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PROCESS OF RETARDING CORROSION OF COATED METAL ARTICLES AND COATED METAL ARTICLE

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This application is a continuation-in-part of our co-pending application Serial No. 266,111, filed January 11, 1952, and entitled A Process of Retarding Corrosion of Galvanized Metal Articles.

The principal object of our invention is the provision of a means and process for inhibiting the "white rusting" of galvanized and aluminum coated ferrous materials, sheets and shapes, which will be less expensive and more effective than procedures hitherto current in the art.

Another object of the invention is to provide a means and process for inhibiting such corrosion which will not affect the normal use of the coated articles. Still another object of the invention is to provide such a means and process as will preserve the freshly made appearance of the galvanized and aluminum coated articles, as well as contribute to the safety of handling and use operations.

These and other objects of the invention, which will be pointed out hereinafter or will be apparent to one skilled in the art upon reading these specifications, we accomplish by that procedure and by the means, of which we shall hereinafter describe certain exemplary embodiments.

The white rusting of galvanized materials, sheets and shapes has been a problem of long standing in the art. The development of white rust occurs most rapidly when water or moisture is confined against the coated metallic surface by some immediately overlying member. It is particularly severe where sheets or shapes are stacked in such a way that moisture can collect between the layers and remain there for long periods of time. Galvanized articles are ordinarily made with a high surface luster which is rapidly and seriously damaged by this type of corrosion. As sheets, for example, begin to corrode in packs, an initial very thin film of corrosion reaction products presents a blackish appearance. As corrosion proceeds, however, the thickening layer of corrosion products becomes a whitish deposit which is very difficult to remove and in many instances completely destroys the good appearance of the product. A zinc coated iron or steel surface directly exposed to weather is capable of giving long service under most circumstances without great loss of its appearance value. This is because thin films of corrosion products are more or less continuously removed by the elements which produce them; but the conditions within a pack of sheets or a stack of shapes where these are subjected to high moisture conditions are such as more or less permanently to ruin their appearance within a very short time. Moreover, the rapid formation of white rust and deposits shortens the useful life of the corrosion resistant coatings when the articles are placed in service.

With the more recent development of ferrous stocks coated with aluminum, a similar phenomenon has become important, arising from the same cause. When water or moisture is confined against the surface of an aluminum coated sheet or the like, the first effect to be observed is a darkening of the surface. As the corrosion proceeds, the layer becomes lighter in hue so that

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the term "white rusting" is not inappropriate as applied to the corroded or tarnished materials. It goes without saying that white rusting is not confined to ferrous bodies coated with aluminum but will occur on the surfaces of solid aluminum bodies as well. We have found that by the practice of the teachings hereinafter set forth the problem of white rusting can be solved or greatly minimized on aluminum surfaces as well as zinc surfaces.

Where hereinafter we refer to "galvanized" or "zinc coated" articles, we desire to be understood as including not only pure zinc but also the less pure zincs of any of the commercial spelters or zinc sources as well as alloys of zinc with minor amounts of other metals such, for example, as aluminum. When herein we refer to "aluminum," we mean a surface consisting principally of that metal. Our interest lies chiefly in the field of ferrous sheets or other bodies coated with aluminum and in this connection our disclosure is that the procedures and practices hereinafter taught are effective with base metal bodies coated with any aluminum or aluminum alloy which is suitable for hot dipping. For hot dipping purposes aluminum is sometimes alloyed with minor amounts of silicon and to such alloys magnesium is sometimes added to control the spangle. Alloys of aluminum and beryllium are used for hot dipping as well as alloys of aluminum containing both silicon and beryllium. The exigencies of processes of coating with so-called "pure" aluminum frequently result in contamination of the aluminum with iron, the contamination frequently reaching a saturation point at around 3%. Our teachings are applicable to all such aluminum alloys as well as to aluminum itself containing the normal impurities characteristic of the commercial metal.

The phenomenon of "white rusting" is very frequent in the building trades. It is common practice to pile down building sheets or galvanized or aluminum coated panels at the building site without protection from the weather. Such materials may lie on the site for periods of time ranging from a few days up to several months before they are employed in the erection of the building. Extensive damage frequently results from this practice. In many instances also building panels are subjected to yard storage without cover at their place of manufacture. Moreover, galvanized and aluminum coated sheets are being shipped to an increasing extent in open gondola cars. Waterproof paper wrappings, which are intended to protect such shipments from exposure to the weather, fail to do so for various reasons, or at least do not prevent the confining of water or moisture between the sheets.

Many attempts have been made to protect galvanized materials, sheets and shapes from white rusting. These attempts usually involve covering the galvanized surfaces with protective films of foreign materials. Oils, waxes, varnishes, greases, gelatin and protein films have all been tried, as have materials known as polar compounds and cationic compounds.

One difficulty with treatments hitherto known lies in their comparatively great expense. Another difficulty inherent in the imposition of coatings of foreign substance on the galvanized surfaces is that many normal operations cannot be performed upon such surfaces without removal of the coating, which is inconvenient and expensive. Thus, coatings of lacquers, protective paints, waxes and resins tend to interfere with soldering, brazing, and welding operations. Frequently a treated galvanized surface cannot be painted until a tenacious protective coating has been removed. Almost universally the imposition of the coating substances of the prior art destroys or obscures the bright metallic luster of the freshly made galvanized materials.

Chemical treatments have hitherto been proposed con-

sisting in the treatment of the galvanized surfaces with soluble chromates in water solution with or without some carrying or thickening agent such as sodium silicate, methyl cellulose or the like. Such chromate treatments have an effect in minimizing white rust; but they dis-
 5 color the zinc coating and adversely affect the sales appeal of the zinc coated articles. The only way in which the undesirable colored films produced by such chemical treatments can be removed is by a second treat-
 10 ment, such as a mild alkali wash. The second step, however, serves to remove a major part of the protective film from the surfaces of the articles.

Considering economy, one of the most effective ways hitherto in use for minimizing the production of white rust has entailed the practice of oiling the galvanized
 15 sheets or shapes. It will be obvious that this practice not only results in an oily or greasy surface on the galvanized sheets or articles, but because of the very low coefficient of friction produced by the oiling, the sheets or shapes so treated become very difficult to handle and
 20 represent a safety hazard. In the mill, for example, all oiled galvanized sheets which are to be moved from place to place in buggies must be banded to the buggies. There is extra cost in shipping such sheets or shapes; and hazards attend their use in construction work.
 25 Hitherto, therefore, there has been no satisfactory solution of the white rusting problem in this field.

We have found that surfaces of aluminum or galvanized or aluminum coated materials, sheets and shapes may be usefully protected from white rust and attendant
 30 forms of corrosion by treating such surfaces under certain conditions with a solution of chromic acid in pure water. The chromic acid solution may be formed, if desired, by dissolving chromium trioxide in pure water. In any event, the water solution of the chromic acid
 35 should be substantially free of mineral and organic acid radicals, such as chlorides, sulfates, nitrates, fluorides, formates, acetates and the like, and this is what we mean by the use of the term "pure water" herein. Briefly, the clean surface to be treated is brought into contact
 40 with the solution by immersion, spraying or roller coating.

The solution has been found by us to be most active in the temperature range of 150-200° F. Temperatures
 45 below 150° F. may give rise to the need of a longer reaction time and, hence, are undesirable. If the article has a temperature substantially in excess of 200° F., we have found that it may not be readily wetted by the solution.

The chromic acid solution may contain from about
 50 ½% to 4% or 5% of the chromic acid by weight, our preference being for a range of concentration of from 1% to 3%. Optimum results are obtained, by way of example, from a 1% solution of chromic acid at 170° F.

It is essential in the practice of our invention that the water used to form the chromic acid solution be thor-
 55 oughly purified and freed of extraneous ions as set forth above. Tap waters and well waters used in forming chromic acid solutions will frequently impart fair rust resistance, but have strong and variable tendencies to form colored films impairing the appearance of the galvanized or aluminum-surfaced articles.

The exact mechanism by which inorganic and organic acid radicals in the water cause discoloration in the presence of chromic acid is not understood. It is believed
 60 that such impurities in the water catalyze the reaction between chromic acid and the zinc or aluminum surface to form colored salts. In pure water chromic acid does not appear to react with zinc or aluminum to more than a very slight extent, and appears merely to dry on the surface without imparting appreciable color.

While there are various ways of purifying a water supply for the purposes of our invention, we prefer to treat the water we use in ion exchange apparatus of known types so
 70 as to reduce its content of foreign materials to a very low

figure. By way of example, we have found that the combined chloride and sulfate content of the water we use should not exceed 15 parts per million. When a solution of chromic acid in "de-ionized" water is made and
 5 used as taught by us, a protective film is made on the surfaces of the zinc or aluminum-surfaced articles which is very low in color and substantially invisible to the eye. It does not impair the bright appearance of the articles while affording substantial protection against corrosion.

In practicing our process, we apply the solution of chromic acid in pure water to the surfaces of the galvanized material or articles in any of the ways set forth above,
 10 but preferably while the articles are in continuous motion. The required temperatures are attained by preheating the solution and/or by preheating the articles. The time of contact between the treating solution and the surface to which it is applied is not important in the usual sense,
 15 providing thorough wetting is obtained. For example, if the articles are dipped in a bath, it is not necessary that they be held beneath the surface of the bath for any specified interval of time once thorough wetting has occurred. In commercial practice we usually apply the treating solution by spraying. Here again it is not necessary
 20 to continue the spraying beyond the point of securing intimate wetting contact between the solution and all areas of the surfaces being treated. Ordinarily a time of treatment with an excess of the solution of from 5 to 10 seconds is sufficient for the purpose. We believe that to the extent that reaction occurs between the chromic acid and the surfaces being treated, it occurs in important
 25 measure during or even after the drying of the solution on the surfaces.

To increase wetting, it is possible to use a wetting agent in the treating solution. However, the wetting agent
 30 must be one which is stable in the presence of chromic acid in solution, and must not ionize in solution to produce ions corresponding to the deleterious radicals mentioned above, including the sulfonate. The choice of wetting agents, therefore, appears limited, and, so far as our investigations have extended, is probably confined to the
 35 so-called "nonionics." Good results may be attained with poly-ether alcohols such, for example, as the material sold under the trade name "Triton NE" by Rohm & Haas Co.

Most methods of applying the treating solution to the surfaces to be treated result in the application of an excess,
 40 which is removed after thorough wetting is assured. This is preferably done by squeegeeing with soft rubber rolls or other wiping equipment. If unequal quantities of the solution are dried upon different areas of the surfaces of sheet stock, for example, different surface appearances
 45 in such areas are likely to be encountered. The sheets or other articles are therefore wiped or squeegeed, and only the thin, controlled layer of solution left upon their surfaces by such treatment is allowed to dry thereon. Water rinsing after the treatment is not desirable and is not
 50 practiced by us.

It is essential that the metal surfaces be clean when treated in accordance with our process, especially in the sense of being free from oily, greasy, or other materials
 55 which would interfere with wetting. Where the surfaces of the sheets or articles have been contaminated or soiled, as from handling, they should be cleaned in a mild alkali before the chromic acid treatment in order to secure maximum protection. A sodium cyanide bath is preferred by us as a pre-cleaner. If the chromic acid treatment is practiced immediately after the hot coating of the articles and before they have had an opportunity to become contaminated or soiled, the cleaning operation
 60 can be avoided. Great quantities of galvanized and aluminum coated strip are today produced in accordance with the processes and apparatus of the Sendzimir Patents 2,110,893, 2,136,957 and 2,197,622. It is readily possible to include equipment for the practice of our process in the
 65 production line of such operations, at a point where the

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freshly coated surface of the strip has cooled to a temperature of approximately 200° F. or lower.

Tests have indicated that in the practice of our process the consumption of chromic acid amounts to about 1/2 of a pound per 2500 square feet of the metal surface, so that it will be seen that the cost thereof is very low.

Sheet, strip, or other metal coated material or articles treated in accordance with our process is substantially unchanged in appearance, while significantly increased in corrosion resistance. The surfaces of such materials are dry, so that they do not present the handling problems of previous waxed, lacquered or greasy sheets. Soldering, brazing and welding operations are not affected by our treatment. Our treatment should not be practiced upon sheet or strip or other materials which are intended to be phosphated, Bonderized or otherwise chemically treated. Atmospheric and under-water corrosion resistance are improved. While it is not intended that our process be relied upon for the indefinite protection of sheets or shapes which are repeatedly wet by rain, as when stored outside or transported for indefinite periods of time without any protection from the weather, our treatment does give satisfactory protection from white rusting under conditions of moisture condensation in warehouses, shipments in boxcars, or with other weather protection, accidental wetting from roof leaks and the like, and normal periods of unprotected storage on construction jobs.

Laboratory tests readily demonstrate the performance of the rust resistant coatings formed in our procedure. In the tests used by us, twelve 4 x 12-in. metal coated sheets are treated as desired for corrosion resistance, stacked, and bound tightly with wire or pressure-sensitive tape. The prepared pack is put into a humidity cabinet maintained at 90% to 100% relative humidity at 120° F. After 12 to 16 hours in the humidity cabinet, it is removed and stored indoors for a week at room temperature. The pack is then opened and inspected for white rust. It may be completely dry; but if the sheets have been tightly bound, some moisture is likely to remain. When examination indicates that white rusting has not occurred, the pack is rebound, re-exposed in the humidity cabinet, and then stored as previously described. Resistance to corrosion may be measured in terms of the number of cycles required for the production of observable white rust.

In making a test for purposes of comparison, a control pack of untreated sheets is run through the procedure along with other sheets which have been treated with the rust inhibitor being tested.

If a humidity cabinet is not available, a similar test may be performed by wetting the sheets, by spraying them with distilled water before assembling the pack and then storing the pack for a week as described.

By such tests all such sheets which have been treated in accordance with the teachings of this application have resisted rust for as many cycles as the best oiled sheets hitherto produced, while many of them have withstood as many as three times the number of cycles. The specimens which have given these extraordinarily long test results have been those, in the laboratory, which were cleaned in mild alkali prior to the chromic acid treatment.

Modifications may be made in our invention without departing from the spirit thereof. Having thus described our invention in an exemplary embodiment, what we claim as new and desire to secure by Letters Patent is:

1. A process of increasing the corrosion resistance of articles having surfaces of a material chosen from a class consisting of zinc, aluminum and alloys thereof, which comprises treating the clean surfaces of the said articles

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with a solution of chromic acid as the solute and water as the solvent, which water is substantially free of organic and inorganic acid radicals and in which the combined sulfate and chloride content does not exceed about 15 p. p. m., so as to form a film of the solution thereon, the concentration of the said solution being substantially 1/2% to 5%, and drying the said film, whereby to produce upon the surfaces of said articles a thin and substantially colorless rust-resistant coating.

2. The process of claim 1 in which the said solution is formed by dissolving chromium trioxide in de-ionized water.

3. The process claimed in claim 1 wherein the surfaces of said articles are wiped after the application of said solution and before drying to insure the drying of a thin and uniform film of the solution thereon.

4. The process claimed in claim 1 in which the temperature of said treatment is substantially in the range of 150° to 200° F.

5. The process claimed in claim 4 in which the time of treatment prior to drying is substantially 5 to 15 seconds.

6. A process of treating articles having surfaces of a material chosen from a class consisting of zinc, aluminum and alloys thereof to impart rust resistance thereto, which comprises bringing the said surfaces into contact with a solution of chromic acid in water substantially free of organic and inorganic acid radicals and in which the combined sulfate and chloride content does not exceed about 15 p. p. m., said solution having a concentration of substantially 1% to 3% and a temperature of substantially 150° F. to 200° F., for a time of substantially 5 to 15 seconds, thereupon removing excess solution from the said surfaces and drying said surfaces without rinsing.

7. The process claimed in claim 6 including a preliminary step of subjecting the said surfaces to cleaning in mild alkali.

8. The process claimed in claim 6 including a preliminary step of subjecting the said surfaces to cleaning in mild alkali, the said alkali being a water solution of a cyanide.

9. The process claimed in claim 1 wherein the said solution is applied by spraying and wherein the surface of the article is wiped to provide a thin and controlled film of the said solution before drying.

10. An article having a surface of a metal chosen from a class consisting of zinc, aluminum and alloys thereof, said surface being protected against the formation of white rust by a protective coating formed in accordance with claim 1.

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