United States Patent Office 3,036,934
Patented May 29, 1962

3,036,934
COATED ARTICLE AND METHOD OF MAKING SAME

James B. Horton, Allentown, and Seymour C. Frye, Coopersburg, Pa., assignors to Bethlehem Steel Company, a corporation of Pennsylvania

No Drawing. Filed Mar. 17, 1958, Ser. No. 721,701
6 Claims. (Cl. 117—132)

This invention relates to the treatment of zinc and other non-ferrous surfaces, and more particularly to the coating of such surfaces with a composition which will inhibit the formation of white rust without materially changing the normal appearance of zinc surfaces.

One object of the invention is to apply a thin, substantially colorless, transparent passivating film on finished zinc surfaces so that the formation of white rust upon such surfaces is inhibited.

Another object of the invention is to apply a passivating film on zinc surfaces wherein there is substantially no attack of the zinc by the film forming solution.

A further object of the invention is to produce a passivating film for zinc surfaces which will not hinder subsequent operations, such as forming and painting.

In the manufacture of zinc-coated steel articles such as sheets or wire, coated by either the hot dip or electrolytic method, frequently a material develops on the zinc surface known as white rust. The white rust may appear when the zinc-coated article has been in transit or storage, in a wet or moist atmosphere, for as short a time as a single day. While the exact chemical composition of white rust is open to dispute among various authorities, it is believed to be principally a mixture of zinc hydroxide and zinc carbonate formed by the joint action of moisture and the carbon dioxide, or other corrosive gases, in the air. While the white rust itself does not necessarily promote additional corrosion on the zinc coating, it does mar the commercially pleasing appearance of the zinc surface, and in some cases may interfere with finishing operations.

In the prior treatment of zinc-coated articles, wherein attempts were made to inhibit the formation of white rust thereon, it is known that such articles have been immersed in a chromic acid solution of considerable strength, and then water rinsed. However, the use of strong chromic acid on zinc surfaces produces two serious defects; first, the zinc will in all likelihood be attacked by the chromic acid, and second, a yellow or brownish film appears on the zinc surface. Such treatment is also relatively ineffective in inhibiting white rust.

We have found a treatment for zinc surfaces wherein formation of white rust is effectively inhibited, and the zinc surface remains free of any visible chromic acid or chromate film. Our method comprises immersing the zinc surface in a water emulsion of an acrylic resin to which has been added a controlled amount of a dichromate. A thin film of acrylic resin and dichromate develops on the zinc sulfate. White rust does not appear on a zinc-surfaced article which has been treated by our method, even when the treated article is subsequently subjected to severely humid conditions. Furthermore, when the amount of dichromate in the film does not exceed about 8 mg./sq. ft. no noticeable coloration, or yellow stain, appears in the resultant film.

Our process may be used with equal efficiency on zinc surfaces of the hot-dipped, electroplated or sherardized type. Zince-coated articles of any configuration may be treated in which the zinc surface is readily exposed to the treating solution, the method being particularly adaptable to the treatment of galvanized sheet, strip or wire. Our treatment is useful also in the prevention of the white rust effect on cadmium and aluminum.

When treating zinc articles, on the surface of which

foreign matter has been allowed to accumulate after manufacture, it is of course necessary to clean the metal surface prior to introducing the article in the described emulsion. One of the advantages of our invention resides in the fact that the manufactured zinc article can be immersed in the treating solution right after the zinc coating has been applied, as an in-line operation, for in such case no cleaning of the zinc surface is required. Any zinc base metal coating, such as one formed from high purity zinc (99.9% Zn), technical grade, or high zinc alloys, is adaptable to the described passivating treatment.

The manner by which our invention may be performed is shown by the following illustrative examples:

Example I

Sixty parts of a water emulsion containing 46% of an interpolymer of acrylic resin, in this case the product known by the trade name of Rhoplex AC–33, are added to 940 parts of water, to which have been added 4.5 parts of ammonium dichromate. A zinc-coated article is immersed in the thus-prepared aqueous dispersion for a few seconds to wet the surface completely, and is then withdrawn, allowed to drain, and air dried. A thin film will be formed on the zinc article which will offer a high degree of protection against white rust. This film will have a weight of approximately 32 mg./cq. ft., or 27.5 mg./sq. ft. of acrylic resin and 4.5 mg./sq. ft. of dichromate.

Example II

Two hundred and fifty parts of the water emulsion in Example I are added to 750 parts of water, to which have been added 19 parts of ammonium dichromate. A zinc-coated article is immersed in the thus prepared aqueous dispersion for a few seconds to wet the surface completely, and is then withdrawn, passed through soft rubber squeegee rolls to remove the excess aqueous dispersion and then air dried, or furnace dried below 325° F. This gives a thin film, approximately 32 mg./sq. ft. in weight.

It is important that the amount of ammonium dichromate in the film be held within the limits of 2 to about 8 mg./sq. ft. of zinc surface. Below 2 mg., only partial protection against white rusting is obtained. Above 8 mg., excessive yellow color develops in the film due to the dichromate. We prefer to have from about 3 to 4.5 mg./sq. ft. of dichromate in the film for best performance against white rusting and for best appearance.

Comparable results can be obtained by substituting other soluble dichromates or chromates, such as those of sodium and potassium, for the ammonium dichromate.

The amount of acrylic resin in the film can be varied over broad limits without impairing the appearance or performance of the film. However, if the aqueous dispersion from which the film is formed is very dilute, for example less than 1% to 2% resin solids, in which case the film would have less than 15 mg. of resin per square foot of metal surface, the films are very thin and tend to show a bluish discoloration. We prefer, therefore, to have about 27 mg./sq. ft. of acrylic resin in the film, this being an economic amount which is free of any bluish discoloration.

The film itself may act as a very good paint base for either brush application or baked coatings, while the film appears to have no substantial effect on solderability. Where optimum painting properties are desired, greater amounts of acrylic resin are desirable in the film.

The high degree of resistance to white rusting conferred on galvanized sheet, by this invention, may be demonstrated as follows:

One foot square sheets of galvanized sheet were coated as in Example I. These were wetted with distilled water and stacked one upon another, weighted down and permitted to stand for eleven days. Examination after this

eleven day period showed that the sheets coated in the manner of Example I were still wet, but were completely free of white rusting. Plain galvanized sheet was 100% covered with white rust. Commercially treated galvanized sheets were also white rusted, in this case to the extent of 5% of the area of the sheet.

Similarly 48 inch wide sheets, having a length of 48 inches, coated according to Example II, were wetted with distilled water and stacked. No white rust was observed on these sheets after being yet for four weeks. Commercially treated material showed extensive white rusting in this time.

Our film-forming method probably has as its chief application, the treatment of zinc-coated steel strip. Our method is quite useful in the treatment of zinc-coated strip made by the hot dip method, for the film may be applied to the strip as the strip leaves the zinc bath without any preliminary treatment of the strip, other than to cool it to room temperature to facilitate the passivating operation.

In applying our treatment to hot-dip coated strip, the strip, as it leaves the zinc bath, is run through a water bath to cool the strip below about 80° F. As the strip leaves the cooling tank, it is rinsed with clean water and then run directly into the treatment tank a few seconds, or long enough to wet the strip uniformly with treatment solution. The strip, with its newly-formed, wet protective film, is withdrawn from the bath in a vertical direction, and it passes through a pair of rubber squeegee rolls, and then through an air drier.

The acrylic resin, in the form of a water emulsion, may be a polymer or an interpolymer. Water-insoluble polymerized esters of acrylic acid, such as methyl acrylate, ethyl acrylate and butyl acrylate, or their homologs, such as methyl, ethyl and butyl methacrylate, as well as esters of certain higher alcohols, may be used as the resin. Mixtures and products of interpolymerization of the foregoing compounds may be used as well.

One type of acrylic resin in the form of an interpolymer which is useful in our method, can be made by emulsifying, in balanced proportions, in an aqueous medium containing 1 to 12% of a water soluble non-ionic polyethoxyethanol emulsifying agent, the following ingredients:

(A) A polymerizable, α,β-unsaturated monovinylidene carboxylic acid, including acrylic, methacrylic and itaconic acids, and water soluble salts thereof,

(B) At least one polymerizable neutral monomeric monovinylidene ester which by itself forms soft polymers and which is selected from the class consisting of esters of acrylic acid and primary alkanols of 1 to 18 carbon atoms, esters of acrylic acid and secondary alkanols of 1 to 18 carbon atoms, esters of methacrylic acid and pirmary alkanols of 5 to 18 carbon atoms, and esters of methacrylic acid and secondary alkanols of 5 to 18 carbon atoms, and

(C) At least one polymerizable monovinylidene compound, which by itself forms a hard polymer and which is selected from the class consisting of alkyl methacrylates in which the alkyl group has 1 to 4 carbon atoms, tert-amyl methacrylate, tert-butyl acrylate, tert-amyl acrylate, cyclohexyl acrylate and cyclohexyl methacrylate, the carboxylate units constituting between 0.5% and 2.5% of the interpolymer, the ratio of parts from said ester to parts from said compound being between 9:1 to 1:20.

Other emulsifying agents which may be used are ethylene oxide derivatives of long-chain carboxylic acids.

As polymerization catalysts, one or more inorganic or organic peroxides may be used as well as ammonium, or alkali metal persulfates, or perborates.

In order to effect interpolymerization at a temperature below that at which coagulation might occur, it is desirable to activate the catalyst. This may be done by using a system in which a reducing agent is present in addition to the catalyst. Examples of reducing agents which may be used are sodium hydrosulfite, potassium sulfite and calcium bisulfite.

The acrylic resin emulsion which we prefer to use is one which results in a dispersion of an interpolymer of ethyl acrylate, methyl methacrylate, and methacrylic acid. This resin is made by first preparing a solution of 25 parts of an octylphenoxypolyethoxyethanol, having about 30 ether groups, in 1000 parts of water. A mixture is made of 280 parts of ethyl acrylate, 140 parts of methyl methacrylate, and 5.5 parts of methacrylic acid. This mixture is added, with stirring, to the solution and the resulting mixture cooled to 15° C. A solution of 0.5 part of ammonium persulfate in 1.5 parts of water is then added, followed by addition of a solution of 0.6 part of sodium hydrosulfite in six parts of water. Stirring is continued, and the temperature rises to about 65° C. in approximately one-half hour, after which the mixture is cooled to about 15° C. There are now added 35 parts of octylphenoxypolyethoxyethanol (the same compound as used in preparing the water solution), 315 parts of ethyl acrylate, 155 parts of methyl methacrylate, 6 parts of methacrylic acid, a solution of 0.6 part of ammonium persulfate in 1.5 parts of water, and 0.8 part of sodium hydrosulfite in six parts of water. The temperature of the mixture rises, again reaching a maximum of approximately 65° C. Stirring is continued for an hour and the batch cooled to 30° C. While the batch is cooling, ammonium hydroxide solution is added until a pH of 9.5 is reached. The resultant resin is then made into a water emulsion and mixed with the required amount of dichromate or chromate.

We claim:

1. The method of forming a protective film on a metal surface which comprises applying to an article having a metal surface of the group consisting of zinc, cadmium and aluminum a water mixture consisting essentially of a water emulsion of an acrylic resin and a soluble compound of the group consisting of chromates and dichromates and drying and thereby forming a transparent white rust-preventive film of acrylic resin and said soluble compound containing not less than 10 mg. of resin and from 2 mg. to 8 mg. of said soluble compound per square foot of metal surface.

2. The method of forming a protective film on a metal surface which comprises applying to an article having a metal surface of the group consisting of zinc, cadmium and aluminum a water mixture consisting essentially of a water emulsion of an acrylic resin in the form of one of the group consisting of polymers, interpolymers and mixtures of polymers and a soluble compound of the group consisting of chromates and dichromates and drying and thereby forming a transparent white rust-preventive film of acrylic resin and said soluble compound, said film containing not less than 10 mg. of resin and from 2 mg. to 8 mg. of said soluble compound per square foot of metal surface.

3. The method of forming a protective film on a metal surface which comprises applying to an article having a metal surface of the group consisting of zinc, cadmium and aluminum a water mixture consisting essentially of a water emulsion of an acrylic resin in the form of an interpolymer of an acrylate, methacrylate and a monovinylidene carboxylic acid and ammonium dichromate and drying and thereby forming a transparent white rust-preventive acrylic resin-dichromate film containing not less than 10 mg. of resin and from 2 mg. to 8 mg. of said dichromate per square foot of metal surface.

4. The method of forming a protective film on a metal surface which comprises applying to an article having a metal surface of the group consisting of zinc, cadmium and aluminum a water mixture consisting essentially of a water emulsion of an acrylic resin in the form of an interpolymer of ethyl acrylate, methyl methacrylate and methacrylic acid and ammonium dichromate and drying and thereby forming a transparent white rust-preventive acrylic resin-dichromate film containing not less than 10 mg. of resin and from 2 mg. to 8 mg. of said dichromate per square foot of metal surface.

5. The method of forming a protective film on a metal surface which comprises applying to an article having a zinc surface a water mixture consisting essentially of a water emulsion of an acrylic resin in the form of an interpolymer of ethyl acrylate, methyl methacrylate and methacrylic acid and ammonium dichromate and drying and thereby forming a transparent white rust-preventive acrylic resin-dichromate film containing not less than 10 mg. of resin and from 2 mg. to 8 mg. of said dichromate per square foot of metal surface.

6. A zinc-surfaced article having a transparent protective film, said film consisting essentially of not less than 10 mg. of an acrylic resin and from 2 mg. to 8 mg. of ammonium dichromate per square foot of metal surface.

References Cited in the file of this patent

UNITED STATES PATENTS

2,481,323	McCoy	Sept. 6, 1949
2,535,794	Hempel	Dec. 26, 1950
2,760,886	Prentiss et al.	Aug. 28, 1956
2,902,390	Bell	Sept. 1, 1959

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,036,934 May 29, 1962

James B. Horton et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 57, for "sulfate" read -- surface --; line 66, for "Zince-coated" read -- Zinc-coated --; column 2, line 26, for "32 mg./cq. ft." read -- 32 mg./sq. ft. --; column 3, line 10, for "yet" read -- wet --; line 51, for "pirmary" read -- primary --.

Signed and sealed this 4th day of September 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents