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GALVANIZING PROCESS

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The present invention relates to a method of coating a base metal with another metal and more particularly to a method of galvanizing a ferrous metal strip or sheet on one side only.

Galvanized sheet metal is conventionally used in applications where the metal is exposed to corrosive atmospheres and the like conditions. One potential use for corrosive resistant one-side galvanized material is in the manufacture of automotive bodies, particularly for the surfaces of the body where rusting is generally most severe. The conventional galvanized sheet material which is coated on both sides with zinc has not been widely accepted for automobile body construction because of the relatively poor exterior finish which results when a galvanized surface is enameled or painted. It would therefore be highly desirable to provide an inexpensive galvanized sheet material in which zinc is coated on one side only, thereby leaving the other side uncoated and in condition for providing a suitable enamel finish.

Heretofore, ferrous sheet metal material has been galvanized on one side only by applying to one side of a sheet of ferrous metal an alkali metal salt solution and drying said solution before subjecting the sheet to the galvanizing bath. Since the large scale production of galvanized sheet material requires continuously passing an endless strip of the sheet material through a galvanizing line in which the strip is heated to an elevated temperature in a reducing atmosphere to remove oxides from the free metal surface immediately prior to galvanizing, it is essential that any zinc barrier coating applied to the strip be highly stable and adherent under the foregoing heating conditions. The prior art coatings, however, lose their ability to adhere securely to a ferrous metal surface when heated in a reducing atmosphere at temperatures above about 1450° F. and cause the zinc plating bath to become contaminated. Consequently, the known zinc repellent coating methods for producing one-side galvanized sheet material are entirely unsatisfactory for use in any galvanizing operation where it is necessary to heat to temperatures above about 1450° F.

It is therefore an object of the present invention to provide an improved method of galvanizing ferrous metal sheets on one side only.

It is also an object of the present invention to provide a method of galvanizing ferrous metal sheets on one side only which can be used in conjunction with a high temperature continuous galvanizing line.

It is a further object of the present invention to provide a method of galvanizing a ferrous metal sheet on one side only which provides a firmly adherent zinc barrier coating which does not contaminate the galvanizing bath and which nevertheless can be readily removed from the ferrous metal sheet after the sheet passes through a galvanizing bath leaving one side of the sheet free of a zinc coating and in a clean condition for satisfactory surface finishing.

Other objects will be readily apparent to those skilled in the art from the detailed description and claims to follow.

The foregoing objects and other objects which will be apparent to one skilled in the art are achieved by providing on only one side of a ferrous metal sheet a thin, continuous coating of a refractory metal oxide composi-

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tion which is firmly held on the surface of the ferrous metal sheet during the passage thereof through the galvanizing processing line but which is readily removable therefrom after completion of the galvanizing process. The novel binding agent which removably secures the said metal oxides on the surface of the ferrous metal sheet is a reaction product formed in situ on the surface of the ferrous metal sheet in the presence of the refractory metal oxide which is essentially the product of the chemical combination of an oxy-mineral acid and the iron in the surface of the ferrous metal sheet. Thus, it has been discovered that a thin, continuous coating of silica, alumina, or manganese oxide, for example, when applied as a fine powder suspension or colloidal solution, and dried is effective for preventing the wetting of a ferrous metal sheet by molten zinc. However, a coating of the said oxides when applied to a ferrous metal sheet by previously devised means, such as when suspended in a starch solution, leaves a residue in the zinc plate bath which seriously interferes with the proper coating of the zinc and is entirely objectionable. When, however, any of the herein disclosed refractory metal oxides or a combination of said oxides is prepared in the form of an aqueous colloidal solution or suspension having an oxy-mineral acid, such as a phosphoric acid or chromic acid dissolved in said colloidal solution or suspension, the refractory metal oxide is securely held on the ferrous metal sheet during a galvanizing process employing temperatures as high as 1900° F. without forming a residue in the galvanizing bath and can also be readily removed following the galvanizing step.

While the improved zinc barrier coating of the present invention can be applied to a ferrous metal sheet as a thin continuous, uniform coating and thereafter dried in any desired manner which will be apparent to one skilled in the art, it has been found that a very effective and convenient manner of applying the said barrier coating is by means of an electrostatic spray apparatus. For best results, the ferrous metal sheet should, of course, be completely free of rolling oils or grease at the time the colloidal suspension is applied, since for economic reasons, the colloidal solution is preferably prepared with an aqueous vehicle. The ferrous metal sheet is therefore treated with a standard alkaline-type cleaner or subjected to flame treatment to remove the grease or oil by oxidation.

It has also been found desirable to have the metal sheet heated to a surface temperature of about 200–300° F. when the said colloidal suspension is applied thereto in order to provide the desired adherent, continuous coating. It appears that by having the sheet heated to a temperature within the indicated range, the reaction between the phosphoric acid or other oxy-mineral acid and the iron of the sheet metal is accelerated so so that the acid reacts substantially completely with the iron in the surface before the colloidal solution is completely dried. If the sheet is heated to substantially above 350° F. before being coated with the colloidal solution or if the sheet being coated with the colloidal solution is heated too rapidly, the water in the colloidal solution is removed by vaporization before the reaction between the acid and the iron is substantially completed, thus resulting in a poorly adherent zinc barrier coating.

The foregoing pre-heating of the ferrous metal sheet prior to applying the zinc barrier coating is of particular importance in the preferred embodiment of the present invention in which an endless strip of sheet metal is moved continuously through a galvanizing line without interruption. If a batch type zinc coating operation were employed where a prolonged period can elapse between application of the colloidal suspension and the

immersion in a zinc coating bath, the necessity of rapidly completing the reaction between the iron and the acid would, of course, be absent. It will also be understood that it is not required to heat the colloidal solution coating in a reducing atmosphere in order to provide a satisfactory zinc barrier coating, as the reducing atmosphere is primarily for the purpose of preventing the formation of and removing oxides from the free metal surface which is to be coated with zinc.

The amount of zinc barrier coating used to provide a complete zinc repellent surface can be varied considerably. The ferrous metal sheet should preferably have a coating weight of at least 0.3 gram (dry weight) per square foot of sheet surface area. Excellent results have been achieved with the zinc barrier coatings providing between about 0.3 and 0.4 gram (dry weight) per square foot of sheet surface area. When substantially heavier coatings of the herein disclosed composition are applied, there is a tendency for the outer portion of the coating to flake, probably as a result of the outer portion of the coating not reacting completely with the iron. It is therefore preferred to maintain the weight of the barrier coating below about 0.5 gram per square foot of ferrous metal surface area for both practical and economic reasons.

If the herein disclosed zinc barrier coating has been applied to a pre-heated steel strip by electrostatic spraying, rolling, or the like, the coating dries rapidly and the strip is passed through the normal continuous in-line high or low temperature heat treatment cycle conventionally employed on continuous galvanizing lines. The barrier coating of the present invention is in no way impaired by heating to a temperature of between 1200 and 1900° F. in a reducing atmosphere containing 75 percent hydrogen with the remainder being substantially nitrogen and having a dew point of -10° F. to -20° F., such as provided in the normal galvanizing atmosphere formed by dissociating ammonia.

After the ferrous metal strip has been heat treated in the conventional manner, as described above, the strip or sheet is immersed in a molten zinc bath in accordance with the usual galvanizing practice. On emerging from the galvanizing bath, only the uncoated side of the metal sheet is coated with zinc. The zinc barrier coating on the opposite side of the sheet is readily removed by contacting the barrier coating with rotating brushes or other abrading means. The resulting ferrous metal sheet having one side only galvanized and the other side free of zinc can be stored and handled in the usual manner.

The zinc barrier coating of the present invention comprising a fine refractory metal oxide and an oxy-acid composition is preferably applied to the surface of the ferrous metal sheet as an aqueous colloidal solution or colloidal suspension. The colloidal solution or suspension is preferably formed by diluting with water a concentrated active colloidal silica sol (50% by weight silica) until the silica concentration is between about 5 and 20% by weight silica and preferably having about 10% by weight silica. To the thus diluted aqueous colloidal solution of silica is then added a concentrated solution of an oxy-mineral acid, such as commercial grade phosphoric acid or chromic acid. The oxy-mineral acid is dissolved in the colloidal solution in amounts varying between 1 and 10% by volume, with the optimum or preferred concentration of phosphoric acid being about 2-3% by volume thereof. The phosphoric acid used is readily available in concentrated aqueous solutions containing about 85% by weight phosphoric acid. A chromic acid aqueous solution is readily prepared from chromium trioxide (CrO_3) in flake form.

In order to further illustrate the present invention and to show a preferred embodiment thereof, the following specific examples are given:

Example I

An oil-free steel sheet (24 gauge) in roll form is mounted for continuous passage through a continuous galvanizing line and is first introduced into a preheated zone to raise the surface temperature to about 250-300° F. The sheet is then immediately passed through an electrostatic spray booth (Ransburg No. 1 system) equipped with four atomizing spray guns (Binks) which form a very fine spray of an aqueous colloidal solution of silica having phosphoric acid dissolved therein. Each of the spray guns is adjusted to discharge about 400 cc. of said colloidal solution per minute and thereby provide the said moving sheet with a coating having about 0.35 gram per square foot of surface area (dry weight basis).

The aqueous colloidal solution of silica and phosphoric acid is preferably prepared by diluting a concentrated (50% by weight silica) active colloidal silica sol (sold under the trade name "Nalcoag," by the National Aluminate Chemical Company) with water until the silica concentration of the colloidal solution is substantially 10% by weight. To the diluted silica solution is then added slowly with agitation concentrated commercial phosphoric acid (85% by weight phosphoric acid) until the composition contains three parts by volume phosphoric acid solution for every 97 parts of diluted colloidal silica solution.

The ferrous metal sheet having the colloidal solution coating thereon is then passed through a continuous in-line heat treating zone wherein the sheet is heated in a heat treating zone having a temperature up to about 1850° F. while in a reducing atmosphere containing about 75 percent hydrogen and about 25 percent nitrogen with a dew point of -10° F. After the sheet is thus treated, the sheet is immersed in a molten zinc bath which may or may not contain minor amounts of additives to improve the zinc coating. Thereafter, the zinc barrier coating is removed by applying an abrasive force thereto, as by contacting the zinc barrier coating with a rotating abrasive roll. If desired, the zinc repellent coating can be treated with a mild acid solution to facilitate removal thereof by the abrasive roll. The resulting sheet has only one side galvanized with the opposite side being completely free of zinc and in condition for receiving an enamel or paint finish.

Example II

The process of providing a zinc coating on one side only of a steel strip (24 gauge) was carried out in the same manner as in Example I except that in place of the aqueous colloidal solution of silica having phosphoric acid dissolved therein, the said 10% (by weight) silica colloidal solution has admixed therewith a chromic acid aqueous solution until the said colloidal coating solution comprises 10 percent by weight chromium trioxide (CrO_3). The chromic acid solution is prepared by dissolving chromium trioxide flakes (CrO_3) in water to provide a chromic acid aqueous solution.

It will be understood that other phosphoric acids and water soluble phosphate compounds and chromic acid compounds in addition to those employed in the specific examples can be used in the present invention. For example, phosphorous acid, hypophosphorous acid, metaphosphorous acid, hypophosphoric acid, metaphosphoric acid, pyrophosphoric acid, and orthophosphoric acid, in addition to the water soluble salts thereof, can be employed in providing the present zinc barrier coating composition. If necessary, concentrated phosphoric acid can be mixed with the other phosphoric or phosphorous acid compounds to increase the rate of reaction with the iron in the ferrous metal sheet.

It will also be understood that other refractory metal oxides, which are characterized as being unaffected by elevated temperatures and strongly reducing atmospheres,

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can be used in place of the silica, provided the said oxides are prepared in a finely divided form so as to remain in colloidal solution. For example, the silica employed preferably has a particle size of about 20 to 25 microns. Among the other refractory metal oxides which can be used in the present invention are aluminum oxide, chromium oxide, manganese oxide, magnesium oxide, and zirconium oxide. Also, combinations of the metal oxides, such as silica and manganese oxide, can also be used where, for cost reasons or otherwise, it might be desirable to reduce the concentration of one of the components of the colloidal solution or suspension. It is also within the purview of the present invention to form the refractory metal oxide in situ during the drying or heating step by using a refractory metal compound which is readily decomposed to the oxide.

Others may practice the invention in any of the numerous ways which are suggested to one skilled in the art, by this disclosure, and all such practice of invention are considered to be a part hereof which fall within the scope of the appended claims.

We claim:

1. A process of continuously producing a one side galvanized strip of ferrous metal while leaving the other side of said strip uncoated which comprises; continuously applying to only one side of a ferrous metal strip preheated to a temperature of between about 200° and 300° F. a thin continuous film consisting essentially of about 97 parts of an aqueous colloidal solution of silica having a silica concentration of about 10% by weight of said solution and about 3 parts of an aqueous phosphoric acid solution containing about 85% by weight phosphoric acid and allowing said film to dry to provide a thin continuous barrier coating before heating said strip to a substantially elevated temperature, continuously passing said strip through a treating zone having a temperature between about 1200° and 1900° F. before galvanizing, continuously immersing said strip in a galvanizing bath wherein only the other side of said strip is coated with zinc, and thereafter removing said barrier coating from said one side of said strip by applying an abrading force thereto without changing the physical characteristics of said strip to provide a one side galvanized ferrous metal strip.

2. A process as in claim 1, wherein said film is applied to said strip in an amount sufficient to form a dry barrier coating having a weight of between about .3 gram and .5 gram per square foot.

3. A process as in claim 1, wherein said silica has a maximum particle size of about 25 millimicrons.

4. A continuous process of producing a one side galvanized strip of ferrous metal while leaving the other side uncoated which comprises; continuously applying to only one side of a ferrous metal strip preheated to a temperature of between about 200° and 300° F. a thin continuous film consisting essentially of a colloidal solution of silica having a silica concentration of between about 5 to 20% by weight of said solution and having

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dissolved therein between about 2 and 3% by volume of an aqueous phosphoric acid solution containing 85% by weight phosphoric acid and allowing said film to dry to provide a thin continuous barrier coating before heating said strip to a substantially elevated temperature, continuously passing said strip through a treating zone having a temperature between about 1200° and 1900° F. before galvanizing, continuously immersing said strip in a galvanizing bath wherein only the other side of said strip is coated with zinc, and thereafter removing said barrier coating from said one side of said strip by applying an abrading force without changing the physical characteristics of said strip to provide a one side galvanized ferrous metal strip.

5. A continuous process of producing a one side galvanized strip of ferrous metal while leaving the other side uncoated which comprises; continuously applying to only one side of a ferrous metal strip preheated to a temperature of between about 200° and 300° F. a thin continuous film consisting essentially of a colloidal solution of at least one refractory metal oxide selected from the group consisting of silicon oxide, aluminum oxide, chromium oxide, manganese oxide, magnesium oxide, and zirconium oxide, said oxide being present in a concentration of between about 5 to 20% by weight of said solution, and containing a minor proportion of an aqueous solution of an oxy-mineral acid selected from the group consisting of phosphoric acid, phosphorous acid, and chromic acid, said acid solution when selected from phosphoric acid and phosphorous acid being between about 2 and 3% by volume of said colloidal solution and when chromic acid being between about 1 and 10% by volume of said colloidal solution, and allowing said film to dry to provide a thin continuous barrier coating before heating said strip to a substantially elevated temperature, continuously passing said strip through a treating zone having a temperature between about 1200° and 1900° F. before galvanizing, continuously immersing said strip in a galvanizing bath wherein only the other side of said strip is coated with zinc, and thereafter removing said barrier coating from said one side of said strip by applying an abrading force thereto without changing the physical characteristics of said strip to provide a one side galvanized ferrous metal strip.

6. A process as in claim 5 wherein said acid solution is an aqueous phosphoric acid solution containing about 85% by weight phosphoric acid and is present in an amount between about 2 and 3% by volume of said colloidal solution.

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