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PROCESS FOR COATING METAL SURFACES

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ABSTRACT OF THE DISCLOSURE

A process for treating zinc, aluminum, or ferrous metal surfaces in which a layer of an aqueous mixture of chromic acid and phosphoric acid is applied to the surface to be treated. The water content of the layer is adjusted to within the range of about 4 to 20% by weight and an organic film forming resin is then applied to the water-containing surface. The aqueous chromic acid-phosphoric acid coating material desirably also contains a filler, such as titanium dioxide.

This invention relates to a method for coating metal surfaces to provide thereon a protective and/or paint base coating, and more particularly it relates to a method for coating surfaces of ferrous metal, zinc or aluminum, which is particularly adapted for application in a strip line process.

In recent years, interest has developed in the prefinishing of metal sheet and strip and there has been a rapidly increasing market for this product. By "prefinished," it is meant metal, generally ferrous metal, zinc or aluminum, which is painted in the sheet or strip form and then fabricated. The prefinish applied may be a primer, a one or two coat finish paint or a laminate such as a plastic film or the like. Since the metal is fabricated after painting, severe requirements are placed both on the paint used, and to an even greater extent on the metal surface treatment before painting. The paint should be flexible yet tough and give corrosion resistance, while the surface treatment must provide excellent adhesion and formability, and also good corrosion resistance.

Presently, a variety of metal surface treatments are applied commercially to obtain a suitable surface for the application of strip line paint finishes and laminates. For the most part, however, these differ, depending on the metal to be treated. For example, on steel, zinc phosphate coatings generally give the best corrosion resistance but are surpassed in formability by the less corrosion resistant iron phosphate coatings. Similarly, on galvanized surfaces, the corrosion resistant zinc phosphate coatings are generally surpassed in formability by the alkaline-complex oxide coatings. Additionally, aluminum is generally treated with a chromic-aluminum oxide system, which is quite different than the treatments for either steel or zinc. Not only are each of these treatments different depending on the metal treated, but additionally, in many instances the treatment used for one metal may be ineffective or even detrimental when used on a different metal.

Generally, however, all of these treatments are dependent on a definite reaction with the metal surface being treated so that contact of the treating solution with the metal for a definite reaction time is essential. Thus, in a conventional process for treating sheet or strip, the metal surface is contacted with the treating solution for a time sufficient to form a coating and, thereafter, the excess coating solution is removed and returned to the main body of coating solution. Because of the reaction which takes place, the concentration of the active components of the solutions change during use, each at a different rate, so that careful control of the solution make-up may be required to insure proper functioning. Additionally, sludge formation may also take place, requiring periodic clean out.

The equipment required for using these processes on a variety of metals normally includes a long series of treating stages, with those not needed for the particular metal in process being by-passed. Alternatively, hold tanks may be provided to store treating solutions not needed for a particular metal. Although this makes it possible to eliminate many of the treating stages and, thus, requires less space, it involves appreciable expensive downtime while tanks are cleaned and solutions are changed.

Accordingly, at the present time, there is not available a single process for treating ferrous metal, zinc and aluminum, and the methods now used generally require either a long series of treating stages or a number of hold tanks, with the inherent disadvantages of each. Moreover, since the speed at which the process can be carried out is normally dependent on reaction time, speed variations may be limited and the processes are often not suited for high speed, e.g. 1000 feet per minute, sheet or strip line application. Additionally, in some cases, the processes which give the best corrosion resistance on a particular metal may not also give the best formability.

It is, therefore, an object of the present invention to provide a method for producing a paint base and/or protective coating on metal surfaces, which coating may be applied to aluminum, zinc and ferrous metal surfaces in the form of sheet and strip and overcomes the difficulties of the prior art methods.

A further object of the present invention is to provide a multimetal coating process which may be used in the prefinishing of painted sheet and strip to give a coating having good adhesion, physical properties, and resistance to salt fog.

These and other objects will become apparent to those skilled in the art from the description of the invention which follows.

Pursuant to the above objects, the present invention includes a process for treating a metal surface which comprises applying to the surface to be treated a layer of an aqueous coating mixture containing chromic acid and phosphoric acid, adjusting the water content of the thus-coated surface so as to provide thereon water in an amount within the range of about 4 to 20% by weight of the coating on the surface, thereafter, applying to the water-containing surface an organic film forming material in an amount sufficient to seal the surface and curing the coatings thus-formed on the surface. This method is found to be particularly applicable to use in strip lines and the coatings produced thereby are found to be excellent paint base and protective coatings.

More specifically, in the practice of the method of the present invention, the aqueous coating solution which is applied to the metal surface, desirably contains CrO_3 in an amount within the range of about 4 to about 35% and H_3PO_4 in an amount within the range of about 4 to about 35%. Preferably, the CrO_3 is present in the coating mixture in an amount within the range of about 6 to about 15% while the H_3PO_4 is present in an amount within the range of about 6 to about 15%. In many instances, it has been found to be desirable to use solutions in which the CrO_3 and H_3PO_4 are present in substantially equal amounts by weight. It is to be appreciated, however, that the aqueous coating mixtures used may contain the CrO_3 and H_3PO_4 in a weight ratio of CrO_3 to H_3PO_4 within the range of about 0.5:1 to about 2:1.

In addition to the chromic acid and the phosphoric acid, the aqueous coating mixtures also desirably contain an inorganic filler material, which material may be present in the composition in amounts within the range of about 1 to about 40%, with amounts within the range of about 15 to about 25% being preferred. Exemplary of such filler materials which may be used are titanium dioxide, colloidal silica, attapulgus clay, aluminum metal powder, zinc metal powder and the like. Additionally, it has been found that metal salts of organic fatty acids, such as zinc stearate, lead acetate, sodium acetate and the like, may also be used. In a most preferred embodiment, the aqueous coating solution for use in the method of the present invention contains 8% by weight CrO_3, 8% by weight H_3PO_4, and 20% by weight of titanium dioxide.

The aqueous coating solution may be applied to the metal surface to be treated in any convenient manner, as for example, by roller coating, spraying, flowing, immersion, and the like. Inasmuch as many strip lines have facilities for roller coating applications, in many instances this method of applying the coating solution is preferred. Accordingly, primary reference hereinafter will be made to applying the coating solution by roller coating. In such operations, the normal roller coating techniques, as are known to those in the art, may be used, and the solutions may be applied by either direct or reverse roll coating. The temperature of the chromic acid-phosphoric acid coating solutions have not been found to be critical. Accordingly, temperatures from room temperature, e.g., about 20° centigrade up to a boiling point of the solution may be used. The coating operation with these solutions, whether by roller coating or other means, is desirably carried out so that a coating weight within the range of about 5 to about 200 milligrams per square foot and preferably within the range of about 30 to about 60 milligrams per square foot is formed on the metal surface.

In applying the chromic acid-phosphoric acid coating solutions to the metal surfaces to be treated, it has been found to be desirable that the coating is applied evenly over the surface of the metal. In some instances, it also has been found to be desirable to ensure this even application by passing the coated surface through one or more rolls after the application of the coating solution.

Following the application of the chromic acid-phosphoric acid coating solution to the metal surface, any excess coating solution is desirably removed from the surface and the water content of the thus-coated surface is adjusted so as to provide on the surface water in an amount within the range of about 4 to about 20% by weight of the coating on the surface. Preferably, the water content is adjusted so as to provide water on the surface in an amount within the range of about 6 to about 10% by weight of the coating. This adjustment of the water content of the surface may be effected in any convenient manner, and will depend upon the conditions under which the coating has been applied. Thus, for example, where the coating is applied under conditions of high humidity, it may be necessary to remove water from the surface so as to bring the water content within the 4 to 20% by weight range. This may be done by drying the surface in any convenient manner, as for example by passing heated air over the surface. Where the coating has been applied under conditions of low humidity, however, water may have to be added to the surface in order to bring the water content within the desired 6 to 20% by weight range. Here again, the addition of water to the surface may be effected in any convenient manner, as for example, by contacting the surface with moist air or steam.

After the moisture content of the coating on the metal surface has been adjusted within the ranges as has been indicated hereinabove, an organic film-forming material is applied to the wet surface. Quite surprisingly and in contrast to the teachings of the prior art, it has been found that when the surface to which the organic film forming material is applied has a moisture content within the range of about 4 to 20% by weight of the chromic-phosphoric acid coating on the surface, the film adhesion and formability of the final coated metal surface are excellent. Additionally, when the moisture content of the surface is appreciably above 20% the corrosion resistance is greatly reduced and when it is less than about 4% the adhesion, formability and resistance to blistering on water immersion are reduced. Accordingly, it is quite important in the present process that the moisture content of the chromic acid-phosphoric acid coated surface be adjusted as has been indicated hereinabove and that this moisture content be maintained while the organic film forming material is applied on the surface.

As with the chromic acid-phosphoric acid coating solution, various application techniques may be used in applying the organic film forming material, including spraying, roller coating, brushing, and the like. Various organic film forming materials may be used, such as alkyd resins, acrylic resins, epoxies, vinyls, urethanes, and other commonly used film forming resins. These materials may be pigmented or unpigmented, as is known in the art, and are applied in an amount sufficient to seal the metal surface being treated. In many instances, it has been found that coating weights of the film forming material as low as about 500 milligrams per square foot may be sufficient to effect the desired sealing of the metal surface. Obviously, greater amounts of the film forming material, such as are sufficient to provide dry films of one mil thickness or even higher, may also be used if desired. It is to be appreciated that the film forming materials used may be in the form of paints, lacquers, enamels or the like, and are applied as solutions or dispersions of one or more of the above indicated resin materials in a suitable solvent.

Following the application of the organic film forming material, the film forming material on the coated metal surface is then cured. This curing may be effected by heating, baking or the like, depending upon the nature of the particular film forming material used. It is to be appreciated, that there is considerable latitude in the choice of the organic film forming material used and in the amounts which are applied to the metal surface. Thus, in some instances, it is possible to obtain a treated metal surface having a finished top coat thereon by using a relatively heavy film of a film forming material which is a finish or top coat paint. In other instances, when using a film forming material which is normally a primer paint, a primed metal surface is obtained after the curing step which is then suitable for the application of the top or finish coat. In other instances, the film-forming material applied may be unpigmented and applied in a relatively thin film, sufficient only to seal the metal surface. Such coatings, however, have been found to be substantially equivalent to the primed coatings so that in many instances only a single top or finish coating is required on the surface. It has been found that with one coat of paint, however, there is sometimes a slight tinting, and a reduction in gloss of the paint film by the chromic acid. Thus, when light colors are used, it is preferable to use a very light coat of paint as the initial film former on the CrO_3-H_3PO_4 mixture. Once this is baked subsequent paint coats are not affected.

An obvious application of this process is the high speed treatment of strip metal at the mill, where the process of this invention is used in conjunction with a light prime coat of paint. A further application in the use of the process of this invention in conjunction with an adhesive, as the film former, to provide a suitable surface for the adhesion of lamination film such as vinyls, polyethylenes and Tedlar®.

It is to be appreciated that the process of the present invention may be used on various metal surfaces, including surfaces of aluminum, aluminum alloys which are predominantly aluminum, zinc, zinc alloys, which are prodaminantly zinc, and ferrous metal surfaces such as iron, steel and the like. Additionally, in some instances, metal surfaces other than those set forth hereinabove, may also be coated by this process. The present process has been found to be particularly applicable in the coating of metallic strip and sheet, and has particular utility in the coating of metal strip at relatively high line speeds.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. In these examples, unless otherwise indicated, temperatures are in degrees centigrade, and parts and percent are by weight. It is to be appreciated, however, that these examples are merely exemplary of the present invention and are not to be taken as a limitation thereof.

EXAMPLE 1

Clean steel panels, 4 inches by 10 inches, were treated with a solution containing 10% CrO_3, 10% H_3PO_4 to

coated with the same paint finish used for the seal coat, which top coat was then cured by baking.

By way of comparison, other steel panels were given a commercial zinc phosphate treatment and a commercial iron phosphate surface treatment; other galvanized panels were given a commercial zinc phosphate treatment and a commercial amorphous complex oxide treatment; and other aluminum panels were treated with commercial chromic-aluminum oxide treatments. All of these panels were then top coated as were the previous panels and all of the thus-prepared panels were tested for adhesion, formability and resistance to water immersion and salt fog. Using this procedure, the following results were obtained:

Metal	Surface treatment	Paint	Adhesion [1]	Formability [2]	Resistance to— Water immersion [3]	Salt fog [4]
Steel	Process of present invention	Acrylic	Excellent	Excellent	V. good (micro)	Excellent (1–2).
Do	Commercial iron phosphate	do	do	do	Excellent (10)	Fair (13–45).
Do	Commercial zinc phosphate	do	do	V. good	do	Fair (7–22).
Do	Process of present invention	Vinyl	do	Excellent	do	V. good (2–5).
Do	Commercial iron phosphate	do	V. good	Fair	do	Good (4–10).
Do	Commercial zinc phosphate	do	Excellent	V. good	do	Good (5).
Galvanized steel	Process of present invention	do	do	Excellent	do	Good (0–8).
Do	Commercial zinc phosphate	do	do	do	do	Good (5+).
Do	Commercial amorphous oxide.	do	do	do	do	Good (0–12).
Do	Process of present invention	Acrylic	do	V. good	V. good (micro)	Excellent (0–2).
Do	Commercial zinc phosphate	do	do	Poor	Excellent (10)	Good (0–12).
Do	Commercial amorphorus oxide.	do	Good	V. good	do	Good (10+).
Aluminum	Process of present invention	do	do	do	do	Excellent (0).
Do	Commercial Al-chromic-oxide.	do	do	do	do	Excellent (0–1).
Do	do	do	do	do	do	Do.
Do	Process of present invention	Vinyl	do	do	do	Excellent (0).
Do	Commercial Al-chromic-oxide.	do	do	do	do	Do.
Do	do	do	do	do	do	Do.

[1] Knife adhesion rating.

[2] Formability, combined crack and peel observed when metal deformed.

[3] Water immersion, blistering on immersion in water at 100° F. for approximately 400 hours; rated using ASTM rating which is given in parenthesis (10 is perfect).

[4] Salt fog testing for 400 hours usng ASTM procedure and rated on overall quality and the average width of undercutting in millimeters, which is given in parenthesis.

which 30% by volume of titanium oxide had been added. The coating was effected by passing the panels through a roll coater, for a total of four passes, so as to work the coating into the surface of the panels. Excess coating solutions were then removed from the panels and the coating weights of the panels was determined to be about 40 milligrams per square foot. Thereafter, the coated panels were humidified with a steam jet to provide a water content on the surface of the panels of about 9% by weight of the coating. The panels were then immediately painted, while moist, with a white alkyd baking enamel, the enamel being applied by spraying in an amount sufficient to provide a coating of about 600 milligrams per square foot on the panel. The alkyd enamel coating was cured by baking for about 5 minutes at 150° centigrade. Thereafter, a top coat of the same alkyd enamel was applied to the panels. The top coated panels were then tested and gave excellent results in the knife adhesion test and the water immersion test after immersion for 16 hours at 60° centigrade. Additionally, in the standard 5% salt fog test, the panels exhibited only from 0 to 4 millimeters creepage after 117 hours in the test.

EXAMPLE 2

A series of runs were made to compare the process of the present invention with commercially available processes for treating steel, galvanized steel (zinc) and aluminum. In these runs, panels of the three metals were treated by applying thereto a composition containing 12% CrO_3, 8% H_3PO_4, 20% TiO_2 and 60% H_2O, using a forward roll coater at a surface speed of 200 feet/minute. The panels were then passed through two smoothing rolls and then under a hot air blast which reduced the water content of the surface to within the range of 6–10%. Thereafter, about 600 milligrams/square foot of the particular paint finishing being tested was applied to the moist surface by spraying, and the surface was baked for 5 minutes at 150° centigrade. The panels were then cooled and top

EXAMPLE 3

The procedure of Example 2 was repeated using the following coating compositions, which were applied in the amounts indicated:

Composition:	Coating weight in milligrams per sq. ft.
(A) 2% CrO_3, 8% H_3PO_4, 20% TiO_2, balance H_2O	30
(B) 4% CrO_3, 8% H_3PO_4, 20% TiO_2, balance H_2O	52
(C) 6% CrO_3, 8% H_3PO_4, 20% TiO_2, balance H_2O	53
(D) 8% CrO_3, 8% H_3PO_4, 20% TiO_2, balance H_2O	59
(E) 8% CrO_3, 6% H_3PO_4, 20% TiO_2, balance H_2O	52
(F) 8% CrO_3, 4% H_3PO_4, 20% TiO_2, balance H_2O	35
(G) 8% CrO_3, 2% H_3PO_4, 20% TiO_2, balance H_2O	40

These compositions were applied with a roll coater, as in Example 2, to panels of steel, galvanized steel and aluminum. The water content of the surface was adjusted to within the range of 6–10% using an air blast and a sealer film of a white alkyd enamel was applied to the moist surface by spraying. The panels were cured by baking for 5 minutes at 150° centigrade, cooled and then top-coated with the same alkyd enamel. The panels were then tested as in Example 2 and all showed good paint bonding ability.

EXAMPLE 4

The procedure of Example 3 was repeated with the exception that the following coating compositions were used:

(A) 23% CrO_3, 23% H_3PO_4, 33% TiO_2, balance H_2O
(B) 28% CrO_3, 28% H_3PO_4, 33% TiO_2, balance H_2O
(C) 35% CrO_3, 35% H_3PO_4, balance H_2O

The panels thus treated were sealed with vinyl and alkyd paint films, using both one and two coats after adjusting the surface moisture to 6–10% and the paint bond obtained was calculated. In each instance, good adhesion, formability and corrosion resistance were obtained.

EXAMPLE 5

A number of fillers were examined in a series of experiments using the procedure of Example 4. The following compositions were prepared:

(A) 10% CrO_3, 10% H_3PO_4, 5% pyrogenic silica
(B) 10% CrO_3, 10% H_3PO_4, 10% synthetic calcium silicate
(C) 10% CrO_3, 10% H_3PO_4, 20% hydrated magnesium aluminum silicate
(D) 10% CrO_3, 10% H_3PO_4, 4% silica

These compositions were applied to steel test panels, the surface water adjusted to 6–10%. A film of a strip line paint applied and the combined coating cured 5 minutes at 150° C. The panels were then cooled and top coated with the same strip line paint. Evaluation of the paint bonds obtained was carried out and it was found that all compositions exhibited good paint bonding.

It is to be noted that because the CrO_3-H_3PO_4 mixture is simply applied in the present method and no reaction time is required, the speed of the process can be readily varied without change in the time of the treatment and thus equipment length. Furthermore, the process is suited to the treatment of metals at very high speeds, the limiting speed being dependent mainly on the curing of the film former. Also the mixture is applied directly in the desired quantity so there is no depletion of active chemicals and consequent difficulty in control.

In addition all three of the common metals can be treated with the same mixture and the resulting paint bonds are equivalent to the combined best features of those commercial treatments now in use.

While there have been described various embodiments of the invention, the compositions and methods described are not intended to be understood as limiting the scope of the invention as changes therein are possible and it is intended that each element recited in any of the following claims is to be understood as limiting the scope of the invention as changes therein are possible and it

is intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A method for treating zinc, aluminum and ferrous metal surfaces which comprises applying to the metal surface to be treated a layer of an aqueous coating mixture which consists essentially of from about 4 to 35% by weight CrO_3 and from about 4 to 35% by weight H_3PO_4, adjusting the water-content of the thus-coated surface so as to provide thereon water in an amount within the range of about 4 to about 20% by weight of the coating on the surface, thereafter, applying to the water-containing surface an organic film-forming resin in an amount sufficient to seal the surface and curing the coating thus-formed on the metal surface.

2. The method as claimed in claim 1 wherein the aqueous coating mixture also contains an inorganic filler or metal salts of organic acids in an amount within the range of about 1 to about 40% by weight of the coating mixture.

3. The method as claimed in claim 2 wherein the inorganic filler material is titanium dioxide.

4. The method as claimed in claim 3 wherein the aqueous coating mixture is applied to the metal surface in an amount sufficient to provide a coating weight within the range of about 5 to about 200 milligrams per square foot.

5. The method as claimed in claim 4 wherein the organic film forming resin is a resin selected from the group consisting of vinyl, alkyd and acrylic resins.

6. The method as claimed in claim 5 wherein the water content on the surface coated with the chromic acid-phosphoric acid coating solution is within the range of about 6 to about 10% by weight of the coating.

7. The method as claimed in claim 6 wherein the aqueous coating solution contains 6–15% CrO_3, 6–15% H_3PO_4 and 10–30% titanium dioxide.

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