Sept. 29, 1970 W. WILSON, JR 3,530,569

METHOD OF COATING STEEL FOR PREVENTION OF CORROSION

Filed Sept. 27, 1967 3 Sheets-Sheet 1

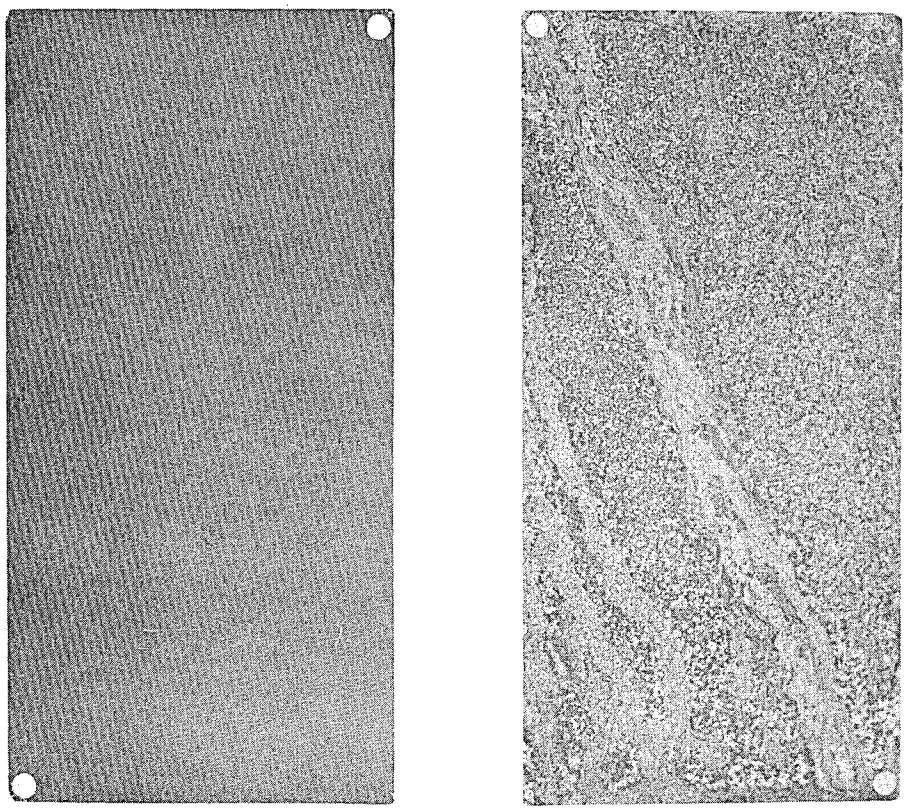


FIG. 1

METHOD OF COATING STEEL FOR PREVENTION OF CORROSION

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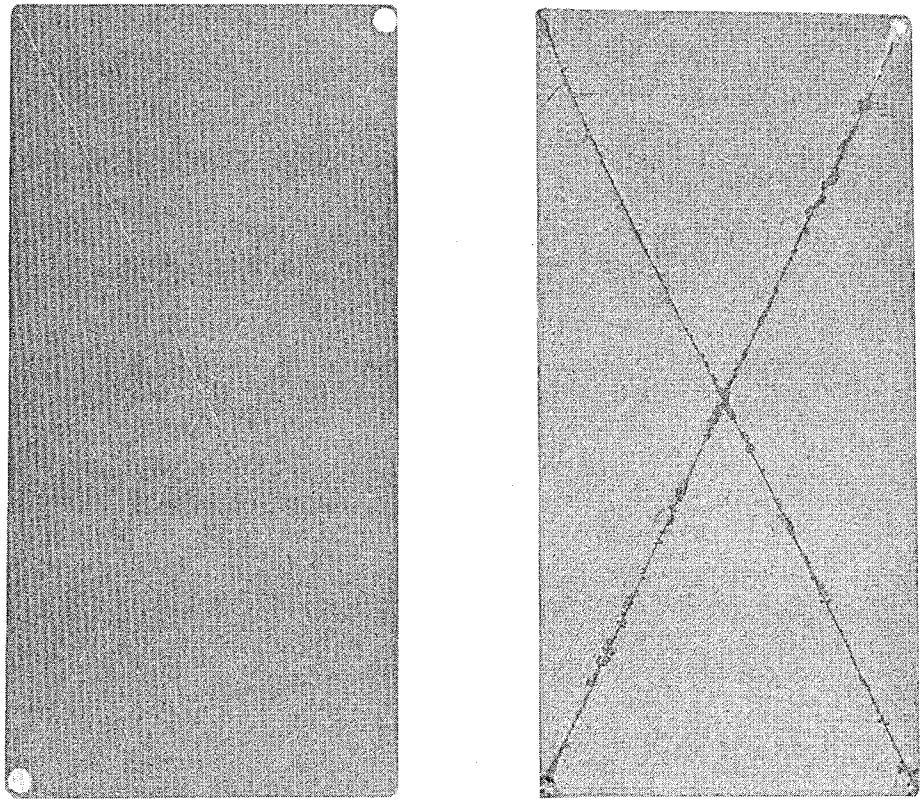


FIG. 2

METHOD OF COATING STEEL FOR PREVENTION OF CORROSION

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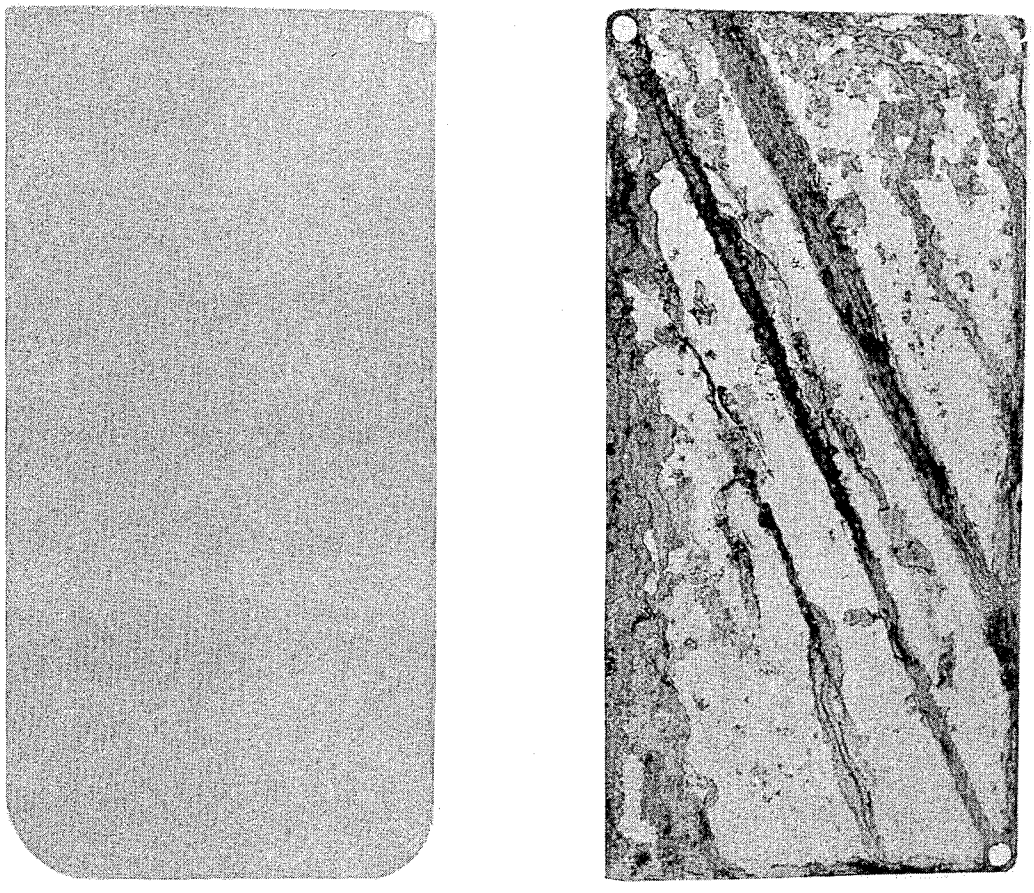


FIG. 3

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METHOD OF COATING STEEL FOR PREVENTION OF CORROSION

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U.S. Cl. 29—527.1 7 Claims

ABSTRACT OF THE DISCLOSURE

The corrosion of sheet steel is prevented by hot rolling the steel in an inert gas enclosure, cooling the steel to about 200° F. and thereafter temporarily protecting the steel from corrosion and the like by coating the cooled sheets of steel with a composition comprising 15 to 30% of a phenolic vinyl resin, 1 to 10% of metal chromate, 1 to 10% molybdenum disulphide, and a liquid vehicle. The coated steel is next cold-rolled and reduced, after which a coating of the same composition is applied to the surface of the steel to protect the same during the subsequent cold working operations such as stamping and cutting. The finally formed article is given a primer coating consisting of the same coating mixture without the molybdenum disulphide, with the article thereafter being covered by a conventional paint film.

BACKGROUND AND OBJECTS OF THE INVENTION

In the ordinary or conventional steel rolling operation wherein the steel is rolled in the ordinary atmosphere which contains oxygen and traces of water vapor and carbon dioxide, there is a continuous oxidation of the hot surface of the steel, which causes a loss of steel as rust or scale and necessitate subsequent pickling or acid treatment of the teel in order to remove the scale. This also requires the use of an alkaline bath to neutralize the acid deposits.

The rolled steel produced in the above manner is generally oiled for lubrication purposes. Oil is also used as a lubricant during the cold rolling operation for effecting a reduction in metal thickness. After annealing and tempering, the sheets must again be oiled or otherwise lubricated before they are sent to fabrication.

After fabrication, which may, for example, comprise stamping parts from the sheet steel, the material is washed in an alkaline bath and given several water rinses. The fabricated parts are then bathed in a phosphate solution, and washed again in water. After rinsing in chromic acid they are washed once more with fresh portions of water. The article is now primed and baked, which also involves several repetitions of cleaning and washing. The article then must be washed, for example in a phosphate primer, wet sanded, dry baked and then top coated with a resinous material which must have a sufficient degree of shear strength and flexibility in the cured condition. Following the coating operation, the article is baked. This involves a sand touch-up process and the application of as many as six top coats. As a matter of practice, as many as 35 baths, coats, etc., are employed in the typical automotive part production process. Nevertheless the final product exhibits little corrosion resistance under service use.

It is therefore an object of the present invention to eliminate a majority of the various operations above noted presently required and provide a new coating composition and method of applying the same to sheet steel. Specifically, in accordance with the present invention, a coating composition is applied to the sheet steel immediately following hot rolling, with such coating providing temporary protection during the subsequent and cold rolling operations and eliminating previously required cleaning

and washing steps preceding and following each of these operations. A second coating of the same composition is preferably applied after the cold rolling operations, with such coating serving similarly to temporarily protect the sheet steel and, in addition, to serve as a lubricator for subsequent cold working operations. In this regard, it may be desirable, as will be discussed in more detail hereinbelow, to apply a further coat of such composition just prior to such cold working operations as stamping to provide additional lubrication. A final coat is applied to the finally formed article, which final coat serves as a primer for conventional paint or the like and renders the article highly resistant to corrosion.

It should be noted that the idea of rolling steel in an inert atmosphere is not entirely new. However, the prior art proposals for rolling steel in an inert atmosphere required external cooling of the rolls by spraying water or other cooling liquid directly on the rolls, as well as cooling the inert gas or atmosphere. This has the disadvantage of contaminating the inert gas by the moisture resulting from the spray cooling of the rolls which, together with oxygen and other gases, defeats the purpose of the instant invention.

The prior art proposals for improving the surface finish of steel, incident to the working of the steel for effecting a reduction in cross-sectional area thereof, have used molybdenum disulphide, mostly in the form of a dry powder, to coat the steel prior to working. The molybdenum disulphide coating acts as an improved lubricant and surface treating composition. From tests made by applicant it is believed that the coating of such a material does not withstand salt spray tests of even 24 hours.

The function of the molybdenum disulphide in the instant invention is not solely that of a lubricant per se. It is combined, as will be seen below, with a phenolic resin and a metal chromate or mixture of metal chromates to form a ferrous-molybdenate-chromic sulphate ion complex on the steel surface. This provides a greatly superior adherence of the primer to the coated article without adversely affecting the corrosion protection afforded by the coating.

It is also conventional practice to surface treat steel, to provide a corrosion resistant coating thereon, by spraying or dipping with compositions containing chromic acid or metal chromates, including zinc chromate. Known methods of protecting steel against corrosion also include the application of organic coatings containing resinous materials, e.g. phenolic resins.

The applicant has discovered, however, that when zinc chromate or a metal chromate mixture including zinc chromate is combined with the phenolic resin in the maner described, greatly improved corrosion protection is afforded in comparison with phenolic resin alone. The applicant's resin-containing formulations are even further improved by the inclusion of molybdenum disulphide. The lubricating properties of molybdenum disulphide, in combination with the particular phenolic resin used, render the metal articles more adaptable to cold working operations, without detracting from the corrosion-resistant properties of the coating.

The practice of the applicant's method results in significent economies in manufacture, both in terms of time and expense. As stated, many of the conventional steps after hot rolling are made unnecessary, a large part of the chemical treatment and oiling being eliminated from operations, without detracting from the corrosion-resist-manufacture of sheet steel.

SUMMARY OF THE INVENTION

The invention is based on the discovery that following the hot rolling of sheet steel in an inert gas enclosure and allowing the temperature thereof to fall below

200° F., the application to the steel surface of a composition obtained by adding 1 to 10% of a mixture preferably comprising 50% zinc chromate and 50% lead silica chromate, 1 to 10% molybdenum disulphide and 15 to 30% of a suitably plasticized liquid phenolic resin to a liquid vehicle, provides a corrosion-inhibiting film on the article which is to be subsequently subjected to cold rolling.

The present preferred practice of making the sheet steel base includes hot rolling the sheet steel to an intermediate gage of 0.080" at a temperature of approximately 1800° F. The hot rolling is done in an inert gas atmosphere, such as argon gas. As the sheet is allowed to cool below 200° F., a coating having the above composition is applied by spraying or dipping, with such coating being cured at such temperature without additional heat being required. Immediately, or after prolonged storage, the coils of steel can be shipped to cold rolling mills where the steel is reduced to final gage.

A second coating of the coating composition of the present invention is applied after the cold rolling operation, after which the sheet steel is rendered temporarily resistant to corrosion and ready for further processing, normally comprising cold working operations such as stamping, cutting, welding or the like. An important feature of the invention is that the steel article can be welded without removing the protective coating. If desired, a further coat can be applied if the sheet steel is to be stamped, primarily to provide additional lubrication for the stamping operation.

After the final formation of the steel product, a final coat of the above composition, without the molybdenum disulphide, is applied to the article as a primer and anti-corrosion base for final painting.

It is estimated that by using the above-described steps as many as twenty operations can be eliminated from the present standard practices in processing steel.

DETAILED DESCRIPTION OF THE INVENTION

As stated in the summary above, the composition includes a phenolic vinyl resin which can be conveniently produced by condensing a phenol and formaldehyde in the presence of a catalyst such as morpholine. The mole ratio is about 0.75 mole of formaldehyde per 1 mole of phenol. The reaction is catalyzed with 1% morpholine based on the weight of the phenol. The condensation reaction is carried out at 60% C. and is terminated at the point where the resulting resin is soluble in alcohol.

Heretofore the poor flexibility characteristics of phenolic resin has limited considerably the scope of usefulness of such resins in coating compositions. The phenolic resins of the present invention are therefore plasticized with 10 to 20% polyvinyl butyl to give greater flexibility to the primer.

Substantially the same result as that set forth herein can be gained by the use of other plasticizers. Some of the lower polymers of acrylic acids form salts which are relatively flexible and these classes of resins may be advantageously employed to plasticizer more inflexible resins as exemplified by the hardened phenolic resins.

The condensation reaction product of a phenol and foremaldehyde which, when plasticized with polyvinyl butyral, or the like, yields the phenolic resin of this invention, is conveniently dissolved in a water-immiscible solvent. The solvent employed can be any organic solvent in which the phenolic resin is soluble. Commonly employed as solvents are toluene, xylenes, denatured ethyl alcohol, isopropanol, aromatic hydrocarbon mixtures, such as "Solvesso," and also various aliphatic, naphthenic and aromatic naphthas.

As noted, the phenolic resins can be conveniently produced by condensing a phenol with formaldehyde. Among phenols suitable for reaction with formaldehyde are the tri-functional phenols, that is phenols having at least 3 unsubstituted positions, illustrative of which are the following: phenol; meta-substituted phenols such as the alkylated phenols exemplary of which are m-cresol, m-ethyl phenol, m-n-propyl phenol, m-isopropyl phenol, m-sec.-butyl phenol, m-tert.-butyl phenol and the like; meta-substituted alkoxy phenols such as m-methoxy phenol, m-ethoxy phenol and the like; also suitable is resorcinol.

Formaldehyde in any of its available forms, i.e. formal and para-formaldehyde can be used.

In accordance with the present invention, 15 to 30% of a phenolic resin of the type described is combined with 1 to 10% of a metal chromate, or a mixture of metal chromate, and 1 to 10% molybdenum disulphide, all of which are dissolved in a water-immiscible liquid vehicle. The preferred mixture of metal chromates contains, for example, 50% zinc chromate and 50% lead silica chromate. When the coating composition is used as a primer, molybdenum disulphide is excluded therefrom, with the indicated ranges of the metal chromate or chromate and the resin remaining the same. The molybdenum disulphide is preferably of a semi-colloidal grain size, e.g. under 1 micron. The coating mixture also contains a thinner, such as any quickly evaporating alcohol, which is satisfactory for most applications of the coatings.

EXAMPLES

Various methods of applying the applicant's corrosion inhibiting coatings will be described below with reference to specific examples.

The sheet steel is first hot-rolled to an intermediate gage of 0.080" at a temperature of approximately 1800° F. To secure maximum protection, the steel should be hot-rolled in an inert gas enclosure. The flat-rolled product is cooled to about 200° F., also preferably in an inert gas atmosphere, and then coated with a coating mixture having the following formulation, with the percentages being indicated by weight:

	Percent
Molybdenum disulphide	2
Zinc chromate	5
Lead silica chromate	5
Plasticized phenolic resin	20
Mixture of 50% xylene and 50% "Solvesso"	68

The above mixture is preferably applied at about 200° F. by known dip, spray or roller coating techniques.

The steel, hot-rolled and provided with a protective coating as described, is rolled and reduced to final gage by one or more passes through a reducing stand or stands, in accordance with usual cold-rolling practice. After coming off the tempering rolls, the surface of the steel is sprayed, dipped or otherwise coated, using essentially the same formulation referred to above. The steel at this point is at a temperature determined by the tempering operation, which temperature is sufficiently high to cure the resin.

The coated sheets produced in the above manner showed no tendency to stick together during the recoiling. Moreover, the metal thus protectively coated is characterized by being highly resistant to corrosion and also unusually ductile, withstanding conventional cold working operations.

Although not absolutely necessary, superior results are obtained when an additional coating is applied, without the use of other lubricants, in advance of cold working operations as stamping, cutting, bending, pressing and the like.

The protective coatings are not damaged, nor is their adherence impaired, during such cold forming operations. As stated, the coated sheets present no problem of fragmentation of the coating and, consequently, even the freshly sheared surfaces of the steel are protected from corrosion.

For further protection and, if necessary, for providing the ultimate adhesion with overlying paints, a primer coating is applied to the finished article by dip, spray or

roller coating techniques. The following is representative of a primer coating of the present invention with the percentages again being by weight:

	Percent
Zinc chromate	5
Lead silica chromate	5
Plasticized phenolic resin	20
Mixture of 50% xylene and 50% "Solvesso"	70

The coated surface is baked for 20 minutes at approximately 350° F. to thermally cure the coating.

For some purposes the coating of the present invention need not have any additional top coating applied over it. However, where a top coating is applied, the improved paint adhesion of the present invention is obtained with any kind of paint, enamel, varnish, lacquer or other resin films. Acrylic enamels, melamine-formaldehyde paints, nitrocellulose lacquers, tung oil varnish are typical top coatings that are frequently used.

The resulting products exhibit a high degree of corrosion resistance when exposed to outdoor environments, under service use and under accelerated test conditions.

DESCRIPTION OF TESTS AS SHOWN IN PHOTOMICROGRAPHS

The tests were carried out on identical steel samples subjected to the operations referred to above. In each case, one sample was coated with the coating mixture that forms the subject of the present invention and one comparison sample was treated in accordance with conventional methods.

The results of the tests are illustrated in the accompanying figures, where

FIG. 1 is a photomicrograph showing a sample on the left coated with the coating mixture of the present invention on being subjected to hot rolling, and the sample on the right showing a conventional hot-rolled steel covered with scale which must be removed before cold rolling.

FIG. 2 is a photomicrograph showing the sample on the left coated with the resin primer of the present invention and an overlying coating, without signs of corrosion, and the sample at the right, provided with conventional paint, severely corroded on being subjected to scratch tests.

FIG. 3 is a photomicrograph showing the sample on the left coated with the resin primer of the present invention on a previously applied coating of the invention, and the sample at the right provided with a conventional primer coating applied over a conventional cold-worked article wherein the required oil layer was not removed.

CONCLUSIONS

Under present practice steel becomes rusted or corroded a number of times between the various forming and finishing operations. Repeated cleaning never completely eliminates the rust-producing ingredients. It is also well known that paint films over oxides have never eliminated rusting.

The coating process of the present invention secures maximum protection of the metal substrate from hot rolling to finished product. The coating produced in the manner described is not only a surface coating but a lubricant and a sealer. It has superior adhesion and paint bonding properties. It does not have to be removed for stamping, welding or like operations.

The composition and method of the invention having been thus described, modifications thereof will be apparent to those skilled in the art and the invention is to be considered limited in scope only by the scope of the hereinafter appended claims.

What is claimed is:

1. A process for preventing corrosion of sheet steel comprising the steps of

(a) hot rolling said sheet steel in an inert gas atmosphere,

(b) allowing the temperature of said sheet steel to fall below 200° F.,

(c) aplying to the surface of said sheet steel a composition comprising in admixture by weight 1–10% of a mixture consisting of zinc chromate and lead silica chromate, 1–10% molybdenum disulphide, and 15–30% of a plasticized phenolic resin dissolved in a water-immiscible liquid vehicle,

(d) cold rolling said coated sheet to effect a reduction of its thickness, and

(e) applying a second coat of said composition to the sheet steel surface after such cold rolling operation.

2. A process as defined in claim 1 wherein said phenolic resin is a condensation product of phenol and formaldehyde plasticized with 10–20% polyvinyl butyral.

3. A process as defined in claim 1 wherein said liquid vehicle is a water-immiscible solvent selected from the class consisting of toluene, xylene, denatured ethyl alcohol, isopropanol and aromatic hydrocarbon mixtures.

4. A process as defined in claim 3 wherein said liquid vehicle consists essentially of 50% xylene and 50% aromatic hydrocarbon mixture.

5. A process as defined in claim 1 further including the step of applying a further coat of said coating composition to the sheet steel surface just prior to cold working said sheet steel.

6. A process as defined in claim 1 wherein said mixture consists essentially of 50% zinc chromate and 50% lead silica chromate.

7. A process for forming a steel article of predetermined shape with a corrosion resistant coating thereon including the steps of

(a) hot rolling sheet steel in an inert gas atmosphere,

(b) allowing the temperature of said sheet steel to fall below 200° F.,

(c) applying to the surface of said sheet steel a composition comprising in admixture by weight 1–10% of a mixture of zinc chromate and lead silica chromate, 1–10% molybdenum disulphide and 15–30% of a plasticized phenolic resin, dissolved in a water-immiscible liquid vehicle,

(d) cold rolling said coated sheet steel to effect a reduction of its thickness,

(e) applying a second coating of said resinous coating composition to the sheet steel surface,

(f) cold working the coated sheet steel to form a metal article of predetermined shape,

(g) applying to the surface of said steel article a primer coating comprising in admixture about 1–10% of mixture consisting of zinc chromate and lead silica chromate, and 15–30% of a plasticized phenolic resin dissolved in a liquid vehicle,

(h) heating said steel article to about 350° F. to cure said primer coating thereon, and

(i) applying a top coating in the form of a standard paint over said primer coating and baking the final paint layer to obtain a fully cured product.

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