United States Patent [19]

Palisin, Jr.

[11] **3,790,355**

[45] **Feb. 5, 1974**

[54] **COATED METAL ARTICLE AND METHOD OF COATING**

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[22] Filed: **Nov. 18, 1971**

[21] Appl. No.: **200,224**

Related U.S. Application Data

[63] Continuation of Ser. No. 887,397, Dec. 22, 1969, abandoned.

[52] **U.S. Cl.**..... **29/195**, 204/38 E, 148/6.21

[51] **Int. Cl.**..... **B23p 3/00**, C23c 7/26

[58] **Field of Search**..... 204/38 S, 38 E, 38 R, 37; 117/49, 71, 72, 75; 148/6.21; 29/195

[56] **References Cited**

UNITED STATES PATENTS

3,526,486 9/1970 Smith et al. ..... 204/38 S

2,746,915 5/1956 Giesker et al..... 204/56 R

OTHER PUBLICATIONS

Modern Electroplating by Lowenheim, 1963 page 425

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Assistant Examiner—R. L. Andrews
Attorney, Agent, or Firm—Blythe D. Watts et al.

[57] **ABSTRACT**

A metal article having a corrosion-resistant, adherent surface-covering, hydrophobic, thermosetting polymer film.

A method of coating a metal article to make it resistant to corrosion comprising the steps of forming a metallic chromating surface thereof, applying a hydrophobic, thermosetting polymer to a surface thereof and heating the article at a temperature of at least about 300° F. to convert the polymer into a hard, adherent film.

3 Claims, No Drawings

COATED METAL ARTICLE AND METHOD OF COATING

This application is a continuation of my pending application Ser. No. 887,397, filed Dec. 22, 1969 and now abandoned.

BACKGROUND

The prior art most nearly pertinent to this invention and known to me is U. S. Pat. Nos. 3,031,333 and 3,556,869. These patents disclose processes which were not devised to, and would not, produce articles which would meet the severe service conditions met by articles produced by the present invention.

SUMMARY

The present invention provides extremely corrosion-resistant coverings for, and a method of producing such coverings on, metal articles. Such articles may be composed of iron, steel, aluminum, zinc, bronze or copper alloys. The method consists of chromating a surface of the article or of a layer of metal on the article and covering the chromated surface with a heat hardened film of a hydrophobic, thermosetting polymer.

According to the present invention, metal articles when composed of aluminum, cast iron, malleable iron, steel, zinc, bronze or copper alloy are cleaned in any suitable conventional manner, for example, by tumbling the article in caustic soda or by passing an electric current through such a solution with the metal article constituting the anode. After such cleaning, the article is rinsed in cold water, is then dipped in a dilute acid solution, and again rinsed in cold water. When the article is composed of ferrous metal, aluminum, bronze or copper alloys, a 10 percent sulfuric acid solution or a 25 percent hydrochloric solution is sufficient to neutralize the caustic soda. When the article is composed of zinc, a very weak acid solution is used.

In certain instances where even better cleaning of a ferrous metal article is desired or where its surface is to be activated, the article may be reversely treated in an alkaline cyanide bath, i.e., by passing a current through the bath for about 30 seconds while the article is the anode in the circuit and then reversing the current flow for about 30 seconds while the article is the cathode in the circuit. Following this reverse treatment, the article is rinsed in water if it is to be plated promptly thereafter, or it may be rinsed in a dilute sodium cyanide solution to prevent rusting when it is not to be plated promptly.

The thus cleaned metal article composed of iron, bronze or copper alloys is then electrolytically plated in a conventional manner, as by making it the cathode in an electrolytic bath. Preferably cadmium or zinc is the coating metal and either may be deposited on the article from a conventional bath such, for example, as cadmium cyanide or zinc cyanide. Nickel and chromium may also be used as coating metals. Any suitable conventional bath composition may be used for depositing either of these metals, for example, a nickel sulfate bath may serve for the chromium deposition. A current density of about 10 amperes per square foot is suitable and the plating action is continued until between about 0.0002 inch to 0.005 inch layer of the base metal has been deposited on the article.

On aluminum, a layer of another metal such, for example, as copper may be applied before the coating of cadmium or zinc is applied. When the article is composed of zinc, a coating of cadmium, zinc, nickel or chromium is deposited on the surface thereof. After such deposition, the article is rinsed with water and then is rinsed in dilute aqueous nitric acid.

Following the electroplating and rinsing operations, the surface of the coating metal, or of the article if composed of zinc, is chromated. This chromating step consists of treating the cadmium or zinc in such a manner as to convert the metal surface thereof into a clear, stain-free finish with corrosion While properties. Whiel various substances may be used for such chromating action, I prefer to use a chromating material consisting of about 90 percent trioxide and about 10 percent sodium bisulfate dissolved in water, the concentration of this chromating material being between about 6 oz. and about 16 oz. per gallon of water. The article to be chromated is thoroughly rinsed to free it from alkalis and is then dipped into the chromating solution for between about 10 seconds and about 25 seconds. Preferably that solution should be at a temperature between about 65° and about 95° F. Upon removing the article from the chromating bath, it is thoroughly rinsed with water.

The chromated surface on the metal article is then covered with hydrophobic, thermosetting polymer and the article is heated at a temperature between about 300° and about 400° F. until the polymer has been baked and has become a hard film. The heating time depends somewhat on the thickness of the metal article and its variations in thickness. Preferably the heating is continued long enough for all parts of the metal article to be brought within the above specified range of temperatures.

A preferred hydrophobic thermosetting film-forming polymer composition is as follows:

Hexamethoxy methyl melamine	about 15.3%
Ethyl Acrylate	about 16.0%
Methacrylic Acid	about 1.0%
Chromium Trioxide	about 0.1%
Water	about 67.6%

Other film-forming compositions which may be used include the hexamethoxy methyl melamine of the foregoing composition with equivalents of the other ingredients thereof.

The above preferred film-forming composition has given new and unexpected results in terms of corrosion prevention. For example, the films formed by this invention had a pencil hardness of H-3, excellent flexibility, abrasion resistance and adhesion and evidenced no degradation after being exposed for 100 hours to humidity and to salt spray conditions. In contrast therewith, films composed of epoxy solvent lacquer had a pencil hardness of H, good flexibility and abrasion resistance and fair adhesion and were affected when exposed for 100 hours to humidity or to salt spray.

Films composed of nitrocellulose had a pencil hardness of H, poor flexibility and abrasion resistance, fair adhesion and were affected when exposed for 25 hours to humidity or salt spray.

Having thus described this invention in such full, clear, concise and exact terms as to enable any person skilled in the art to which it pertains to make and use the same, and having set forth the best mode contemplated of carrying out this invention, I state that the subject matter which I regard as being my invention is particularly pointed out and distinctly claimed in what is claimed, it being understood that equivalents or modifications of, or substitutions for, parts of the above spe-

cifically described embodiments of the invention may be made without departing from the scope of the invention as set forth in what is claimed.

What is claimed is:

1. The method of making a metal article resistant to corrosion which comprises the steps of electroplating, with a metal selected from the group of metals consisting of zinc, cadmium, nickel and chromium, a surface of an article composed of metal selected from the group of metals consisting of aluminum, iron, zinc, brass and copper alloys, chromating the electroplated surface by treating it for between about 15 seconds and about 25 seconds with water containing between about 6 oz. and about 16 oz. per gallon of a liquid composed of about 90 percent of CrO_3 and about 10 percent of sodium bisulphate, rinsing the resulting chromated surface with water, covering the said chromated surface with hydrophobic thermosetting polymer and heating said article to above about 300° F. to convert the polymer into a hard film.

2. A metal article composed of a metal selected from the group of metals consisting of aluminum, iron, brass, copper alloys and zinc, having an electrodeposited coating on a surface thereof selected from the group of metals consisting of zinc, cadmium, nickel and chromium, said coating having a chromated surface formed by being treated for between about 15 seconds and about 25 seconds with water containing between about 6 oz. and about 16 oz. per gallon of a liquid composed of about 90 percent of CrO_3 and about 10 percent of sodium bisulphate followed by rinsing the chromated surface with water, and a film of hydrophobic thermosetting polymer adhering to said chromated surface, which film has been hardened by heating the article to above about 300° F.

3. A method of protecting a metallic surface to render it highly resistant to salt spray corrosion and to abrasion, wherein the surface is composed of a metal selected from the group of metals consisting of aluminum, iron, zinc, brass and copper alloys, comprising the steps of:

a. electroplating the surface with a metal selected from the group of metals consisting of zinc, cadmium, nickel and chromium;

b. chromating the electroplated surface to produce a clear, blemish free colorless chromate coating thereon by treating it for between about 15 seconds and about 25 seconds with water containing between about 6 oz. and about 16 oz. per gallon of a liquid composed of about 90 percent of CrO_3 and about 10 percent sodium bisulphate;

c. rinsing the chromated surface with water to flush away chromating solution remaining thereon;

d. coating the chromated surface with a transparent colorless hydrophobic thermosetting polymer; and

e. heating the article to above about 300° F to convert the polymer to a hard, colorless transparent film thereby providing the surface with a blemish free corrosion resistant finish.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,790,355

DATED : February 5, 1974

INVENTOR(S) : Stephen P. Palisin, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 10, after "corrosion" insert

- - resisting - -

Signed and Sealed this

sixteenth Day of *September 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,790,355 Dated February 5, 1974

Inventor(s) Stephen P. Palisin, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 60, after "the" insert -- nickel deposition and a chromic acid bath may serve for the --. Column 2, line 10, "Whiel" should read -- While --; same line 10, cancel "While" Column 2, line 13, after the first occurrence of the word "percent" insert -- chromium --.

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
★ U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.