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[73] Assignee **The Dow Chemical Company**
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[54] **METHOD OF PROTECTION OF METAL**
SURFACES FROM CORROSION
8 Claims, No Drawings
[52] U.S. Cl..... **148/6.15 R,**
106/14, 252/389
[51] Int. Cl..... **C23f 7/00**
[50] Field of Search..... **148/6.15;**
106/14; 260/606.5, 961; 252/137, 389

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Primary Examiner—Ralph S. Kendall
Attorneys—Griswold and Burdick, William R. Norris and
Lloyd S. Jowanovitz

ABSTRACT: The present invention is a method of protecting metal surfaces from corrosion which comprises contacting the metal with an organo phosphonic, phosphonous or phosphinic acid.

METHOD OF PROTECTION OF METAL SURFACES FROM CORROSION

BACKGROUND OF THE INVENTION

Thin metal surfaces are reactive and require protection from water corrosion and waterborne corrosive agents. The surface of plastic which has been coated with a thin metal is especially susceptible to corrosion. Aluminum has been found to be an effective coating for polyester plastic films. However, the aforementioned difficulties are quite apparent when aluminum is applied to the polyester film in very thin layers. Present methods of protecting such films include anodization and overlacquering or laminating the aluminum surface with a tough corrosion resistant plastic.

It is known that phosphoric acid may be used to form a corrosion resistant coating on metal surfaces. This method of coating metal surfaces, commonly known as Parkerizing, involves coating the metal by dipping or spraying it with a solution of phosphoric acid. The process is normally used to protect massive forms of metal and coatings having a thickness of from 0.00015 to 0.0003 inch are normally applied to effectively protect the metal substrate. Such a method would not be readily applicable to thin metal films due to the excessive thickness of the coating. The process also employs reagents which would strip the polyester film of its aluminum coating.

U.S. Pat. No. 3,351,558 teaches the use of a phosphonate in combination with a detergency builder. This composition is taught to have the effect of reducing the corrosiveness of the detergency builder by the in situ formation of a protective coating on the metal surface, and is intended for use in aqueous solution wherein the acid salt acts as the corrosion inhibitor.

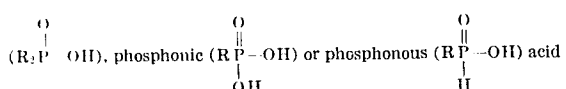
It would be desirable and it is an object of the present invention to provide a method for inhibiting corrosion of metal surfaces.

It is a further object to provide such a method which may readily be carried out without the use of specialized equipment.

An additional object is to provide such a method which will result in a coating which is conveniently applied to thin metal films.

SUMMARY OF THE INVENTION

The present invention is a method for protecting metal surfaces and applying protective coatings to metal surfaces. The method involves contacting the metal with a solution of an



The R group attached to the acid radical is a hydrophobic organic moiety having from one to about 24 carbon atoms. Examples of R groups are a straight or branched chain, substituted or unsubstituted alkyl, aryl, alkaryl or arylalkyl containing from one to about 24 atoms.

Unexpectedly, the acid is much superior to the acid salts of U.S. Pat. No. 3,351,558 in providing corrosion protection to metal surfaces, especially metal surfaces which readily form oxide surface coatings. Particularly useful results are achieved in the instance of thin metal films.

DESCRIPTION OF PREFERRED EMBODIMENTS

While the present invention is not premised on an explanation of its underlying theory, it is believed that the corrosion

inhibition of the process is provided by formation of a hydrolysis resistant M—O—P bond between the metal and the acid, thus setting up a layer of organic moieties of the acid on the metal surface. The layer effectively keeps water and waterborne corrosives out of contact with the metal surface. The protection increases as the length of the carbon chain of the organic moiety increases. However, as the carbon chain becomes exceedingly long, inhibition of corrosion becomes less effective and a less protective coating is provided. Acids in which the organic moiety contains from one to about 24 carbon atoms are preferred. Acids having 10 to 14 carbon atoms in the organic moiety provide especially effective protection, with the acids having 12 carbon atoms being the most preferred.

Phosphonic acids have been found to provide protection superior to that of the phosphinic and phosphonous acid and are the preferred acids for the practice of the present invention.

The organic moiety may be substituted or unsubstituted. Substituents which may form a part of the organic moiety are preferably those which do not significantly decrease hydrophobicity. Fluorine, chlorine, bromine or aryl are preferred. Other substituents include cyano, mercapto and hydroxyl groups.

The invention is normally practiced by practicing a dilute solution of the acid to be applied and dipping the metal into it. Polar organic liquids such as acetone, tetrahydrofuran and the lower ethers, i.e., those ethers containing from two to 10 carbon atoms, are convenient solvents for the acids used in the present method. Water and nonpolar organic solvents may also be used although the acids are somewhat less soluble in these solvents. When water is employed as the solvent, the pH of the solution should be less than 7. A dipping period of from about 10 to 15 seconds is sufficient to impart a protective coating to the metal. Repeated dipping may be employed to provide a more substantial protective coating. The coated metal may then be washed with the solvent and allowed to dry. The metal may be contacted with the acid solution by other means such as spraying, brushing or roll coating. The protective coatings may also be applied in situ such as, for example, by introducing the acid to a fluid contained in a metal vessel. By such addition, the sides of the vessel will be protected from corrosion.

The method can be used to coat any of the metals which form insoluble phosphates. The common construction metals such as iron, nickel, copper, zinc, lead, tin, magnesium, and aluminum may be coated by the present method. The method is especially effective for coating thin sheets of aluminum.

The following examples will serve to more fully illustrate the present invention.

EXAMPLES 1-9

Solutions of acids were prepared by dissolving 0.1 gram of the acid in 100 milliliters of solvent, Examples 1-5 used tetrahydrofuran and examples 6-9 used acetone as the solvent. Aluminum coated polyethylene terephthalate film was dipped into the solution for a period of from about 10 to 15 seconds. In each case the film was cut in half before treatment with the acid solution and one-half left untreated as a control. After the film which had been treated was allowed to dry and washed with acetone to remove unreacted acid, it and the control sample were immersed in boiling deionized water and the time required for removal of the metal coating was visually observed. Table I represents the results of these tests for a number of acids.

TABLE I

Ex. No.	Acid	Formula	Time required to —	
			Demetalize treated film	Demetalize untreated film
1	Methyl phosphonic acid	$ \begin{array}{c} O \\ \\ CH_3P-OH \\ \\ OH \end{array} $	1 min. 42 sec.	1 min. 3 sec.

Ex. No.	Acid	Formula	Time required to	
			Demetalize treated film	Demetalize untreated film
2	Phenyl phosphonic acid...	$\text{C}_6\text{H}_5\text{P} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \\ \searrow \text{OH} \end{array}$	1 min. 12 sec.	1 min. 3 sec.
3	n-Octyl phosphonic acid	$\text{C}_8\text{H}_{17}\text{P} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \\ \searrow \text{OH} \end{array}$	2 min. 7 sec.	1 min. 3 sec.
4	n-Dodecyl ¹ phosphonic acid	$\text{C}_{12}\text{H}_{25}\text{P} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \\ \searrow \text{OH} \end{array}$	16 min. 0 sec.	1 min. 3 sec.
5	n-Octadecyl phosphonic acid	$\text{C}_{18}\text{H}_{37}\text{P} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \\ \searrow \text{OH} \end{array}$	3 min. 0 sec.	1 min. 3 sec.
6	Octyl phosphinic acid	$(\text{C}_8\text{H}_{17})_2\text{P} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array}$	1 min. 30 sec.	54 sec.
7	3,3,3-trifluoropropyl phosphinic acid ...	$(\text{CF}_3)(\text{CH}_2)_2\text{P} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array}$	1 min. 20 sec.	54 sec.
8	Phenyl phosphonous acid.	$\text{C}_6\text{H}_5\text{P} \begin{array}{l} \nearrow \text{H} \\ \searrow \text{O} \\ \searrow \text{OH} \end{array}$	1 min. 58 sec.	54 sec.
9	n-Dodecyl ¹ phosphonic acid ...	$\text{C}_{12}\text{H}_{25}\text{P} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \\ \searrow \text{OH} \end{array}$	16 min. 0 sec.	36 sec.

¹ When dodecyl phosphonic acid was used, no demetalization had occurred in 16 minutes, at which time the experiment was stopped.

EXAMPLES 10-13

In order to compare the effectiveness of the present method, wherein the solvent was either aqueous or nonaqueous, and the method of providing protection by using the aqueous solution of the acid salt, the following experiment was conducted:

A piece of aluminum coated polyethylene terephthalate film was cut into four pieces. The pieces were designated A, B, C and D and treated as follows:

10. A was dipped in a solution of 0.1 gram dodecyl phosphonic acid in 100 milliliters of acetone for 30 seconds.

11. B was dipped in a solution of 0.1 gram of the sodium salt of dodecyl phosphonic acid in 100 milliliters of boiling water for 30 seconds.

12. C was dipped in a solution of 0.1 gram of dodecyl phosphonic acid in 100 milliliters of water for 30 seconds. The water was heated to its boiling point in order to get the acid into solution.

13. D was left untreated and used as a control.

Each of the treated samples was washed with the acid solvent and allowed to dry after treatment. Each sample was dipped into boiling deionized water and the time required for the metal coating to be removed was visually observed. Table II represents the results of these tests.

TABLE II

Sample	Time required for demetalization
A	330 seconds
B	62 seconds
C	160 seconds
D	55 seconds

The above data indicate that the sample treated with a nonaqueous solution of the acid took more than twice as long

to demetalize than did that treated with a water solution of the acid. The acid salt imparted some protection to the metal surface but considerably less than did the unaltered acid.

In a manner similar to that of examples I and II protective coatings can be applied to the surfaces of metals other than aluminum, such as for example, iron, nickel, copper, zinc, lead, tin or magnesium.

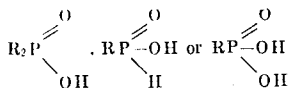
The invention is practiced in a manner similar to that of the above examples wherein the acid employed is characterized of the formula

and R is straight or branched chain, substituted or unsubstituted, pentyl, heptyl, nonyl, undecyl, tridecyl, pentadecyl, nonadecyl, docosyl and tetracosyl. However, R is selected so that the total number of carbon atoms in the molecule does not exceed about 24.

Specific examples of such acids are n-pentyl phosphonic acid, (p-t-butylstyryl) phosphonic acid, hexyl phosphonic acid, n-heptyl phosphonic acid, 3-heptyl phosphonic acid, octyl phosphonic acid, n-nonyl phosphonic acid 4-nonyl phosphonic acid, n-undecyl phosphonic acid, n-pentadecyl phosphonic acid, n-nonadecyl phosphonic acid, n-tetracosyl phosphonic acid, dipentyl phosphonic acid, heptyl butyl phosphonic acid, dinonyl phosphonic acid, benzyl butyl phosphonic acid, benzyl heptyl phosphonic acid, benzyl hexyl phosphonic acid, dibenzyl phosphonic acid, di-n-butyl phosphonic acid, diundecyl phosphonic acid, didocyl phosphonic acid, dihexyl phosphonic acid, di-n-octyl phosphonic acid, bis(2-ethyl hexyl) phosphonic acid, butyl phenyl phosphonic acid, decyl ethyl phosphonic acid, di-t-butyl phosphonic acid, didecyl phosphonic acid, diisobutyl phosphonic acid, diisopropyl phosphonic acid, di-n-propyl phosphonic acid, ethyl isopropyl phosphonic acid, isopropyl phenyl phosphonic acid, n-pentyl phosphonous acid, 6-undecyl phosphonous acid, n-tridecyl phosphonous

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1. A method for protecting thin metal films not adaptable to treatment with phosphoric acid from corrosion which comprises contacting the metal film with a polar organic liquid solution of an acid characterized by the formula



wherein R is a straight or branched chain, hydrophobic, substituted or unsubstituted alkyl, aryl, alkaryl or arylalkyl group containing from 10 to 14 carbon atoms; thereby setting up a layer of organic moieties of the acid on the metal surface.

2. The method of claim 1 wherein R is an alkyl containing from 10 to 14 carbon atoms.

3. The method of claim 2 wherein the acid is characterized by the formula

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4. The method of claim 3 wherein R is an alkyl containing 12 carbon atoms.

5. The method of claim 1 wherein the solvent is acetone, tetrahydrofuran or a lower ether.

6. The method of claim 1 wherein the metal is selected from the group consisting of iron, nickel, copper, zinc, lead, tin, magnesium or aluminum.

7. The method of claim 1 wherein the metal is dipped into the acid solution, rinsed with the acid solvent and allowed to dry.

8. The method of claim 1 wherein the metal film is aluminum.

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CERTIFICATE OF CORRECTION

Patent No. 3,630,790 Dated 28 December 1971

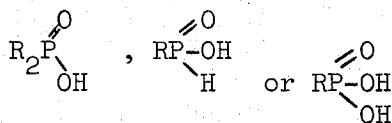
Inventor(s) Donald L. Schmidt and William J. Leahy

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 47, insert --organo phosphinic-- at the end of the line following "an"; line 57 insert --carbon-- between "24" and "atoms.".

Column 2, line 25, delete "practices by" and insert --by preparing-- between "practiced" and "a dilute".

Column 4, line 46, delete "of" and insert --by--; in the blank space between lines 48 and 53 insert the following formulae:



Column 4, line 76, insert the following after the last word in the column, "phosphonous":

-- acid, 10-nonadecyl phosphonous acid, n-docosyl phosphonous acid, and n-tetracosyl phosphonous acid.--

Signed and sealed this 27th day of June 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,630,790 Dated 28 December 1971

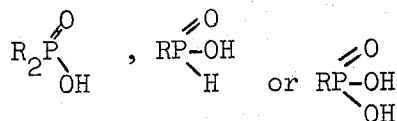
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