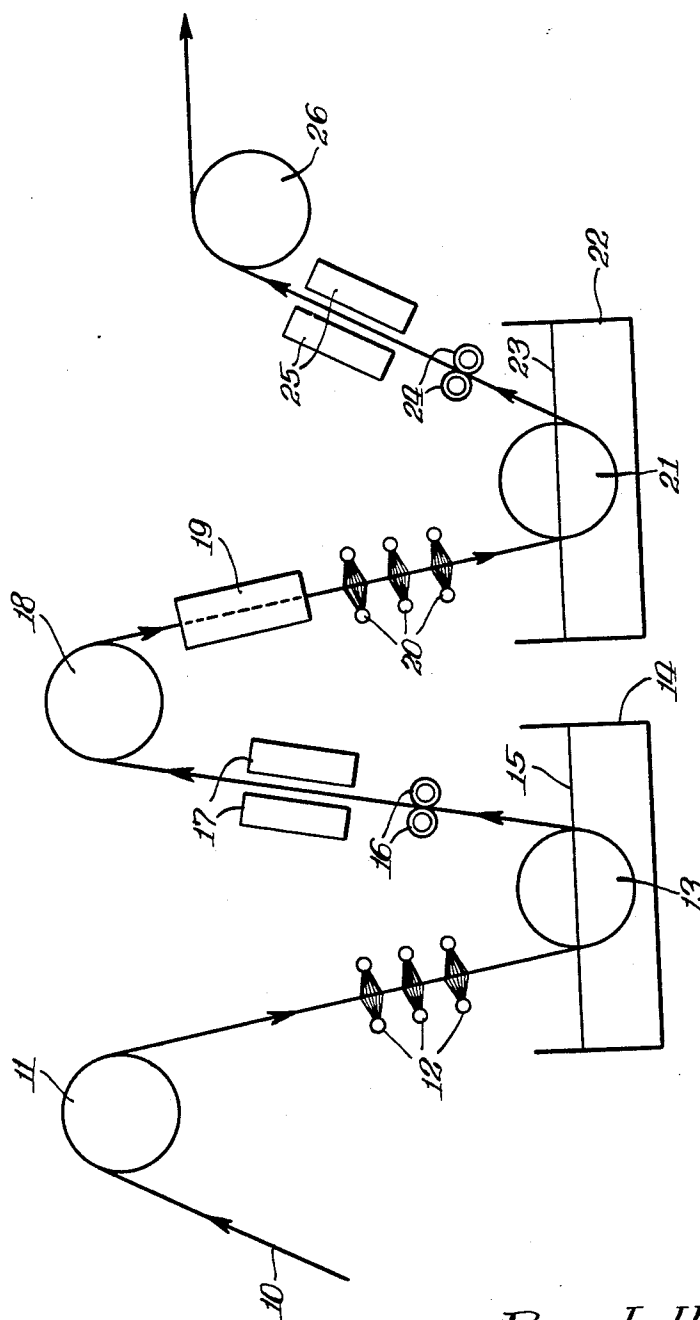


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CORROSION PROTECTION FOR ZINC-SURFACED AND
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CORROSION PROTECTION FOR ZINC-SURFACED AND ALUMINUM-SURFACED ARTICLES

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This invention is a continuation-in-part of my copending application Serial No. 521,435, filed July 12, 1955 and now abandoned, which is in turn a continuation-in-part of my application Serial No. 332,480, filed January 21, 1953 and now abandoned.

This invention relates to the protection of zinc-surfaced and aluminum-surfaced articles against corrosion and more particularly to a coating process for accomplishing the desired protection as well as to the resultant coated article.

It is well known that zinc or zinc-surfaced articles, such as galvanized iron or steel sheets, tend to turn white or grayish-white with age. This white surface coating is frequently referred to as "white rust" and is presumably due to the formation of zinc oxide, hydroxide, carbonate or mixtures thereof on the metal surface. The condition is particularly noticeable when the zinc-surfaced sheets or other articles are stacked or piled in such manner that moisture tends to collect between the articles.

With the relatively recent development of aluminum coated or aluminized ferrous metal, it has been found that a similar corrosion problem exists.

In general, there have been three main approaches to the problem of preventing "white rust" or increasing the resistance of a zinc surface to "white rust." The first approach involves the formation of barrier type films such as coatings of paint, lacquer and the like. Obviously, this technique has only a very limited application since its cost is high and the protection is lost once the film is damaged thereby preventing effective fabrication, soldering, or other uses of the metal articles. Another approach to the problem consists in the use of an inhibitor comprising an oil solution of a polar compound which is adsorbed probably as a monomolecular layer on the metal surface being protected. Although these inhibitors do provide reasonably effective protection, the method possesses serious disadvantages which are inherent in the oily characteristics of these compounds and their carriers. In other words, for many purposes the consumer or user of galvanized steel considers the presence of an oily film on the product to be highly undesirable. A third general approach to the problem comprises the use of a chemical inhibitor such as chromic acid or various soluble chromates or nitrites which are thought to dissolve in the moisture which is part of the corrosive environment to form a corrosion inhibiting solution in contact with the metal.

My invention falls in the last mentioned category and is concerned primarily with a novel technique for utilizing the corrosion inhibiting properties of chromic acid. However, as will hereinafter appear, the present process differs in a number of important respects from the techniques heretofore proposed for the use of chromic acid and other similar chemical inhibitors.

According to certain methods heretofore suggested, chromic acid or chromates are used in such a manner as to cause an actual chemical attack on the zinc surface such that the conventional luster of zinc coated articles is destroyed and in many cases a pronounced stain due to the formation of colored zinc chromate films or the like is left on the article. Such surface discoloration is considered highly undesirable for many commercial purposes. Furthermore, a severe disadvantage of most of the chemical inhibitor methods heretofore proposed is

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that the deposit of chromic acid or other chemical on the zinc surface is so readily soluble that the desired protection is lost if any substantial amount of water or condensate comes in contact with the treated surface.

Accordingly, a primary object of my invention is to provide a novel and improved process for the treatment of zinc-surfaced and aluminum-surfaced articles to protect the same from "white rust" or other corrosion.

A further object of the invention is to provide a novel zinc-surfaced or aluminum-surfaced article having a unique and highly effective corrosion resistant coating.

Another object of the invention is to provide a novel process for utilizing chromic acid or related chromium compounds to protect zinc-surfaced and aluminum-surfaced articles against corrosion while at the same time avoiding detrimental surface discoloration and disfiguration.

Still another object of the invention is to provide a novel process for the utilization of chromic acid or related chromium compounds to protect zinc-surfaced and aluminum-surfaced articles against corrosion, which process makes possible the presence of chromic acid in a soluble form but prevents its rapid solution and loss in moisture or condensate which may reach the metal surface.

An additional object of the invention is to provide a novel continuous process involving a two-stage chemical treatment for the protection of zinc-surfaced and aluminum-surfaced articles against corrosion which is particularly adapted for continuous operation, for example in conjunction with a high speed galvanizing line.

Other objects and advantages of the invention will become apparent from the subsequent detailed description in which connection the accompanying drawing is a schematic illustration of a preferred method of practicing the process.

It should be understood that the corrosion protection treatment hereinafter described is applicable to sheets, articles, and shapes made of zinc or aluminum or alloys of either as well as to sheets, articles, and shapes having merely a surface coating of zinc or aluminum or alloys of either. The terms "zinc-surfaced" and "aluminum-surfaced" as used herein are intended to embrace all of the foregoing.

It has been found that vastly improved results are obtained in protecting zinc and aluminum surfaces by means of a specific two-stage chemical treatment involving the following steps:

(1) Applying to the zinc or aluminum surface a solution of an alkali metal silicate, preferably sodium silicate, having a relatively high silica:soda ratio;

(2) Drying the sodium silicate coating to form a film which is highly resistant to solution or washing off during subsequent treatment or ultimate use of the article;

(3) Applying in situ to the sodium silicate coated surface a chromic acid solution; and

(4) Subjecting the coated article to a final drying step.

The present process is particularly useful for continuous operation. For example, the process may be appended at the end of a high speed galvanizing line and the sheet or strip issuing from the line is subjected to the afore-mentioned sequence of operations in a completely continuous manner regardless of the speed of the galvanizing line. However, it will be readily understood that the basic principles of my invention may also be utilized in the treatment of other types of zinc-surfaced or aluminum-surfaced articles on a batch, semi-continuous, or continuous basis.

The first step of the process involves the formation of an alkali metal silicate film or layer on the zinc-surfaced or aluminum-surfaced article. Sodium silicate is the preferred compound because of its cheapness and avail-

ability. The sodium silicate is applied in aqueous solution by spraying, immersion, or any other suitable technique or combination of techniques. During the second stage of the process the application of chromic acid converts at least a substantial portion of the sodium silicate film to silica gel which functions as a highly effective adsorbent and retaining medium for the chromic acid. Accordingly, in order to expedite the rapid formation of silica gel during the second stage of the process, I prefer to employ a sodium silicate in the first stage of the process which has a relatively high silica:soda ratio. Sodium silicate is available commercially in a wide range of silica:soda ratios, but for purposes of the present invention it is usually desirable that this ratio be within the range of from about 3:1 to about 3.75:1 on a weight basis. Best results are obtained within a preferred range of from about 3.25:1 to about 3.75:1.

Commercial grade sodium silicates also come in various concentrations, but in the first stage of the present invention as used in the treatment of zinc-surfaced articles it is desirable to utilize an aqueous solution of the sodium silicate containing from about 5 to about 50 grams of SiO_2 per liter of solution. For optimum results, the concentration should be within the narrower range of from about 15 to about 35 grams of SiO_2 per liter of solution. In the treatment of aluminum-surfaced materials, the aqueous sodium silicate solution may contain from about 12 to about 95 grams of SiO_2 per liter of solution, and preferably from about 16 to about 80 grams per liter. During application to the zinc-surfaced or aluminum-surfaced article, the sodium silicate solution is maintained at a temperature of from about 115° F. to about 200° F. and preferably within the narrower range of from about 140° F. to about 180° F.

Following the application of the sodium silicate film in the first stage of the process, it is a highly important feature of my invention that the sodium silicate film be dried to a substantial extent. The exact degree of dehydration is not highly critical, but it is necessary that the sodium silicate film be dried sufficiently so that it resists solution or washing off in the second stage of the process. However, the dried, difficultly soluble sodium silicate film must still have sufficient moisture present to facilitate rapid conversion of at least a portion of the film to silica gel during the second stage of the process. When the process is utilized on a continuous scale, as in the treatment of the product from a high speed galvanizing line, the drying operation should be carried out at an elevated temperature in order to effect the desired degree of drying as rapidly as possible. The temperature which may be used in the intermediate drying step is, of course, dependent upon the drying time which in turn is dependent upon the length of the drying zone and the speed of the strip in a continuous line. Broadly speaking, the intermediate drying temperature may be from about 100° F. to about 400° F., it being understood that the temperatures at the lower end of the range will require longer drying times, and vice versa. For a preferred range, I have found that by heating the metal to a surface temperature of from about 125° F. to about 250° F., intermediate the two chemical treatment stages, very effective results are obtained at practical drying times and line speeds. Also, the fact that the sodium silicate solution in the first stage of the process is applied at a temperature of from about 115° F. to about 200° F. further facilitates drying of the film in the intermediate drying step.

A previously mentioned, this intermediate drying step is very important to the successful operation of the invention since without intermediate drying the sodium silicate film is not sufficiently resistant to solution or washing off, with the result that the desired protection is lost by removal of the sodium silicate film either during the second stage of the process or during ultimate

exposure of the product to a moisture-containing corrosive environment.

In the second chemical treatment stage of the process the dried sodium silicate film is impregnated or reacted with an aqueous chromic acid solution. The chromic acid converts at least a substantial portion of the sodium silicate to silica gel which tenaciously retains the chromic acid or possible reaction products thereof so that the latter is readily available for its corrosion protection properties during ultimate use of the coated article. In the treatment of zinc-surfaced articles the concentration of the aqueous chromic acid solution may range from about 0.5 to about 7.5 grams of CrO_3 per liter of solution. Best results are obtained within the lower portion of this range, preferably from about 1.0 to about 3.0 grams of CrO_3 per liter of solution. In the treatment of aluminum-surfaced articles the concentration of the chromic acid solution may be from about 0.6 to about 5 grams of CrO_3 per liter of solution. The residence or contact time during the chromic acid treatment stage is not highly critical inasmuch as the intermediate drying step heretofore discussed renders the sodium silicate film highly resistant to solution. In any event, the time of contact with the chromic acid solution or bath is restricted sufficiently to avoid any possibility of the sodium silicate film being dissolved in or washed off by the chromic acid solution. The temperature during the treatment with the chromic acid solution may be maintained at from about 115° F. to about 200° F. and preferably from about 140° F. to about 180° F.

As hereinbefore described, when a high silica:soda ratio sodium silicate is employed in the first chemical treatment stage, the desired conversion of at least a portion of the sodium silicate by reaction with chromic acid is greatly facilitated because of the higher rate of gelation of the high silica:soda ratio sodium silicate. Moreover, the lower alkalinity of the high silica:soda ratio sodium silicates offers an additional advantage in that lower concentrations of chromic acid may be used in the treating solution for the second stage of the process. The use of the high silica:soda ratio sodium silicate is particularly desirable in the treatment of aluminum-surfaced articles.

After the chromic acid treatment, the product is subjected to a final drying operation to produce a final dried protective coating and the process is then complete. For high speed continuous operation, this final drying operation should likewise be carried out at an elevated temperature, for example by heating the coated strip to a surface temperature of from about 125° F. to about 250° F.

Thus, the final protective coating produced by my process comprises a sodium silicate film which has been dried and converted at least in part to silica gel and impregnated with chromic acid by in situ reaction with the latter. By reason of the intermediate drying step between the two chemical treatment stages, the completed protective coating is strongly adherent to the metal article and is relatively insoluble in moisture or condensate so that the chromic acid is always available for its corrosion inhibiting properties. Moreover, the silica gel component of the protective coating provides a high degree of retention for the chromic acid. Although I do not wish to be bound by any theoretical explanation, it is believed that the conversion of sodium silicate to silica gel is effective to the greatest extent adjacent the outer surface of the sodium silicate film and that the inner surface of the sodium silicate film in contact with the metal may comprise substantially unconverted sodium silicate which serves to cement the protective coating to the metal.

Referring now to the drawing, I have illustrated therein a preferred technique for practicing the invention in conjunction with a high speed galvanizing line. The galvanized strip or sheet issuing from the end of the galva-

nizing line is designated at 10, the sheet traveling in the direction of the arrows. The sheet passes over an upper roll 11 and then downwardly between a plurality of sprays 12 which are disposed on opposite sides of the sheet and which are preferably of the low velocity-high volume type so that effective flooding of the sheet with sodium silicate solution is accomplished. The sheet 10 then travels underneath a roll 13 which is partially immersed in a tank 14 containing an aqueous sodium silicate solution having the characteristics heretofore described. It will be understood that the excess sodium silicate solution from the sprays 12 drains back into the tank 14 wherein the liquid level is designated at 15. By means of recirculating pumps (not shown) the sodium silicate solution is pumped continuously from the tank 14 to the sprays 12. Although the drawing shows applications of the sodium silicate solution to the sheet 10 by means of sprays followed by immersion or dipping in a bath, it will be understood that the sprays alone or immersion alone may be utilized depending upon the equipment and physical facilities available in a given plant.

As the sheet 10 moves upwardly from the roll 13 it passes between a pair of rubber coated squeegee rolls 16 to remove excess solution which then drains back into the tank 14. The sheet then passes through a drying unit designated diagrammatically at 17. This drier is preferably of the forced hot air or hot gas type to obtain rapid removal of all excess moisture so that the sodium silicate film is in a non-tacky state when the sheet 10 passes over an upper roll indicated at 18. The speed of the sheet 10 may be on the order of from about 100 to about 200 ft. per minute, and with gas fired air driers for the drying unit 17 I have found that a surface temperature on the order of about 150° F. will accomplish the desired degree of drying at this point. Next, the sheet 10 passes downwardly from the roll 18 and thence through another heater or drying unit 19 which accomplishes the desired final degree of dehydration of the sodium silicate film. Preferably, the heater 19 is of the radiant heat type, such as electric heating elements or gas fired tubular heating elements, so that the sodium silicate film dries from its inner surface outwardly thereby realizing highly effective drying of the film in a short time.

As the sheet 10 passes from the radiant heat drier 19 it is treated by means of a plurality of spray units 20 with an aqueous chromic acid solution of the type heretofore described. The sheet then passes under a roll 21 partially immersed in a tank 22 containing the chromic acid solution, the liquid level being designated at 23. As before, recirculating pumps may be provided to supply solution from the tank 22 to the sprays 20, and either the sprays or the immersion step may be omitted if desired. The operation is completed by passing the sheet 10 through another set of squeegee rolls 24 and thence through a drier unit 25 which may also be of the forced hot air or hot gas type. Finally, the treated sheet passes over a roll 26 and thence to suitable winding rolls or other equipment for cutting the sheet into desired lengths.

As hereinbefore mentioned, instead of sodium silicate, other water soluble alkali metal silicates or polysilicates such as those of potassium or lithium may be used. Also, the sodium silicate and chromic acid baths may contain added ingredients, if desired, to impart additional properties to the treating solutions. For example, a suitable wetting agent may be employed in either of these baths. In the chromic acid solution, it may be desirable in some cases to employ added acidic ingredients for the purpose of facilitating the conversion of sodium silicate to silica gel.

The following examples will illustrate the beneficial results obtainable by my process as compared with other treating methods.

Example I

The tests were carried out on 4" x 6" samples of gal-

vanized steel from the same galvanizing run. In each case the samples were thoroughly washed with carbon tetrachloride before being subjected to the various protective treatments.

The galvanized steel samples were dipped for five seconds in an aqueous sodium silicate solution containing the equivalent of 23.6 grams of SiO_2 per liter of solution while maintaining the solution at a temperature of 165° F. The sodium silicate employed in preparing the solution was du Pont type "F" sodium silicate having a gravity of 40.6° Bé. and a silica:soda weight ratio of approximately 3.25:1. After dipping in sodium silicate, the samples were passed through a wringer with rubber rolls and then dried by radiant heat from an electric heater for six seconds on each side of each sample. The dried samples were immediately dipped for five seconds in an aqueous solution of chromic acid containing 1.5 grams of CrO_3 per liter of solution, the latter being maintained at 155° F. The treatment was completed by passing the samples once again through a wringer with rubber rolls and then air drying.

For purposes of evaluating the effectiveness of the process in protecting the samples against corrosion, a test method was employed which has been found to provide an accurate approximation of the actual conditions to which galvanized steel is subjected during storage and transportation in industry. The test procedure involves thoroughly wetting a plurality of test samples with distilled water by means of an atomizer and then stacking the wet samples and placing the stack or pile under a bell jar near a muffle furnace. An open container of water is also placed under the bell jar. The furnace heat is controlled to maintain the air temperature within the bell jar at approximately 120° F. so that a high relative humidity on the order of 90 to 100% is maintained within the bell jar. After approximately 40 hours of exposure, the samples are removed from the bell jar, allowed to dry in the air, and then evaluated for corrosion. The relative corrosion is estimated by visual observation on the basis of an arbitrary scale ranging from 1 to 10. On this scale, the value 1 represents substantially no corrosive effect and the maximum value 10 represents a high degree of corrosion corresponding to the results obtained with an unprotected or untreated test sample.

Using the foregoing test method, the average corrosion rating for the samples treated according to the above described procedure of the present invention was about 1. Thus, the method of the present invention provides a high degree of protection against corrosion. Furthermore, the protective coating obtained by this technique is invisible so that the desired bright surface characteristics of the galvanized product are maintained and, in addition, the surface does not possess the objectionable slippery characteristics inherent in the use of an oil inhibitor.

Example II

In this experiment, the treating procedure was substantially the same as in Example I except that after the sodium silicate treatment the galvanized steel samples were dried for four seconds by means of a hot air blast and thereafter the dried samples were dipped for three seconds in a chromic acid solution of the same concentration at a slightly higher temperature of from 165° F. to 170° F. Using the same test method for evaluating the resistance to corrosion but allowing the samples to remain exposed to the humid atmosphere in the bell jar for 45 hours, the average corrosion rating was 2.

Example III

For comparative purposes, galvanized steel test samples were subjected to a single stage treatment representative of a known commercial treatment for corrosion prevention. According to this procedure, the test

Wetting Agent

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 samples were dipped for five seconds in an aqueous treating solution maintained at 120° F. and containing sodium silicate and potassium dichromate. The same commercial grade of sodium silicate described in Example I was used here, and the treating solution contained 7.9 grams of SiO₂ per liter of solution and 3 grams of potassium dichromate per liter of solution. After this treatment, the samples were passed through a wringer with rubber rolls and air dried.

Using the same evaluating method discussed in Example I, the average corrosion rating of the test samples was 4. Consequently, the effectiveness of the single stage treating method is substantially less than that of the process of the present invention.

Example IV

This test was carried out to evaluate the comparative effectiveness of a somewhat different two stage chemical treatment as heretofore proposed in the art. According to this procedure, the galvanized steel test samples were first dipped for 15 seconds in a 75° F. solution of chromic acid containing 300 grams per liter of chromic acid, 30 grams per liter of ammonium persulfate, and 5 ml. per liter of Monsanto Chemical Company's wetting agent known as Santomerse S. These samples were immediately washed in running water and then dripped, without intermediate drying, for five seconds in a 160° F. solution containing du Pont "F" brand of sodium silicate in a concentration of 21.5 grams of SiO₂ per liter and also containing 1 gram per liter of Carbide & Carbon Chemicals' wetting agent known as Tergitol 7. Thereafter, the samples were passed through a wringer with rubber rolls and air dried.

Using the test method described in Example I, these samples had an average corrosion rating of 4.5 which is markedly inferior to the results shown in Example I.

Example V

In this experiment, the process heretofore described in Example I was carried out in reverse order. Thus, the galvanized steel test samples were dipped for three seconds in an aqueous solution maintained at 165° to 170° F. and containing 1.5 grams of chromic oxide per liter. The samples were then passed through a wringer with rubber rolls and dipped for three seconds in a 165° F. aqueous solution of du Pont type "F" sodium silicate containing 23.6 grams of SiO₂ per liter of solution. Again, the samples were passed through a wringer with rubber rolls and air dried.

The corrosion evaluation method was the same as described in Example I except that the samples were maintained in the bell jar for 45 hours. The average corrosion rating of the test samples was 5 so that again the results are inferior to the results obtained by the process of the present invention.

Example VI

The effectiveness of the present invention in protecting aluminum surfaces was shown by a series of tests on 3" x 4" panels of aluminum sheet. The test samples were degreased with carbon tetrachloride and then rubbed successively with emery paper and steel wool to provide a clean, reproducible surface.

One group of test samples was left untreated, another group was treated by dipping in an aqueous chromic acid solution (1% CrO₃) at room temperature and dried by squeegee rolls, and a third group was treated by the process of the present invention substantially as described in Example I. All samples were then subjected to the high humidity stack test at 120° F. for 40 hours as described in Example I.

Using the same evaluation scale described in Example I, it was found that the untreated test samples had an average corrosion rating of about 8 to 10 and the chromic acid treated samples averaged about 8 to 9. However,

the samples which were treated according to my invention were substantially free of all corrosion and were rated at 1.

I claim:

1. A process for treating an article having a surface of a metal selected from the group consisting of zinc, aluminum, and alloys thereof to protect the surface against corrosion, which comprises the steps of coating the surface with an aqueous solution of an alkali metal silicate, drying to form a relatively insoluble and incompletely dehydrated silicate film on said surface, and thereafter impregnating the silicate coated surface with an aqueous chromic acid solution, said incompletely dehydrated silicate film containing sufficient water so that at least a portion of the alkali metal silicate is converted to silica gel by the action of said chromic acid solution.
2. The process of claim 1 further characterized in that said alkali metal silicate comprises sodium silicate.
3. The process of claim 2 further characterized in that said sodium silicate has a silica:soda weight ratio of from about 3:1 to about 3.75:1.
4. The process of claim 3 further characterized in that said sodium silicate has a silica:soda weight ratio of from about 3.25:1 to about 3.75:1.
5. The process of claim 1 further characterized in that the temperature of the alkali metal silicate and chromic acid solutions is from about 115° F. to about 200° F.
6. The process of claim 5 further characterized in that said temperature is from about 140° F. to about 180° F.
7. The process of claim 1 further characterized in that said drying step is carried out at a temperature of from about 100° F. to about 400° F.
8. The process of claim 7 further characterized in that said temperature is from about 125° F. to about 250° F.
9. The process of claim 1 further characterized in that said drying step is carried out by first contacting the surface of the article with hot gases to effect removal of a substantial portion of the water and thereafter heating the surface of the article by radiant heat to complete the drying step.
10. A process for protecting a zinc-surfaced article against corrosion which comprises the steps of coating the zinc surface with an aqueous solution of sodium silicate containing from about 5 to about 50 grams of SiO₂ per liter of solution, drying to form a relatively insoluble and incompletely dehydrated silicate film on said surface, and thereafter impregnating the silicate coated surface with an aqueous chromic acid solution, said incompletely dehydrated silicate film containing sufficient water so that at least a portion of the silicate is converted to silica gel by the action of said chromic acid solution.
11. The process of claim 10 further characterized in that said sodium silicate solution contains from about 15 to about 35 grams of SiO₂ per liter of solution.
12. A process for protecting an aluminum-surfaced article against corrosion which comprises the steps of coating the aluminum surface with an aqueous solution of sodium silicate containing from about 12 to about 95 grams of SiO₂ per liter of solution, drying to form a relatively insoluble and incompletely dehydrated silicate film on said surface, and thereafter impregnating the silicate coated surface with an aqueous chromic acid solution, said incompletely dehydrated silicate film containing sufficient water so that at least a portion of the silicate is converted to silica gel by the action of said chromic acid solution.
13. The process of claim 12 further characterized in that said sodium silicate solution contains from about 16 to about 80 grams of SiO₂ per liter of solution.
14. A process for protecting a zinc-surfaced article against corrosion which comprises the steps of coating

the zinc surface of the article with an aqueous solution of an alkali metal silicate, drying to form a relatively insoluble and incompletely dehydrated silicate film on said surface, and thereafter impregnating the silicate coated surface with an aqueous chromic acid solution containing from about 0.5 to about 7.5 grams of CrO_3 per liter of solution, said incompletely dehydrated silicate film containing sufficient water so that at least a portion of the alkali metal silicate is converted to silica gel by the action of said chromic acid solution.

15. The process of claim 14 further characterized in that said chromic acid solution contains from about 1.0 to about 3.0 grams of CrO_3 per liter of solution.

16. A process for protecting an aluminum-surfaced article against corrosion which comprises the steps of coating the aluminum surface of the article with an aqueous solution of an alkali metal silicate, drying to form a relatively insoluble and incompletely dehydrated silicate film on said surface, and thereafter impregnating the silicate coated surface with an aqueous chromic acid solution containing from about 0.6 to about 5.0 grams of CrO_3 per liter of solution, said incompletely dehydrated silicate film containing sufficient water so that at least a portion of the alkali metal silicate is converted to silica gel by the action of said chromic acid solution.

17. A process for protecting a zinc-surfaced article against corrosion which comprises the steps of coating the zinc surface of the article with an aqueous solution of sodium silicate containing from about 5 to about 50 grams of SiO_2 per liter of solution, said sodium silicate having a silica:soda weight ratio of from about 3:1 to about 3.75:1, drying to form a relatively insoluble and incompletely dehydrated silicate film on said surface, and thereafter impregnating the silicate coated surface with an aqueous chromic acid solution containing from about 0.5 to about 7.5 grams of CrO_3 per liter of solution, said incompletely dehydrated silicate film containing sufficient water so that at least a portion of the sodium silicate is converted to silica gel by the action of said chromic acid.

18. A process for protecting an aluminum-surfaced article against corrosion which comprises the steps of coating the aluminum surface of the article with an aqueous solution of sodium silicate containing from about 12 to about 95 grams of SiO_2 per liter of solution, said sodium silicate having a silica:soda weight ratio of from about 3:1 to about 3.75:1, drying to form a relatively insoluble and incompletely dehydrated silicate film on said surface, and thereafter impregnating the silicate coated surface with an aqueous chromic acid solution containing from about 0.6 to about 5.0 grams of CrO_3 per liter of solution, said incompletely dehydrated silicate film containing sufficient water so that at least a portion of the sodium silicate is converted to silica gel by the action of the chromic acid.

19. An article having a surface of a metal selected from the group consisting of zinc, aluminum, and alloys thereof, and a protective coating over said surface comprising a dried alkali metal silicate film converted at least in part to silica gel and impregnated with chromic acid.

20. The article of claim 19 further characterized in that said alkali metal silicate comprises sodium silicate.

21. An article having a surface of a metal selected from the group consisting of zinc, aluminum, and alloys

thereof, and a protective coating over said surface comprising a dried alkali metal silicate film, the outermost portion of said film being substantially converted to silica gel and impregnated with chromic acid, and the innermost portion of said film in contact with said surface being substantially unconverted alkali metal silicate for firmly adhering the coating to said surface.

22. The article of claim 21 further characterized in that said alkali metal silicate comprises sodium silicate.

23. A continuous process for treating a metal strip having a surface of a metal selected from the group consisting of zinc, aluminum, and alloys thereof to protect the surface against corrosion, comprising the steps of coating the surface of the strip with an aqueous solution of an alkali metal silicate, advancing the strip in an upwardly directed path, thence over a guide roll, and thence in a downwardly directed path, drying the silicate solution on the strip to a non-tacky state during movement of the strip in said upwardly directed path and before it reaches said guide roll, further drying the silicate solution on the strip during movement of the strip in said downwardly directed path to form a relatively insoluble and incompletely dehydrated silicate film on said surface, and thereafter impregnating the silicate coated surface with an aqueous chromic acid solution, said incompletely dehydrated silicate film containing sufficient water so that at least a portion of the alkali metal silicate is converted to silica gel by the action of said chromic acid solution.

24. The process of claim 23 further characterized in that said first-mentioned drying step is carried out by contacting the strip with hot gases to effect removal of a substantial portion of the water from the silicate solution on the strip and said second-mentioned drying step is carried out by radiantly heating the strip.

25. A continuous process for treating a moving strip having a surface of a metal selected from the group consisting of zinc, aluminum, and alloys thereof to protect the surface against corrosion, comprising the steps of coating the surface of the strip with an aqueous solution of an alkali metal silicate, drying the silicate solution on the strip during movement of the strip at a temperature of from about 100°F . to about 400°F . to form a relatively insoluble and incompletely dehydrated silicate film on said surface, and thereafter impregnating the silicate coated surface with an aqueous chromic acid solution, said incompletely dehydrated silicate film containing sufficient water so that at least a portion of the silicate is converted to silica gel by the action of said chromic acid solution.

26. The process of claim 25 further characterized in that said alkali metal silicate comprises sodium silicate and said temperature is from about 125°F . to about 250°F .

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