

# UNITED STATES PATENT OFFICE

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## METHOD OF COATING ZINC OR CADMIUM BASE METALS

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This invention relates to the coating of zinc or cadmium base metals, or zinc or cadmium coated metal, and has for its object the provision of an improved method of producing a useful coating or film on such metals. By "zinc or cadmium base metals" I mean metals and alloys composed principally of zinc or cadmium, including metals (e. g. other than zinc) coated with a zinc or cadmium base metal as for example by galvanizing, electroplating, etc.

In my co-pending application, Serial No. 65,138, filed February 21, 1936, I have described and claimed generally the production of visible protective coatings on malleable non-noble heavy metals by methods analogous to those herein described.

The invention is particularly concerned with the production of a visible film or coating on zinc or cadmium metals, including zinc or cadmium base alloys, for the purpose of retarding corrosion and particularly the formation of white corrosion products resulting from atmospheric or moisture exposure. Ordinary commercial zinc (in particular, rolled or strip zinc), zinc base alloys such as die-casting alloys containing aluminum, magnesium and/or copper (for example, the alloys of United States Patents Nos. 1,596,761, 1,663,215, 1,779,525, 1,852,434, 1,852,441 and Re. 18,600), and rolled zinc-base alloys of United States Patent No. 1,716,599, may be advantageously coated by the method of the invention.

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.

During the course of my investigations I have found that if sulphate anions (in the form of sulphuric acid or a soluble sulphate that does

not form a precipitate with chromic acid) be added in gradually increasing amounts to a chromic acid solution in which zinc is dipped, that the action of the solution on the zinc varies with the sulphate anion concentration. When the amount of sulphate anions is very small, very little zinc is dissolved and the zinc surface is found to be slightly passivated. As the concentration of the sulphate is increased the amount of zinc dissolved increases and the zinc begins to be visibly etched. This etching action continues until a certain sulphate concentration is reached, when a visible coating begins to form. Within the range of sulphate concentrations which produces the most desirable coatings, the amount of zinc dissolved no longer increases appreciably with the increase in sulphate concentration. Within a narrow range of sulphate concentration beyond that at which the coating first forms, the coating is semi-transparent and has a noticeable blue tinge. After this range has been passed, the coating becomes iridescent and finally develops a golden-brown (bronze or brass color). Further increase in the sulphate concentration causes the film to dissolve, so that the action on the zinc is merely an etching.

I have found that the appearance of the coating as to color and iridescence varies slightly with the metal employed for a given concentration of chromic and sulphuric acids. Moreover, the range of sulphate concentration, within which coatings are formed, varies slightly with the metal employed, whether it be cadmium, zinc, or a zinc-base alloy, and closely parallels that described for zinc. If the metal treated be a zinc-base alloy containing copper, for example a rolled zinc-base alloy containing 1 per cent copper and 0.01 per cent magnesium, the disappearance of the film due to the presence of an excessive amount of sulphate ions is indicated by a change in color of the treated metal from the golden-brown of the film to black due to the solution of copper from the alloy and its reprecipitation in finely divided black form.

If a solution of sodium dichromate be employed in place of chromic acid, and successive additions of sulphuric acid be made, the reactions of the metal immersed in the solution are in general similar to those hereinbefore described for chromic acid solutions. With a sodi-

um dichromate solution, however, the amount of zinc dissolved is much less than with a chromic acid solution. Moreover, in the range of sulphuric acid concentrations within which the most desirable coatings are formed, the amount of zinc dissolved continues to increase as the sulphuric acid concentration is increased.

In carrying out the treatment according to the invention the metal appears to undergo the following actions: (1) Etching of the metal, (2) passivation of the metal, and (3) the formation of a visible protective coating. I attribute these actions which appear to occur in the formation of a protective coating, to the character of solution employed in the treatment.

As a result of my investigations I have discovered that a visible, colored, protective film can be formed on zinc or cadmium base metals that is resistant to the corrosive action of the atmosphere or moisture. I have found that if the metal be immersed for a relatively short time in an acid solution containing chromate or dichromate ions and the anions of a mineral acid, that a visible film or coating will be formed thereon. By "mineral acid" I mean sulphuric acid, hydrochloric acid, and nitric acid. Based upon these discoveries, my present invention involves, in its broad aspect, the formation of a visible coating on zinc or cadmium base metal by immersing the metal in an acid solution containing chromate or dichromate ions and the anions of a mineral acid. Solutions for practicing the invention may contain chromic acid and the anion of the salt of a mineral acid, or a dichromate and a free mineral acid.

In carrying out the invention the articles of zinc or cadmium base alloys to be coated are subjected to an immersion treatment in an acid solution having an appropriate ratio of chromate, or dichromate, ions to the anions of a mineral acid to form a visible coating. The films or coatings formed may vary from a golden-brown (bronze or brass color) to black and tend to display iridescence.

An appropriate solution for carrying out the invention may be formed of chromic acid and a salt of a mineral acid such, for example, as sodium sulphate, sodium chloride, ammonium chloride or sodium nitrate. Free mineral acid may be added if desired. A satisfactory solution may contain from about 25 grams of chromium trioxide per liter of water up to 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 produce less attractive films than the solutions of higher concentration. With relatively highly concentrated solutions the loss by drag-out is unnecessarily high. The quantity of mineral acid anion in the solution should be proportional to the amount of chromic acid present. With solutions containing, for example, about 50 grams of chromium trioxide per liter of water, from 2 to 10 cc. of sulphuric acid (specific gravity 1.84) may be added per liter of water, and in the case of a solution containing about 200 grams of chromium trioxide per liter of water, about 8 to 50 cc. of sulphuric acid may be added per liter of water. The sulphate ion may be added in the form of a salt, such as sodium sulphate, in amounts equivalent to the above indicated amounts of sulphuric acid.

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.

If hydrochloric acid or an equivalent amount of a salt such as sodium chloride be added to the chromic acid, the amount necessary to produce a film having a given color or appearance is slightly greater than if sulphuric acid or sodium sulphate be employed.

If nitric acid be added to the chromic acid, very much larger amounts of nitric acid must be used in order to obtain satisfactory coatings, and in general the coatings are less desirable than those produced by the addition of sulphate or chloride ions.

The invention may be carried out by employing a solution containing a dichromate, for example sodium or potassium dichromate, in which the acidity is provided by a mineral acid, for example sulphuric, hydrochloric or nitric acids. If the sodium salt be used, the solutions may contain from about 25 to 300 or more grams of sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) per liter of water, the range from about 50 to 300 grams per liter being preferred. The films formed on zinc by means of such solutions may vary from a pale and iridescent nature to a uniform, very slightly iridescent bronze color, depending upon the amount of sulphuric acid in solution. Thus, with a solution containing about 50 grams of sodium dichromate per liter of water, the quantity of sulphuric acid (specific gravity 1.84) required to be added to the solution varies from about 1.0 to 19.5 cc. per liter of water; however, an amount of acid within the range of from 1.5 to 7.5 cc. per liter of water is generally preferred. When using a solution containing about 300 grams of sodium dichromate per liter of water, the quantity of sulphuric acid (specific gravity 1.84) required to be added to the solution may vary from 2 to 80 cc. per liter of water, while a preferred amount of acid will generally be found within the range of from 3 to 19 cc. per liter of water. This latter range of acid content also applies to solutions containing from about 100 to about 200 grams of sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) per liter of water.

If hydrochloric acid be added to the dichromate solution instead of sulphuric acid, sufficient hydrochloric acid must be added to make the chloride ion concentration somewhat greater than the concentration of the sulphate ion as indicated in the examples immediately preceding.

If nitric acid be added to the dichromate solution, the amount required to produce a satisfactory film is much greater than that of either sulphuric or hydrochloric acid.

Before immersion the metal articles to be treated should be cleansed to remove dirt or grease. This is preferably done by a cathodic treatment of the article for  $\frac{1}{2}$  to 3 minutes in a hot solution of trisodium phosphate, using enough current to cause 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, while periods of from 2 to 30 seconds

are 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 composition of the metal being treated. The longer immersion periods may be used with rolled cadmium or zinc, galvanized iron, or a rolled zinc-base alloy containing, for example, about 1 per cent copper and 0.01 per cent magnesium. With zinc-base alloys of the type suitable for die-casting, for example those containing aluminum, magnesium and/or copper, the immersion period must be considerably reduced in order to prevent loosening of the film which first forms. Thus, with a solution containing about 200 grams of chromic acid per liter of water and an appropriate amount of sulphuric acid, it may be desirable to limit the immersion time to as little as 2 seconds. With a solution containing about 50 grams of chromic acid per liter of water, the immersion time may be extended to about 10 seconds. When employing a solution containing sodium dichromate and sulphuric acid, the immersion time for the die-casting alloys may be extended to 30 seconds or more. The metal and solution may be at 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 by rinsing in cold water, and then dried by any appropriate means as 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.

As an illustration of the enhanced protection against corrosion which is offered by the presence of the above described type of visible film on cadmium, zinc and zinc-base alloys, the following examples may be given:

If a clean piece of rolled zinc be exposed outdoors, the surface is rapidly tarnished, and white corrosion products form in a few days. If a similar specimen be immersed in a solution of chromic acid containing 200 grams of chromium trioxide (CrO<sub>3</sub>) per liter of water, rinsed, dried, and then be exposed outdoors, the rate of tarnishing may be very slightly retarded, but white corrosion products will form in a few days as before.

If, to the above described chromic acid solution containing 200 grams of chromium trioxide (CrO<sub>3</sub>) per liter of water, a small amount of sulphuric acid be added (for example, 5.5 cc. per liter of water of sulphuric acid of sp. gr. 1.84), a rolled zinc specimen immersed therein will be slightly etched. This amount of sulphuric acid is sufficient to produce on the zinc a condition which is on the borderline between that of simple etching and that of visible film formation. If a specimen of zinc be treated in this solution and then exposed outdoors, traces of white corrosion products will be observed in a few days, especially if a rainfall occurs, and the surface of the specimen gradually becomes dull, and in from three to four months is covered with a gray film of corrosion products.

If the amount of sulphuric acid per liter of water in the above solution be increased (for example, to 17.5 cc. of sulphuric acid of sp. gr. 1.84), a rolled zinc specimen immersed therein

acquires an iridescent, brown coating. If such a treated specimen be exposed outdoors it has been found that after as much as six months the coating still retains its original appearance and that no white corrosion products have formed.

A similar solution, in which the sulphate was added in the form of sodium sulphate instead of sulphuric acid, was used to treat a specimen of a rolled zinc alloy containing 1 per cent copper and 0.01 per cent magnesium. After exposure of this specimen outdoors for more than two years, it was found that, except for adhering particles of dust and dirt, the specimen had changed very little in appearance and no white corrosion products were to be seen.

The protection of zinc against corrosion according to the method of the present invention has been further studied by determining the changes in weight which occur upon outdoor exposure of treated and untreated specimens. With untreated specimens it is found that during the first month or more of outdoor exposure there is an increase in weight due to the accumulation of white corrosion products; with continued exposure the specimens slowly lose in weight, corresponding to the solution of zinc and the removal of the ensuing corrosion products.

The same phenomena regarding changes in weight were observed in the case of specimens of rolled zinc passivated by immersion for three minutes in a chromic acid solution (200 g. of chromium trioxide (CrO<sub>3</sub>) per liter of water) before exposure outdoors.

Specimens treated by immersion in a chromic acid solution containing sufficient sulphuric acid to produce a visible film, according to the method of the present invention, show no increase in weight due to the formation of white corrosion products upon exposure outdoors; on the contrary these specimens lose in weight from the beginning of the exposure, but at a rate which was very much less, over a period of months, than the rate at which untreated specimens lose weight.

The following examples illustrate the practice of the invention with different solutions and different zinc-base alloys.

*Solution I*

Water..... 1000 cc.  
Sulphuric acid (94% H<sub>2</sub>SO<sub>4</sub>, sp. gr. 1.84) -- 6 cc.  
Sodium dichromate (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O) -- 200 grams

*Solution II*

Water..... 1000 cc.  
Sulphuric acid (94% H<sub>2</sub>SO<sub>4</sub>, sp. gr. 1.84) -- 3 cc.  
Chromic acid (CrO<sub>3</sub>)..... 50 grams

*Nature of metal treated*

Metal	Composition			Balance zinc
	% Al	% Cu	% Mg	
No. 1, die cast.....	4.10	2.70	0.03	99.99% pure.
No. 2, die cast.....	4.10	.....	0.04	Do.
No. 3, die cast.....	4.10	1.00	0.03	Do.
No. 4, die cast.....	4.10	1.25	.....	Do.
No. 5, rolled zinc.....	.....	1.0	0.01	Zinc with about 0.05% lead.

No. 6, rolled zinc containing about 0.05% lead.

The following tables show the types of coatings obtained by immersing the alloys and the rolled zinc in the above described solutions at

room temperature. All the coatings were firmly adherent and afforded good protection against corrosion:

*Solution I*

Metal	Duration of immersion (in seconds)	Description of coating
No. 1.---	10-20	Dull iridescent coating
No. 2.---	10-20	Iridescent coating with brass tinge
No. 3.---	10-20	Iridescent coating
No. 4.---	10-20	Do.
No. 5.---	20-30	Slightly iridescent brass colored coating
No. 6.---	20-30	Slightly iridescent bronze colored coating

*Solution II*

No. 1.---	2-5	Iridescent coating
No. 2.---	2-5	Iridescent coating with yellow tinge
No. 3.---	2-5	Iridescent coating
No. 4.---	2-5	Do.
No. 5.---	20-30	Iridescent brass colored coating
No. 6.---	20-30	Slightly iridescent bronze colored coating

The films or coatings of the invention not only protect the zinc or cadmium base metal from corrosion but are also useful for decoration. The coatings produced in accordance with the invention retard the formation of corrosion products that form on bright zinc or cadmium base metal surfaces exposed to the atmosphere or moisture. Zinc coated according to the method of the invention can be soldered as readily as uncoated zinc.

I claim:

1. The method of producing a visible protective coating on a zinc or cadmium base metal which comprises subjecting the metal to immersion treatment in a solution containing about 25 grams or more of chromium trioxide per liter of water, and a mineral acid of the group comprising sulphuric acid, hydrochloric acid and nitric acid.

2. The method of producing a visible protective coating on a zinc or cadmium base metal which comprises subjecting the metal to immersion treatment in a solution containing about 25 grams or more of chromium trioxide per liter of water, and 2 to 50 cc. of sulphuric acid (specific gravity 1.84) per liter of water.

3. The method of producing a visible protective coating on a zinc or cadmium base metal which comprises subjecting the metal to immersion treatment in a solution containing from 25 to 300 grams per liter water of a dichromate, for example sodium or potassium dichromate, and a mineral acid of the group comprising sulphuric acid, hydrochloric acid and nitric acid.

4. The method of producing a visible protective coating on a zinc or cadmium base metal which comprises subjecting the metal to immersion treatment in a solution containing from 25 to 300 grams of sodium dichromate, and from 1 to 80 cc. of sulphuric acid (specific gravity 1.84) per liter of water.

5. The method of producing a visible protective coating on a zinc or cadmium base metal which comprises subjecting the metal to immersion treatment in a solution containing about 50 grams of chromic acid plus 2 to 10 cc. of sulphuric acid (specific gravity 1.84) per liter of water.

6. The method of producing a visible protective coating on a zinc or cadmium base metal which comprises subjecting the metal to immersion treatment in an aqueous solution containing from 25 to 200 grams of chromic acid plus 2

to 80 cc. of sulphuric acid (specific gravity 1.84) per liter of water.

7. The method of producing a visible protective coating on a zinc or cadmium base metal which comprises subjecting the metal to immersion treatment in an aqueous solution containing about 200 grams of sodium dichromate and from 3 to 19 cc. of sulphuric acid (specific gravity 1.84) per liter of water.

8. The method of producing a visible protective coating on a zinc or cadmium base metal which comprises subjecting the metal to immersion treatment in an aqueous solution containing 25 to 300 grams of sodium dichromate and 1 to 80 cc. of sulphuric acid (specific gravity 1.84) per liter of water.

9. The method of treating an object having a surface of zinc or cadmium base metal which comprises subjecting the surface of the object to the action of an aqueous solution containing sulphuric acid and from 25 to 300 grams of sodium dichromate per liter of water until a visible corrosion-retarding coating is formed on said surface.

10. The method of forming a corrosion-resistant coating on an object having a surface of zinc or cadmium base metal which comprises subjecting the surface of the object to the action of an acid solution containing chromic acid ions and the anions of a mineral acid of the group consisting of sulphuric acid, hydrochloric acid and nitric acid, regulating the ratio between chromic acid ion concentration and the concentration of mineral acid anions in said solution within predetermined limits, and leaving the surface of the object in contact with the solution until a color ranging from yellow to black appears on said surface.

11. The method of forming a corrosion-resistant coating on an object having a surface of zinc or cadmium base metal which comprises subjecting the surface of the object to the action of an acid solution containing chromic acid and a salt of a mineral acid of the group consisting of sodium sulphate, sodium chloride, ammonium chloride and sodium nitrate, regulating the ratio between the chromic acid concentration and the concentration of the salt of a mineral acid in said solution within predetermined limits and leaving the surface of the object in contact with the solution until a color ranging from yellow to black appears on said surface.

12. The method of forming a corrosion-resistant coating on an object having a surface of zinc or cadmium base metal which comprises subjecting the surface of the object to the action of an acid solution containing chromic acid, a salt of a mineral acid, and a mineral acid of the group consisting of sulphuric acid, hydrochloric acid and nitric acid, regulating the ratio between the concentration of chromic acid, the concentration of the salt of a mineral acid, and concentration of the mineral acid in said solution within predetermined limits and leaving the object in contact with the solution until a color ranging from yellow to black appears on said surface.

13. The method of forming a corrosion-resistant coating on an object having a surface of zinc or cadmium base metal which comprises subjecting the surface of the object to the action of a solution containing dichromate and a mineral acid of the group consisting of sulphuric acid, hydrochloric acid, and nitric acid, regulating the ratio between the concentration

of the dichromate and the concentration of the mineral acid in said solution within predetermined limits and leaving the surface of the object in contact with the solution until a color ranging from yellow to brown appears on said surface.

14. The method of forming a corrosion-resistant coating on an object having a surface of zinc or cadmium base metal which comprises subjecting the surface of the object to the action of an aqueous solution containing a dichromate and hydrochloric acid, regulating the ratio between the dichromate concentration and the hydrochloric acid concentration in said solution and leaving the surface of the object in contact with the solution until a color ranging from yellow to black appears on said surface.

15. The method of forming a corrosion-resistant coating on an object having a surface of zinc or cadmium base metal which comprises subjecting the surface of the object to the action of an aqueous solution containing a dichromate and nitric acid, regulating the ratio between the dichromate concentration and the nitric acid concentration in said solution within predetermined limits and leaving the object in contact

with the solution until a color ranging from yellow to black appears on said surface.

16. The method of forming a corrosion-resistant coating on an object having a surface of zinc or cadmium base metal which comprises subjecting the surface of the object to the action of an acid solution containing dichromate ions and the anions of sulphuric acid, regulating the ratio between the dichromate ion concentration and the concentration of the anions of sulphuric acid in said solution within predetermined limits and leaving the surface of the object in contact with the solution until a color ranging from yellow to black appears on said surface.

17. The method of forming a corrosion-resistant coating on an object having a surface of zinc or cadmium base metal which comprises subjecting the surface of the object to the action of a solution containing chromic acid and a sulphate, regulating the ratio between the chromic acid concentration and the concentration of the sulphate in said solution within predetermined limits and leaving the surface of the object in contact with the solution until a color ranging from yellow to black appears on said surface.

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