid and nitric acid, the acidity of said solution being at least equivalent to 3 ccs. per liter of water of sulphuric acid having a specific gravity of 1.84, regulating the ratio between the concentration of the dichromate and the concentration of the anions of the mineral acid in said solution within limits at which a colored coating is formed and leaving the surface of the metal in contact with the solution until a visible colored protective coating appears on said surface.

5. The method of producing a visible colored protective coating on a malleable non-noble heavy metal which comprises subjecting the metal to immersion treatment in an acid aqueous solution containing from 10 to 300 grams per liter of water of water soluble dichromates, said solution also containing from 100 to 500 grams per liter of water of a mineral acid of the group consisting of sulfuric acid, hydrochloric acid and nitric acid, and leaving the metal in contact with the solution until a visible colored protective coating appears on said surface.

6. The method of producing a visible colored protective coating on a ferrous metal which comprises subjecting the metal to the action of an acid aqueous solution containing from 10 to 200 grams per liter of water of chromic acid and from 10 to 300 grams per liter of sodium chloride and leaving the surface of the metal in contact with the solution until a visible colored protective coating appears on said surface.

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