United States Patent

[11] 3,622,401

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[54] **CHEMICAL TREATMENT OF METAL**
10 Claims, No Drawings

[52] **U.S. Cl.** ..... **148/6.15 R,** 106/14, 252/389
[51] **Int. Cl.** **C23t 7/08**
[50] **Field of Search** ..... 252/389; 21/2.7; 148/6.15 R; 106/14

[56] **References Cited**

UNITED STATES PATENTS

3,351,558	11/1967	Zimmerer	252/389 X
3,413,231	11/1968	Kolodny et al.	252/389 X
3,416,974	12/1968	Scott	252/389 X

Primary Examiner—Ralph S. Kendall
Attorney—Frank M. Van Riet

ABSTRACT: A method for preparing metal surfaces for receipt of a coating such as a paint or adhesive (whereby increased coating adhesion and corrosion resistance is achieved) and the treated metal per se, are disclosed. The method comprises contacting the metal surface with various hydroxyalkyl phosphine oxide derivatives.

CHEMICAL TREATMENT OF METAL

BACKGROUND OF THE INVENTION

The use of various chemical materials in the treatment of metal surfaces is well known to those skilled in the art. For example, U.S. Pat. No. 1,798,218 describes a method whereby certain molybdenum compounds are utilized, whereas U.S. Pat. No. 1,911,537 discloses the use of dicarboxylic and hydroxy-dicarboxylic acids for a multiplicity of purposes. Phosphoric acid salts, (U.S. Pat. Nos. 1,936,533; 1,936,534; 2,952,669) phosphates, (U.S. Pat Nos. 2,224,695; 2,472,099; 2,769,737) and orthophosphoric acid-chlorinated hydrocarbon solutions, (U.S. Pat. No. 2,789,070) have also been disclosed as useful for metal treatment.

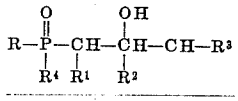
While these prior art techniques generally provide to the metal such characteristics as corrosion resistance, they usually fail in regard to the adhesion of surface coatings such as paints, varnishes, enamels, adhesives etc. thereto. Additionally, many of these antiquated systems are severely polluted by water, i.e. when contacted with water they tend to peel, blister etc.

SUMMARY

We have found that the adhesion of coatings to metals can be materially increased or strengthened by first treating the metal with a chemical material which is chemisorbed, i.e. chemically reacted with or absorbed via strong bonds thereto. In this manner, a foundation or integral chemical or chemically bound coating is formed on the metal surface via reaction with the metal, which foundation is then more susceptible to an ultimate or surface coating such as a paint or adhesive, than materials utilized in the past. Our method results in coatings which are more securely bonded or adhered to the foundation layer because the foundation is chemically bonded to the metal and, in a preferred embodiment, an ultimate coating is chemically bonded to the foundation. That is to say, upon treating the metal according to our novel method, a reaction, as mentioned above, causes a strong bonding of the hydroxyalkyl phosphine oxide derivative layer to the metal. There then remains, in our preferred embodiment, a second reactive group in the hydroxyalkyl phosphine oxide derivative layer, which group is free to react with an exterior surface coating. This free reactive group chemically combines with the surface coating applied thereto to produce a metal having a coating tightly bonded thereto. Additionally, the corrosion resistance of the metal treated according to the present invention, with or without an extraneous coating on its surface, is at least as effective and in many cases, better than known corrosion resistant systems.

DESCRIPTION OF THE INVENTION INCLUDING PREFERRED EMBODIMENTS

Our novel process comprises treating a metal surface, such as that of aluminum, steel, iron, copper, titanium, etc. with a reactive hydroxyalkyl phosphine oxide derivative. The useful derivatives have the formula



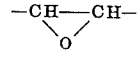
wherein R is an alkyl group of one to four carbon atoms, inclusive, an alkylene group of two to four carbon atoms, inclusive, or a hydroxyalkyl group of one to four carbon atoms, inclusive, R^1 and R^2 are hydrogen, an alkyl group of one to four carbon atoms, inclusive, or a hydroxyalkyl group of one to four carbon atoms, inclusive, R^3 is hydrogen or an alkyl group of one to four carbon atoms, inclusive, and R^4 is an alkyl group of one to four carbon atoms, inclusive, a vinyl group, or a substituted alkyl group of one to four carbon atoms, inclusive, said substituents comprising $N(R^5)_2$, OH, SH, or a polymerizable α, β-ethylenically unsaturated aliphatic group, R^5 being hydrogen or an alkyl group of one to four carbon atoms, inclusive.

While not wishing to be bound by any particular theory, we believe that the COH and P=O groups of the hydroxyalkyl phosphine oxide derivatives react with the oxide layer formed on the surface of the metal to be treated. The existence of such oxide layers is well recognized by cogent workers in the art. Such layers form upon exposure of the metal to the atmosphere. After the phosphine oxide derivative-metal oxide bonding is complete, the reactive groups of the phosphine oxide foundation layer, if any, are than free to react with the surface coating, i.e. paint, adhesive etc. applied thereto, thereby chemically bonding the coating to the metal. The phosphine oxide derivative-metal oxide bonding is pseudochemical in nature and can be more accurately described as a chemisorption or chelation of the derivative by the metal.

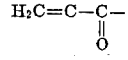
The phosphine oxide derivative foundation layer may be applied to the metal surface, the metal first being thoroughly cleaned such as by degreasing with trichlorethylene etc. or other common techniques, by immersing, dipping, painting, brushing, wiping, spraying etc. the metal article to be treated with solutions of one or more of said phosphine oxide derivatives, for a length of time such that the metal surface absorbs or reacts with a sufficient amount of the derivative. The metal is then merely removed from the solution and allowed to dry.

Additionally, the phosphine oxide derivative can be applied to the metal by first incorporating it into the surface coating material, e.g. the paint or adhesive, and then applying the surface coating. In this manner, the phosphine oxide derivative can be added, for example, to the paint vehicle, and the paint then can be sprayed etc. onto the metal. Similarly, the phosphine oxide derivative can be added to one part of a two-part adhesive system and the adhesive can then be applied to the metal. In each instance, the reactive groups of the surface coating material will react with the appropriate groups of the phosphine oxide derivative, if present, while the derivative itself reacts with the oxide on the metal surface, as more specifically described above. The solution of the hydroxyalkyl phosphine oxide derivative can comprise from about 1 part to about 50 parts of the derivative per 1000 parts of solvent, e.g. ethanol, methanol, water, etc. The treatment is preferably conducted at room temperature although higher or lower temperatures may be utilized, if desired. Complete chemisorption of the phosphine oxide derivative onto the metal surface is generally achieved in from about 10 to about 20 minutes, the lower the derivative concentration, the longer the reaction time necessary.

As mentioned above, when a group reactive with the surface coating or layer is present on the phosphine oxide derivative, there is afforded a chemically available site whereby the reactive group of a paint or adhesive layer may chemically react to thereby form a tightly adhering coating or layer. Examples of paints, adhesives or other coatings which may be used include epoxy paints and adhesives, i.e. those containing chemically available



groups; urethane paints and adhesives, i.e. those containing chemically available NCO groups; acrylic paints and adhesives, i.e. those containing chemically available



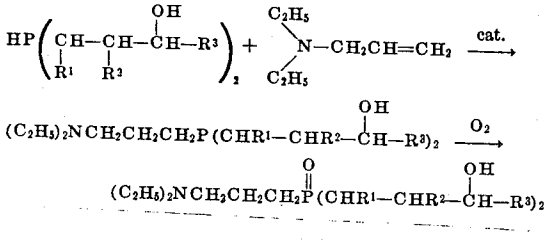
groups; vinyl paints and adhesives, i.e. those containing chemically available –CH=CH– groups and the like. As is clear from the enumeration of the chemically available groups of the above-mentioned coatings, the available group may be free to react with the available group of the phosphine oxide derivative layer previously applied to the metal surface. These reactive groups are explicitly represented, as discussed above,

by $N(R^5)_2$, OH, SH and unsaturated aliphatic groups and in the case of epoxy and urethane paints and adhesives would be $-N(R^5)_2$, –OH or –SH substituted groups, while in the case of acrylic or vinyl paints and adhesives, the reactive group of the phosphine oxide derivative would be the unsaturated substituent, including vinyl, allyl etc.

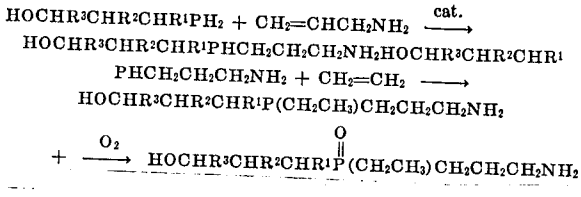
The coating, e.g. a paint, can be applied in a condition such that the reaction concurs while the paint vehicle evaporates or in a condition that the paint must more completely polymerize or cure before it forms a useful coating. In the latter case, if the functional group of the phosphine oxide derivative is such that it initiates polymerization of the paint, the paint may be applied in a prepolymer or semipolymer condition. An example of such a treatment is illustrated by the use of an hydroxy group containing derivative and an epoxy prepolymer. In this case, the hydroxy group both reacts with and cures (polymerizes) the epoxy prepolymer.

Additionally, we have found that our novel processing procedure can be utilized in conjunction with known procedures to obtain a pseudosynergistic effect. For example, we can improve the corrosion resistance of metals treated according to our invention by first treating the metal with an inorganic chromate in a manner known in the art. Furthermore, the chromate (e.g. potassium dichromate; chromic acid solution, etc.) may be incorporated into the solution of phosphine oxide derivative of our novel method before treating the metal according to our invention. In this manner, the corrosion resistance of the metal is further increased without loss of the enhanced surface coating adherence mentioned above.

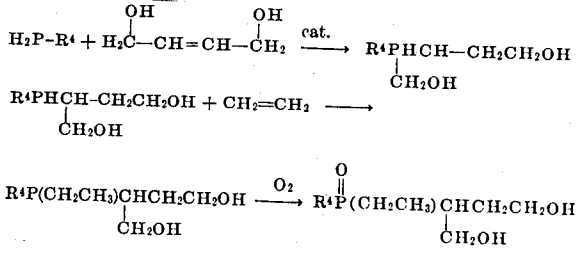
The hydroxyalkyl phosphine oxide derivatives utilized in the present invention are well known to those skilled in the art as are methods for their production. Generally, they may be produced according to procedures set forth in Kosolapoff; Organophosphorus Compounds; J. Wiley & Sons; pgs. 10–105; 1950. Generally, the procedure may consist of reacting an appropriately substituted primary or secondary phosphine (Rauhut et al.; Jour. Org. Chem.; Vol. 26; pg. 5138; 1961) with appropriately substituted amines, diols or Grignard reagents etc. at temperatures ranging from about 50° C.–90° C. in the presence of a free-radical generating catalyst and oxidizing the resultant tertiary phosphines as is known in the art to the corresponding phosphine oxide. Additional starting materials useful in preparing the compounds utilized herein are set forth in U.S. Pat. No. 3,160,666, which reference, and those specified above, are hereby incorporated herein by reference. A typical reaction would proceed according to the equation:



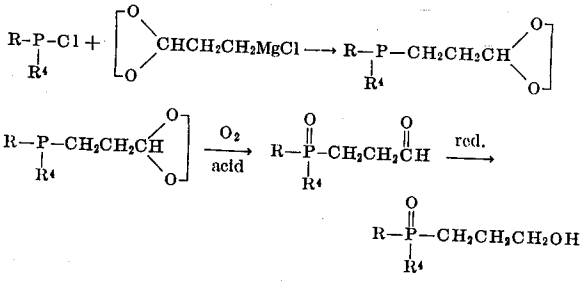
Use of a primary phosphine as the starting material would proceed according to the equation:



Similarly, a primary phosphine may also be reacted according to the equation:



The reaction utilizing a Grignard reagent proceeds according to the formula:



The pretreating process and products of the instant invention find utility in military, industrial and consumer fields such as aircraft and ship surfaces, cooling towers, heat exchangers, window screens, siding etc.

The following examples are set forth for purposes of illustration only and are not meant to be construed as limitations on the present invention except as set forth in the appended claims. All parts and percentages are by weight unless otherwise specified.

EXAMPLE I

Aluminum panels, 3 inches × 5 inches, are degreased by dipping in benzene and further cleaned by dipping in a hot 10 percent solution of a commercially available aluminum cleaner. The panels are then allowed to dry in air. One panel is then immersed in a solution of bis(3-hydroxybutyl) methyl phosphine oxide in water. After 15 minutes the panel is removed and allowed to dry.

The panel is then spray painted with a commercially available epoxy paint and allowed to dry and cure for 5 days at room temperature.

The painted panel is then subjected to a modified version of the "Cross-Hatch Tape Test" formulated by the National Coil Coaters Association. In the test, the painted surface is cut 10 times vertically and 10 times horizontally with a razor blade, the scratch lines being approximately 5 mm. apart. Scotch cellophane tape No. 600 is applied over the test area and rubbed with sufficient pressure to remove all air bubbles. The panel is allowed to set for 10 minutes and the tape is then removed sharply with a pull at right angles to the test surface. A visual examination allows a reasonably accurate estimation of the percent finish remaining on the panel in the test area.

The average results of tests conducted on panels treated according to example 1, in addition to the results recorded utilizing different hydroxyalkyl phosphine oxide derivatives according to the process of the present invention, are set forth in table I, below.

TABLE I

Example	Phosphine oxide derivative R	R¹	R²	R³	R⁴	R⁵	Average percent of finish remaining	Number of panels tested
Control *							20	2
1	CH_3	H	H	CH_3	$CH_2CH_2\overset{OH}{\overset{\vert}{C}}HCH_3$		100	2
2	$CH_2CH_2CH_2OH$	H	H	H	$CH_2CH_2CH_2N$	CH_2CH_3	92	4
3	CH_2CH_3	H	H	H	Same as above	H	93	2
4	CH_2OH	H	H	H	do	CH_2CH_3	98	2
5	CH_2CH_3	CH_2OH	H	H	do	H	90	2
6	$CH_2=CH$	H	H	H	$CH_2=CH$**		88	2
7	$CH_3CH_2CH_2CH_2$	H	H	H	$CH=CH_2$**		91	2
8	$CH_2CH_2CH_2OH$	H	H	H	$CH_2CH_2CH_2N$	CH_3	85	2
9	$CH_2CH_2CH_2OH$	H	H	H	$CH_2CH_2CH_2N$	$C(CH_3)_3$	88	2
10	$CH_2CH_2\overset{OH}{\overset{\vert}{C}}HCH_3$	H	H	CH_3	$CH_2CH_2CH_2N$	Same	88	2
11	CH_2CH_3	H	CH_3	$CH_2CH_2CH_2CH_3$	CH_2OH		85	4
12	$CH_2CH_2\overset{OH}{\overset{\vert}{C}}HCH_3$	OH	H	H	CH_3		82	4
13	$CH_2CH=CH_2$	$CH_2CH_2CH_3$	H	CH_2	CH_2CHSH***		83	2
14	CH_3	$CH_2CH_2CH_2OH$	CH_3	H	$CH_2CH=CH_2$**		80	2

*No phosphine oxide derivative used.
**Acrylic paint used.
***Polyurethane-based paint used.

EXAMPLE 15

The procedure of example 1 is again followed except that after cleaning the surface of the metal panel with a degreasing agent and an alkali cleaning agent, 3 parts of bis(3-hydroxybutyl)methyl phosphine oxide are added to 100 parts of the catalyst-curing agent package of a commercially available, 2-package polyurethane adhesive composition. After blending the contents of the two packages together, the resultant mixture is applied to the clean aluminum panel and cured under the recommended conditions. The adhesive is bonded more tightly to the metal panel than it is on a control specimen formed without the added phosphine oxide.

EXAMPLE 16

The procedure of example 1 is again followed except that in place of the epoxy paint used therein, a commercially available epoxy adhesive is used. The bonding of the adhesive to the metal is similar to that of the paint of said example.

EXAMPLE 17

The procedure of example 6 is again followed except that a commercially available vinyl paint is used in place of that paint of said example and the metal used is steel. The adhesion of the paint to the steel panel is superior to that of a panel coated without the foundation layer of phosphine oxide.

EXAMPLE 18

The procedure of example 10 is again followed except that the metal treated is stainless steel. Similar results are recorded.

EXAMPLE 19

Following the procedure of example 1 except that the metal treated is carbon steel, effective bonding of the epoxy paint is observed.

EXAMPLE 20

The procedure of example 1 is followed with replacement of the aluminum panels with similar shaped sections of titanium sheet. The adherence of the epoxy paint to the phosphine oxide foundation layer is 65 percent (control — no treatment — 0 percent).

EXAMPLE 21

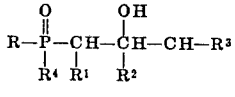
The use of nickel sheet for the aluminum panel of example 3 results in a good bonding of the paint to the panel.

EXAMPLE 22

The process of example 18 is followed except that a commercially available, corrosion resistant nickel-chromium alloy is used in place of the stainless steel panels thereof. The average percent of finish remaining after applying the tape test is 74 percent, six panels tested.

We claim:

1. A method which comprises treating a metal surface with a compound having the formula



wherein R is an alkyl group of one to four carbon atoms, inclusive, an alkylene group of two to four carbon atoms, inclusive, or a hydroxyalkyl group of one to four carbon atoms, inclusive, R^1 and R^2 are hydrogen, an alkyl group of one to four carbon atoms, inclusive, or a hydroxyalkyl group of one to four carbon atoms, inclusive, R^3 is hydrogen or an alkyl group of one to four carbon atoms, inclusive, and R^4 is an alkyl group of one to four carbon atoms, inclusive, a vinyl group, or a substituted alkyl group of one to four carbon atoms, inclusive, said substituents comprising $N(R^5)_2$, OH, SH, or a polymeriza-

ble α, β-ethylenically unsaturated aliphatic group, R^5 being hydrogen or an alkyl group of one to four carbon atoms, inclusive.

An article of manufacture comprising a metal surface having coated thereon a compound having the formula set forth in claim 1.

3. A method according to claim 1 wherein the metal surface is treated with said compound and a surface coating chemically reactive with said compound is coated thereon.

4. A method according to claim 1 wherein said compound is added as a mixture with a surface coating reactive with said compound.

5. A method according to claim 1 wherein said compound is bis(3-hydroxybutyl)methyl phosphine oxide.

6. A method according to claim 1 wherein said metal is aluminum.

7. A method according to claim 3 wherein said surface coating is a paint.

8. A method according to claim 4 wherein said surface coating is a paint.

9. A method according to claim 3 wherein said surface coating is an adhesive.

10. An article according to claim 2 wherein said metal is aluminum.

* * * * *

UNITED STATES PATENT OFFICE

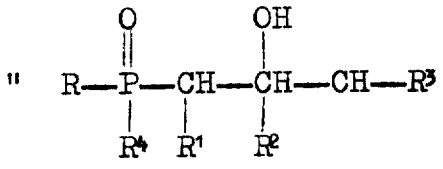
CERTIFICATE OF CORRECTION

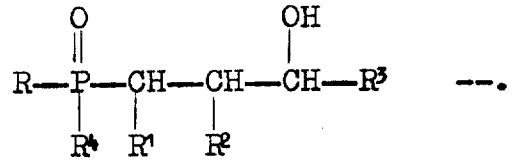
Patent No. 3,622,401 Dated November 23, 1971

Inventor(s) John Edmund McCullough and Francis Clyde Rauch

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

Column 6, the formula in Claim 1

"  " should read

--  --.

Column 7, line 4, "An article" should read -- 2. An article --.

Signed and sealed this 16th day of May 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

USCOMM-DC 60376-P69
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