

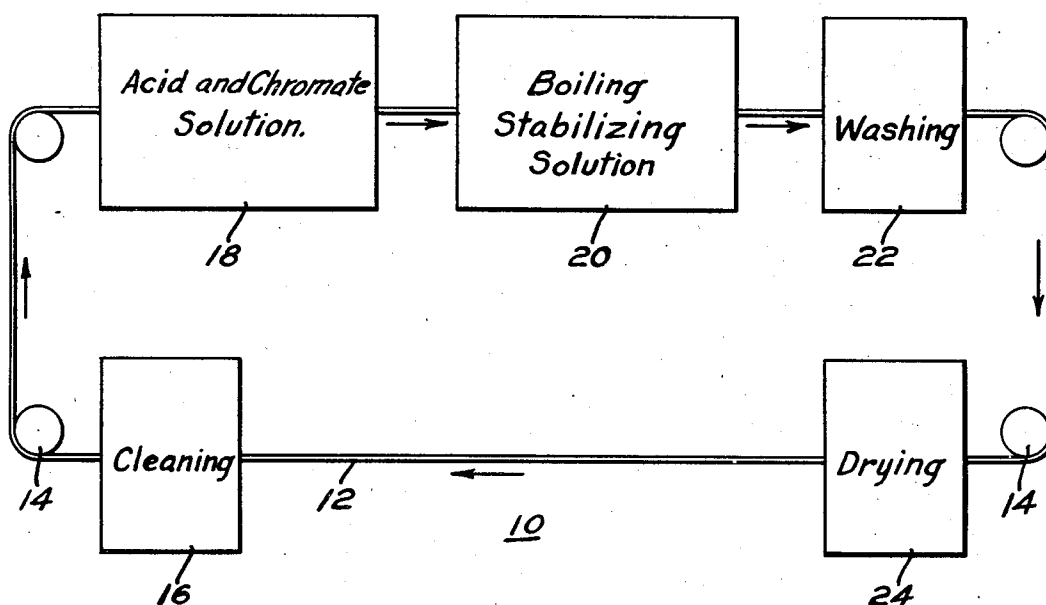
June 30, 1942.

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2,288,007

CORROSION RESISTANT FILMS ON ZINC

Filed Feb. 26, 1941



WITNESSES:

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2,288,007

CORROSION RESISTANT FILM ON ZINC

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Application February 26, 1941, Serial No. 380,653

5 Claims. (Cl. 148—6)

This invention relates to the coating of zinc or cadmium base metals and has for its object the provision of a durable corrosion resistant coating or film on metals. Throughout the specification and claims, by "zinc or cadmium base metals," it is intended to denote metals and alloys composed principally of zinc or cadmium, including other base metals coated with a zinc or cadmium base metal layer applied for example by galvanizing, electroplating and the like.

Under certain atmospheric conditions of high humidity and elevated temperatures, certain metals such, for example, as zinc and cadmium, tend to corrode rapidly with the production of a white chalky surface which gives the metals a very poor appearance. At temperatures above 60° C. and at high humidity zinc will break down with the formation of a white powder in a short period of time. Several processes are known to the prior art in which protective coatings are produced on zinc or cadmium base metals. In particular, the prior art process in which zinc or cadmium base metals are given a protective coating by subjecting the metal to a solution containing a mineral acid and a dichromate has produced coatings which have some value. However, even this type of coating is unstable when the temperature to which the member is subjected exceeds 60° C. and the humidity is fairly high. Furthermore, this latter process does not produce entirely satisfactory permanent protective coatings on zinc or cadmium base metals.

The object of this invention is to provide for stable protective coatings on zinc or cadmium base metals.

Other objects of the invention will be obvious from the specification and claims.

The invention will be understood most readily from the following detailed description thereof, when considered in connection with the accompanying drawing, in which a schematic layout of the several steps of the process is detailed.

This present invention relates more specifically to the treatment of zinc or cadmium base metals or third metals coated with zinc or cadmium base metals by a two-step process, the first of which is substantially the protective coating process outlined in Patent No. 2,035,380 and is followed by a second process which stabilizes and improves the coating provided by the first process as detailed in this patent.

It has been found that when zinc or cadmium base metals are subjected to a solution containing from 1 to 80 cubic centimeters of sulphuric acid and from about 25 to 300 or more grams

of a dichromate per liter of water that the metal acquires a protective coating which is valuable for resisting corrosion within a restricted range of atmospheric conditions. This protective coating lacks adequate corrosion resistance when subjected to temperatures above 60° C. with a relatively high humidity such as is produced by steam at this temperature. Within 24 hours, the surface finish will break down with the formation of the characteristic white powder on zinc base metals.

The sulphuric acid-dichromate coating may be stabilized and rendered exceedingly durable over a wide range of temperatures and at high humidities so that under a test similar to that mentioned above, the stabilized finish merely turns slightly gray after several weeks of suspension in a steam chest at 60° C. and with no evidence of any white corrosion products after a one month test. In addition, the stabilized finish is much more attractive in appearance, being either of a light blue-gray or a greenish-gray color.

The stabilizing after-treatment, following the acid and chromate solution treatment, consists in treating the zinc or cadmium base metal with a boiling aqueous solution containing 1% or more of an alkaline metal hydroxide or some water soluble chromate or dichromate salt.

For a more complete description of the process, reference is made to the single figure of drawing, in which a schematic arrangement suitable for performing the process is shown. In the single figure of the drawing, an endless conveyor system is shown as one possible mode of practicing the process. This is not necessarily the preferred method of treating zinc or cadmium base metal but is merely an example of processing which is adapted to present-day manufacturing operations. The endless conveyor 12 runs on and is guided by pulleys 14. The endless conveyors 12 are constructed so that any desired shape or type of zinc or cadmium base metal object may be suspended thereon for the treatment.

The first process step to which the objects on conveyor 12 are subjected is a cleaning operation at 16, to free them of superficial dirt and grease. One satisfactory method is to submerge the objects in a hot solution of trisodium phosphate for one-half to three minutes while making them a cathode employing enough current to cause a copious evolution of gas. Vapor degreasing and similar cleansing may be employed in order to produce a clean surface for subse-

quent treatment. Any superficial adherent impurities may be removed at the end of the cathodic treatment, for example, by rinsing in hot and in cold water.

The cleansed zinc or cadmium base alloys or members are then carried by the conveyor 12 to the apparatus 18 in which the acid and chromate solution is applied thereto. The mineral acids which have been found to be satisfactory for this coating operation are sulphuric, hydrochloric and nitric acids. Sulphuric acid is superior to the other acids in some respects and is generally preferred. From 1 to 80 cubic centimeters of sulphuric acid of a specific gravity of 1.84 may be added per liter of water. However, from 2 to 10 cc. per liter have given good results. Soluble chromate and dichromate salts and chromic acid are added to the sulphuric acid-water solution. If chromium trioxide is employed, from 25 to 200 grams per liter of water produces satisfactory results. The amount of sulphuric acid is preferably increased in the case of greater concentration of chromium trioxide. If a soluble dichromate salt, such for example, as sodium dichromate is employed, from 25 to 300 or more grams per liter of the salt may be used per liter of water.

Referring to the drawing the zinc or other base metals are immersed in the solution at 18 for a time period ranging from 2 seconds to 3 minutes. A dip of 10 seconds duration has been found to be satisfactory with a solution containing 50 grams of chromic acid and 10 grams of sulphuric acid per liter. If this acid and chromate solution application were depended upon as the sole protective film forming agent, the time of application of the solution is quite critical. Prolonging the immersion beyond a certain optimum time results in a destruction of some of the good characteristics of the protective coating. By following the acid and chromate solution with the stabilizing treatment of this invention, the length of time of the first dip is not at all critical. Accordingly, somewhat prolonged immersion times may be used without suffering adverse effects.

The base metal may be lifted out of the acid and chromate solution and the solution allowed to drip off before application of a boiling stabilizing solution at 20. It has been discovered that the coating produced by the first treatment is greatly improved by following it with a boiling aqueous solution containing 1% or more of sodium or potassium hydroxide or of a soluble chromate or dichromate salt. The following three examples of suitable composition for producing the stabilizing of the acid dichromate coating have produced good results: (1) 10% sodium dichromate, 90% water; (2) 1% sodium hydroxide, 99% water and (3) 10% sodium dichromate, 1% sodium hydroxide, 89% water.

The three examples are not intended to be limitations. Any alkaline metal hydroxide such as sodium and potassium hydroxide may be used for this purpose. Both chromate and dichromate salts which are soluble in water may be employed. The sodium and potassium chromates and dichromates are satisfactory.

The stabilizing solution has been most effective when applied at a boiling temperature. However, temperatures slightly below boiling also produces good results. The stabilizing solution has been effective when the time of application has been varied from 15 seconds to 5 minutes. A 30 second dip in the boiling solution has been used

with consistently good results. The brown coating on zinc as produced by the acid-chromate solution is converted to a bluish-gray surface of pleasing appearance when followed by a sodium hydroxide stabilizing treatment. The same brown surface, when subjected to a 10% sodium chromate stabilizing solution becomes a greenish-gray film. Defects in the base metal are much easier to spot in the case where the boiling stabilization solution has been used following the initial treatment. As previously mentioned, the stabilizing coating exhibits highly superior temperature and humidity resistance characteristics.

The order of the application of the solutions may not be changed since the protective coating is produced only by applying the solution in the order given.

The stabilized coating is washed in hot water at 22 and dried at 24. Heat or a hot air blast may be employed to expedite drying. In some cases wiping with rags or sawdust may be resorted to in order to dry the metal. The articles may be removed from the conveyor 12 and immediately put to use in apparatus.

The protective film produced at stage 18, as taught by the prior art, had only temporary protective value and is not of a permanent character. The stabilized film or coating produced by the entire process disclosed in the present case is satisfactory for use as a permanent protective coating. It is only under extreme corrosive conditions such as exposure to highly corrosive acids and severe abrasive service that the film is destroyed. Average conditions of service, such as result from ordinary weather and atmospheric effects, are adequately met by the protective film produced by the present invention.

In producing the stabilizing solution for use at 20, any or all of the salts and hydroxides listed may be mixed and applied. The main requirement is that the aqueous solution contain 1% or more of the stabilizing chemical in order to produce rapid and satisfactory results.

While I have described and illustrated my invention in connection with a single preferred form of embodiment, it will be understood that various changes and modifications may be made by those skilled in the art without departing from the essential spirit of my invention. It is desired, therefore, that the appended claims shall be accorded the broadest construction consistent with their language and the prior art.

I claim as my invention:

1. The method of providing a stable protective coating on zinc or cadmium base metals which comprises applying a solution containing a chromium compound and a mineral acid to the metal and thereafter applying a hot aqueous solution containing at least one solute selected from the group consisting of alkali hydroxides and chromate and dichromate salts to provide for a durable, heat stable protective coating.

2. The method of providing a stable protective coating on metals of the group consisting of zinc, cadmium and base alloys thereof which comprises applying a solution containing a chromium compound and a mineral acid to the metals to produce a protective coating which is relatively unstable under humid conditions at elevated temperatures and subsequently applying an aqueous solution containing over one percent of a solute selected from the group consisting of alkali metal hydroxides, chromate salts and dichromate salts, the aqueous solution being applied at substantially boiling temperature; the

boiling aqueous solution imparting heat stability in humid atmospheres to the protective coating.

3. The method of producing stable protective coatings on a metal selected from the group consisting of zinc, cadmium and base alloys thereof which comprises applying to the metal a solution containing from 25 to 300 grams of a chromium compound selected from the group consisting of chromium trioxide and dichromates and more than 2 cc. of a mineral acid per liter of water, to provide for a protective coating on the metal, and subsequently applying a hot aqueous solution at about boiling temperature to the metal, the aqueous solution containing 1% or more of one or more selected from the group consisting of alkali metal hydroxides, chromate salts and dichromate salts, the hot aqueous solution imparting stable properties to the coating whereby its resistance to high temperatures and high humidity is increased.

4. The method of increasing the stability of protective chromate coatings on metals selected

from the group consisting of zinc and cadmium base metals, which comprises applying a hot aqueous solution of 1% or more of a solute comprising one or more members of the group consisting of alkali metal hydroxides, chromate salts and dichromate salts.

5. An article of manufacture, comprising in combination, a zinc or cadmium base metal member and a protective surface thereon composed of the reaction product of the zinc or cadmium base metal and an aqueous solution of a chromium compound and a mineral acid and the reaction product being further treated with a substantially boiling aqueous solution containing 1% or more of at least one selected from the group consisting of alkali metal hydroxides, chromates and dichromates, the final reaction product having greater corrosion resistance and more uniform and attractive appearance than the first reaction product.

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