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PROCESS FOR TREATING METALS AND PRODUCT

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This invention relates to a process for treating metals to retard corrosion, and more particularly, to a process for treating material having a zinc surface to inhibit white rust formation and generally improve corrosion resistance. The invention further relates to the novel corrosion inhibited product produced by the process described herein.

The invention will be described and illustrated hereinafter with specific reference to a process for inhibiting "white rust" formation on materials having a zinc surface. However, it will be recognized by those skilled in the art that the process of the present invention also may be useful in retarding or inhibiting other types of corrosion and generally improving corrosion resistance. The term "zinc surface" as used in the specification and claims is intended to include a surface of a material subject to white rusting which is composed of zinc or predominantly of zinc. Examples of materials having a zinc surface subject to white rusting and suitable for treatment in accordance with the present invention include metallic forms or articles composed of zinc or predominantly of zinc, base metals such as ferrous metal or articles fabricated therefrom which are provided with a protective coating of zinc or zinc alloys containing a predominant amount of zinc, etc. It is understood that a suitable material for treatment may have a zinc surface as defined herein on only a portion of its surface area, and that such materials may be treated in accordance with the present invention for the purpose of improving corrosion resistance of at least that portion of the surface area provided with the zinc surface.

A fresh, bright, untreated zinc surfaced material exposed to the atmosphere soon develops a surface film composed of corrosion products which are produced by the action of atmospheric substances such as carbon dioxide, oxygen and moisture. As corrosion proceeds, the surface film tends to increase somewhat in thickness and the layer of corrosion products becomes a white deposit which renders the appearance of the zinc surface less pleasing to the eye. However, a zinc surfaced material directly exposed to weather is generally capable of giving long service without great loss of its appearance value since thin films of the corrosion products are more or less continuously removed by the elements, thereby preventing an appreciable build-up in the thickness of the layer of deposited corrosion products and leaving the zinc surface more or less uniform in appearance.

"White rust" is a term commonly used in the art to refer to a specific form of the above mentioned type of corrosion. It is generally considered to be a relatively thick white deposit of corrosion products composed largely of zinc hydroxide and basic zinc carbonate which forms on unprotected zinc surfaced materials exposed to air and excessive amounts of moisture or water. The development of white rust occurs most rapidly when water is confined against the zinc surface by an overlying member, and it is particularly severe where fresh, bright, untreated zinc surfaced sheets or shapes are arranged during storage or shipment in such a way that water can

accumulate between adjacent surfaces and remain for extended periods of time. For example, galvanized sheets useful in the construction of metallic buildings are commonly stacked in open railway cars, either packaged or without packaging, and shipped over long distances, or stored for long periods of time awaiting shipment or use. Water accumulates between adjacent sheets due to sweating and white rust quickly forms on those portions of the sheets exposed to the water. Over a period of time, the coating of white rust gradually thickens and eventually the appearance of the originally bright galvanized surface is completely destroyed and it takes on the appearance of an inferior product.

The art has long sought a suitable process for treating zinc surfaced materials to effectively inhibit white rust formation. In general, the prior art processes involve the application of either a relatively thick protective coating such as oils, waxes, greases, varnishes, paints, etc., or various chemical treatments which deposit a thin protective coating integral with the zinc surface. In every instance, the prior art processes are unsatisfactory due, for example, to their being ineffective in substantially completely eliminating white rust formation for a reasonable period of time, too expensive, too time consuming for use in high-speed continuous galvanizing operations, or the treatment results in a protective coating which must be removed prior to use of the treated zinc surfaced material. Also, in some instances, the coating substance either destroys or mars the originally bright pleasing finish of the fresh zinc surface. The prior art chemical treatments, in particular, require careful control of operating conditions such as concentration of ingredients and temperature of treatment, and often exhibit a pronounced tendency toward formation of undesirable colored films on the treated zinc surface.

It is an object of the present invention to provide a novel process for treating materials having a zinc surface to improve corrosion resistance which overcomes the above mentioned disadvantages of prior art processes.

It is still a further object of the present invention to provide an improved process for inhibiting white rust formation on a zinc surface which does not discolor or substantially change its appearance.

It is still a further object of the present invention to provide material having a zinc surface which is treated in accordance with the process of the present invention to inhibit white rust formation and generally improve corrosion resistance.

Still other objects of the present invention and the advantages thereof will be apparent to those skilled in the art by reference to the following detailed description.

In accordance with the present invention, material having a zinc surface is treated to deposit a corrosion inhibiting film on the zinc surface and thereby inhibit white rust formation and generally improve corrosion resistance by immersing the material in a body of treating solution consisting essentially of an aqueous solution of zinc nitrate and chromic acid, removing the treated material from the body of treating solution, and then subjecting the treated material to an aqueous rinse to remove excess treating solution. It will be appreciated from the following discussion that certain of the foregoing steps of the process of the invention must be performed under conditions to be fully described hereinafter for generally acceptable results.

The treating solution of the present invention consists essentially of an aqueous solution of zinc nitrate and chromic acid (chromic oxide) having a molar ratio of zinc nitrate to chromic acid between 4:1 and 1:9. However, better results usually are obtained when the zinc nitrate and chromic acid are present in about equimolar quantities. The total molar concentration of the zinc

nitrate and chromic acid may vary over a considerable range. For example, satisfactory results may be obtained when the total molar concentration of zinc nitrate and chromic acid is about 0.5 to 2.0 moles, but better results usually are obtained when the total molar concentration of zinc nitrate and chromic acid is about 1.0. For optimum results, generally the total molar concentration of zinc nitrate and chromic acid should be about 1.0 mole and the zinc nitrate and chromic acid should be present in about equimolar amount.

The treating solution may be prepared by dissolving zinc nitrate and chromic acid in water in the desired molar ratio and amount. The water used as a solvent does not require a special treatment to remove dissolved substances responsible for hardness of water, but generally soft water is preferred over hard water. The resulting solution is acidic and since acidic solutions of chromic acid are generally considered to contain both chromate ion and dichromate ion, and perhaps other species of chromate ion, it is understood that such species of chromate ion may be present in the treating solution of the present invention. Thus, where the treating solution of the present invention is referred to as being an aqueous solution of zinc nitrate and chromic acid, it is understood that these substances are dissolved in water when preparing the treating solution of the present invention and that actually other substances may be present in the resulting solution. However, the substances to be dissolved in water when preparing the treating solution consist essentially of zinc nitrate and chromic acid.

The initial temperature of the zinc surface to be treated is of importance. For example, at least the zinc surface of the material to be treated must be initially at a temperature substantially above room temperature and not over 450° F. at the time of immersion in the treating solution. At temperatures above about 450° F., or at temperatures only moderately above room temperature, generally acceptable results are not obtained. A very satisfactory temperature range which produces excellent corrosion inhibition has been found to be between about 200° F. and 450° F., with even better results usually being obtained at a temperature of about 300° F. The temperature of the treating solution does not appear to be of importance and may vary anywhere between room temperature and substantially the boiling point. In instances where the temperature of the zinc surface to be treated is initially at a temperature substantially above the boiling point of the solution and thus tends to raise the temperature of the treating solution above its boiling point, the treating solution may be recycled if desired, for cooling to a temperature below its boiling point.

The period of treatment may vary considerably. However, once a corrosion inhibiting film is deposited, extended periods of treatment are of no advantage and are to be avoided particularly when treating galvanized steel and the like since the relatively thin zinc coating may be attacked by the treating solution. In most instances, periods of treatment varying between about 2 seconds and 45 seconds are satisfactory, with shorter periods of treatment such as about 3–5 seconds usually being preferred. When the zinc surface to be treated is at an initial temperature between 200° F. and 450° F., the reaction responsible for the effectiveness of the process of the invention appears to take place very rapidly. Often, periods of treatment less than 2 seconds may be as effective as longer periods of treatment where the initial temperature of the zinc surface is approaching the maximum temperature limit.

After the zinc surfaced material has been immersed in the treating solution for a period of time sufficient to result in the formation of a corrosion inhibiting film on the zinc surface, it is then removed from the body of treating solution and subjected to an aqueous rinse for the purpose of removing excess treating solution. It is essential that the treated material be subjected to such an aqueous rinse since otherwise it is not possible to produce a substantially colorless corrosion resistant film on the zinc surface. For best results, the aqueous rinse should follow immediately after removal of the treated material from the treating solution and before the excess treating solution has had an opportunity to dry.

When practicing the present invention, the zinc surfaced material to be treated may be heated to the desired initial temperature and then immersed in the treating solution in any suitable manner. For example, while it is generally more convenient to effect immersion of the material in the solution by passing the material to be treated into a body of treating solution, a body of the treating solution may be flowed over the surface of the material or other suitable method may be used to immerse the material in a body of the solution for the period of time necessary to produce a corrosion inhibiting film. The treated material is then removed and, preferably, immediately subjected to an aqueous rinse for the purpose of removing excess treating solution and assuring that the coating remaining on the treated zinc surface is substantially colorless. The treated material then may be dried and packaged for shipment.

The zinc surfaced material to be treated should be given a suitable conventional pretreatment for the removal of oils, greases, etc. where such are present. However, the presence of a thin film of oxide on the zinc surface usually is not detrimental to the process of the present invention and, in fact, often the presence of a thin oxide film is beneficial. In instances where considerable corrosion has taken place, it may be necessary to remove the major amount of corrosion prior to treatment. In general, freshly galvanized surfaces do not exhibit such a degree of corrosion as to necessitate removal of the oxide film in a pretreatment step.

While the process of the present invention may be used at any suitable time, it is preferred that the zinc surface be treated shortly after the material or article has been manufactured. If desired, the treatment may be successfully incorporated in the manufacturing process. For example, it is possible to incorporate the present invention in the galvanizing of ferrous metal at any suitable stage after application of the zinc coating, provided the proper temperature conditions are met. This may be done at a stage in the galvanizing process after application of the molten zinc coating by first cooling the molten zinc on the ferrous metal base to a temperature sufficient to solidify the zinc coating and allow the proper temperature conditions to be met, and then immersing the galvanized ferrous metal in the treating solution for a period of time sufficient to form a corrosion inhibiting film on the zinc surface. The process of the present invention is particularly desirable for use in a continuous galvanizing line for ferrous metal strip. In the operation of such continuous galvanizing lines, it is customary to use relatively high strip speeds and as a result the time available for treatment is generally very short. The process of the present invention requires a minimum of line space since a corrosion inhibiting film may be deposited on the zinc surface in periods as short as about 2 seconds, thereby allowing economic operation.

The corrosion inhibiting films deposited in accordance with the present invention are substantially colorless and invisible to the naked eye, and do not noticeably change the appearance of the zinc surface. Also, such corrosion inhibiting films have been found to be very resistant to leaching, thereby allowing the treated material to be subjected to the necessary aqueous rinse following deposition of the film without affecting the corrosion inhibiting properties. The corrosion inhibiting films deposited in accordance with the invention exhibit corrosion inhibiting properties over much longer periods of time than those deposited by conventional chemical treatments. Even more important, they offer almost complete protection to the zinc surface.

The manner in which the process of the present invention results in improved inhibition of white rusting is not fully understood at the present time. However, it is assumed that the corrosion inhibiting film contains predominant amounts of zinc chromate, but perhaps some zinc dichromate or still other species of chromate may be present. Whatever the theory, the process of the present invention is highly effective in producing a very thin substantially colorless, invisible corrosion inhibiting film on zinc surfaces in a minimum period of time which is substantially completely effective in inhibiting white rusting.

The foregoing detailed description and the following specific example are for the purpose of illustration only, and are not intended as limiting to the spirit or scope of the appended claims.

EXAMPLE

The various samples treated and tested in accordance with the procedures of this example were prepared from galvanized sheet steel. The sample size was about 4 x 4 inches.

Each sample was treated and tested in accordance with the following general procedure:

(1) The sample was heated 10 minutes in a muffle furnace maintained at the desired temperature (80° F.–550° F.).

(2) The sample was removed from the muffle furnace and immediately immersed for 30 seconds in an aqueous treating solution 0.5 molar in both zinc nitrate and chromic acid, the total molar concentration of zinc nitrate and chromic acid being 1.0 mole. The aqueous treating solution was at room temperature.

(3) The treated sample was withdrawn from the aqueous treating solution, subjected to a water rinse to remove excess treating solution, and dried.

(4) The dried treated sample was placed over tepid water and observed for white rust formation after 7 days. Where the sample exhibited substantially no visible white rusting, the results were recorded as "Good."

If a small amount of white rusting was visible or if considerable white rusting was visible, then the results were recorded as "Fair" and "Bad," respectively.

The results of treating and testing samples in accordance with the above described procedure are tabulated below in Table I. The column headed "Temperature of zinc surface" refers to the temperature of the heated sample to be treated immediately before immersion in the treating solution.

Table I

WHITE RUST INHIBITION

Sample No.	Temperature of Zinc Surface, ° F.	White Rust Inhibition
1	80	Bad.
2	100	Fair.
3	150	Fair.
4	200	Good.
5	250	Good.
6	300	Good.
7	350	Good.
8	400	Good.
9	450	Good.
10	500	Fair.
11	550	Bad.

Controls were run at each of the temperatures mentioned in Table I by immersing the heated sample in distilled water rather than treating solution, rinsing the treated sample with water and drying, and then testing in accordance with the procedure of the example. The samples thus treated and tested were bad after one day exposure.

It may be observed from the data of Table I that the most satisfactory degree of white rust inhibition is produced by treating samples heated to a temperature between 200° F. and 450° F. At temperatures below about 200° F. and above 450° F., generally satisfactory results were not obtained.

We claim:

1. A process for treating material having a zinc surface to improve corrosion resistance comprising immersing the material in a body of treating solution consisting essentially of an aqueous solution of zinc nitrate and chromic acid having a molar ratio of zinc nitrate to chromic acid between 4:1 to 1:9 to produce a corrosion resistant film on the zinc surface, the solution being free of a substance which is a reducing agent for chromate ion, at least the zinc surface of the material to be treated being initially at a temperature substantially above room temperature and less than about 450° F., removing the treated material from the body of solution, and then subjecting the treated material to an aqueous rinse to remove excess treating solution and produce a substantially colorless corrosion resistant film on the zinc surface.

2. The material of improved corrosion resistance produced by the process of claim 1.

3. A process for treating material having a zinc surface to improve corrosion resistance comprising immersing the material in a body of treating solution consisting essentially of an aqueous solution of zinc nitrate and chromic acid having a molar ratio of zinc nitrate to chromic acid between 4:1 and 1:9 to produce a corrosion resistant film on the zinc surface, the solution being free of a substance which is a reducing agent for chromate ion, at least the zinc surface of the material to be treated being initially at a temperature of about 200–450° F., removing the treated material from the body of solution, and then subjecting the treated material to an aqueous rinse to remove excess treating solution and produce a substantially colorless corrosion resistant film on the zinc surface.

4. A process for treating material having a zinc surface to improve corrosion resistance comprising immersing the material in a body of treating solution consisting essentially of an aqueous solution of about equimolar quantities of zinc nitrate and chromic acid to produce a corrosion resistant film on the zinc surface, at least the zinc surface of the material to be treated being initially at a temperature substantially above room temperature and less than about 450° F., removing the treated material from the body of solution, and then subjecting the treated material to an aqueous rinse to remove excess treating solution and produce a substantially colorless corrosion resistant film on the zinc surface.

5. The process of claim 4 wherein the total molar concentration of zinc nitrate and chromic acid in the aqueous solution is about 1.0 mole.

6. A process for treating material having a zinc surface to improve corrosion resistance comprising immersing the material in a body of treating solution consisting essentially of an aqueous solution of about equimolar quantities of zinc nitrate and chromic acid to produce a corrosion resistant film on the zinc surface, at least the zinc surface of the material to be treated being initially at a temperature of about 200–450° F., removing the treated material from the body of solution, and then subjecting the treated material to an aqueous rinse to remove excess treating solution and produce a substantially colorless corrosion resistant film on the zinc surface.

7. The process of claim 6 wherein the total molar concentration of zinc nitrate and chromic acid in the aqueous solution is about 1.0 mole.

8. A process for treating material having a zinc surface to improve corrosion resistance comprising immersing the material for about 2–45 seconds in a body of treating solution consisting essentially of an aqueous solution of about equimolar quantities of zinc nitrate and chromic acid to produce a corrosion resistant film on the zinc surface, at least the zinc surface of the material to be treated being initially at a temperature substantially above

room temperature and less than about 450° F., removing the treated material from the body of solution, and then subjecting the treated material to an aqueous rinse to remove excess treating solution and produce a substantially colorless corrosion resistant film on the zinc surface.

9. The process of claim 8 wherein the total molar concentration of zinc nitrate and chromic acid in the aqueous solution is about 1.0 mole.

10. A process for treating material having a zinc surface to improve corrosion resistance comprising immersing the material for about 2–45 seconds in a body of treating solution consisting essentially of an aqueous solution of about equimolar quantities of zinc nitrate and chromic acid to produce a corrosion resistant film on the zinc surface, at least the zinc surface of the material to be treated being initially at a temperature of about 200–450° F., removing the treated material from the body of solution, and then subjecting the treated material to

an aqueous rinse to remove excess treating solution and produce a substantially colorless corrosion resistant film on the zinc surface.

11. The process of claim 10 wherein the total molar concentration of zinc nitrate and chromic acid in the aqueous solution is about 1.0 mole.

References Cited in the file of this patent

UNITED STATES PATENTS

2,206,064	Thompson, et al.	July 2, 1940
2,393,943	Thomas et al.	Jan. 29, 1946
2,763,569	Bradstreet et al.	Sept. 18, 1956
2,846,342	Curtin	Aug. 5, 1958
2,851,386	Hartman	Sept. 9, 1958
2,904,413	Hampel	Sept. 15, 1959

FOREIGN PATENTS

570,054	Great Britain	June 20, 1945
600,041	Great Britain	Mar. 30, 1948