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[54] **PROCESS FOR TREATING METAL ARTICLES**

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[58] **Field of Search** ..... 148/6.15 R, 6.15 Z; 260/47 P; 117/132 BF

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[57] **ABSTRACT**

Metal articles are coated by a process which comprises treating the metal articles with a non-aqueous phosphatizing solution containing a novolac phenol-formaldehyde resin having a molecular weight of from about 300 to 5,000, and chemically reacting the resin by heating the treated article at a temperature of at least about 190°C in the presence of an oxygen-containing atmosphere.

The articles so treated are rendered exceptionally corrosion resistant and exhibit excellent retention of final finish coatings.

8 Claims, No Drawings

PROCESS FOR TREATING METAL ARTICLES

This invention relates to the chemical treatment of metal articles. Most particularly, this invention relates to the chemical treatment of metal articles to render the articles exceptionally corrosion-resistant, better-suited to retain final finish coatings, and resistant to undercutting when final finish coatings are so applied.

It is well-known that bonding coatings are desirable on metal articles to protect such articles from corrosion and to form a base to promote adherence to such surfaces of organic finishes such as paints, enamels, lacquers, siccative coatings and the like. A variety of processes have been developed for this purpose and many specifically different compositions have been proposed as satisfactory for use in such processes.

Presently, the majority of bonding coatings techniques entail the use of phosphate solutions, or phosphatizing solutions. Such phosphatizing solutions as have been used for the purpose of inhibiting the corrosion of surfaces such as iron and steel result in phosphate coatings which, however, do not provide sufficient protection against corrosion in many cases. In order to obtain sufficient protection against corrosion, the phosphatizing process has been followed in the past, in most instances by rinsing with dilute chromate solutions.

However, this chromate after-rinsing or after-treatment of the phosphate coating has given rise to, among other things, serious disposal problems relative to the resulting waste water. Because of the toxicity of the hexavalent and trivalent chromium, these materials must be removed almost quantitatively from the waste water prior to disposal. Such recovery processes as must be practiced render the chromate rinse economically less desirable. Further, the chromic acid concentrates used for preparing and replenishing the rinsing bath present additional difficulties in handling due to their strongly corrosive properties. The use of chromate rinses in some instances also gives rise to other practical difficulties. During some applications, excessive amounts may tend to either discolor or bleed through subsequently applied topcoats. In other applications, the solutions may also tend to run or to pool in confined areas of the metal article to be treated, which may cause subsequent loss of topcoat adhesion when the completed article is subjected to high humidity conditions. Because of the running and/or pooling of the chromate rinsing solution, certain areas of the metal articles may be inherently left deficient in rinse treatment. Such areas exhibit as a result poor corrosion-resistance and poor resistance to undercutting when exposed to corrosive atmospheres.

Attempts to eliminate or to modify the sealing chromium rinse by post-treating the phosphatized metal articles with solutions of such coating materials as alkene phosphinic acids, acrylics, epoxies and the like have not resulted in the production of entirely satisfactory corrosion-resistant metal articles, generally, having anti-corrosive and paint retention properties attributed to chromium-rinsed phosphatized metal substrates.

It is an object of the present invention to provide for protective coatings for corrodible metal articles.

It is a further object of the present invention to provide protective coatings for corrodible metal articles, which coatings are receptive and retentive to final finish coatings.

It is yet another object of the present invention to provide a chemically reactive metal-treating composition which will, when applied to corrodible metal articles, render such metal articles exceptionally corrosion-resistant.

These and other objects will become readily apparent in view of the following description of the present invention.

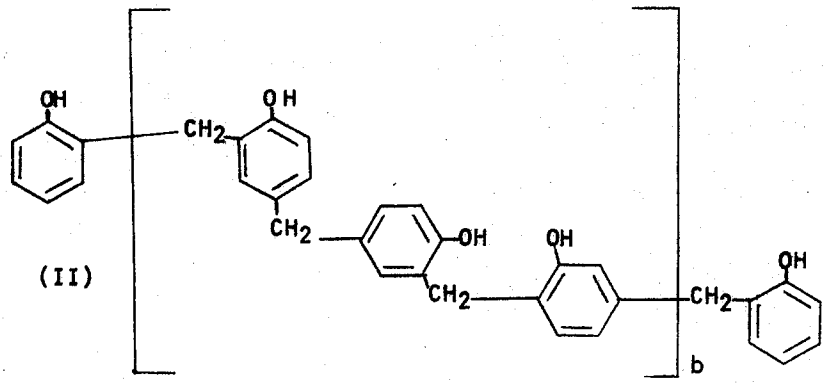
According to the present invention, an anti-corrosive and paint-retentive film is formed on the surface of metal articles by the process comprising:

a. treating the metal article with a non-aqueous phosphatizing solution containing a novolac phenol-formaldehyde resin having a molecular weight of from about 300 to about 5,000; and
b. heating the treated article at a temperature of at least about 190°C in the presence of an oxygen-containing atmosphere.

The use of phenolic resins to prevent corrosion and to provide a measure of protection to metal articles is well known and established in the art. However, such value has been achieved by the use of very high molecular weight phenolic resins with the molecular weight of the resins varying from about 20,000 to greater than about 100,000. Additionally the use of such relatively thick, contiguous films to coat metals with a variety of additional property-altering additives is known, as for example, the providing of lubricant-enhancing materials in phenolic-type carriers.

It has now been found that very low molecular weight novolac phenol-formaldehyde resins applied to metal articles simultaneously with the application of a conventional phosphatizing treatment the resin being deposited in the amounts of from about 4 to about 400 milligrams per square foot, and the treated metal article subsequently heated at temperatures in excess of about 90°C in the presence of an oxygen-containing atmosphere, provide for remarkably superior corrosion protection and other performance properties. Further, such resin depositions do not behave as barrier layers, as do the high molecular weight phenolic resins currently used in the art. Apparently, when the phosphate and low molecular novolac containing compositions are heated to temperatures in excess of about 190°C in the presence of an oxygen-containing atmosphere, the resins tend to exhibit chemical, rather than contiguous film-forming behavior. It is believed that, at temperatures in excess of about 190°C, and in presence of oxygen, the low molecular weight novolac phenol-formaldehyde resins complex and react with the phosphate crystals and iron oxides present to form caustic-insoluble complexes, and that it is this caustic-insolubility of the formed complexes which provides for the excellent undercutting and corrosion resistance properties.

The novolac phenol-formaldehyde resins which have been employed with success in the process of the present invention are those resins having the formula:



(II)

wherein *a* is an integer having a value on the order of from about 1 to about 50 and *b* is an integer having a value of from about 1 to about 20. Such phenol-formaldehyde resins as are represented by formula (I), designated as ortho-novolac phenol-formaldehyde resins, are substantially phenol-terminated chain polymers in which the phenolic nuclei are united by methylene bridges, for the most part located ortho to the phenolic hydroxyl groups. Those resins as are presented by formula (II), designated as random novolacs, are substantially phenol-terminated chain polymers in which the phenolic nuclei are united by methylene bridges for the most part located ortho and para to the phenolic hydroxyl groups.

Such resins are further characterized as permanently soluble and thermoplastic, and curable to insoluble, infusible products upon the application of heat, or upon the addition thereto of a source of formaldehyde.

The resins are of adequate hardness, with a softening temperature of from about 50° to a 100°C, to permit grinding thereof, exhibit good curing properties including a fast rate of cure, and attain a high degree of strength upon being cured.

Such novolac phenol-formaldehyde resins finding utility in the present process can be prepared by any one of a number of suitable methods known in the art, such as those disclosed in U.S. Pat. Nos. 2,475,587 and 3,108,978; in Modern Plastics No. 6,136,220 (1953); and Journal of Polymer Science 22,477 (1956), the teachings of which are herein incorporated by reference. The preparation of a typical acid-catalyzed novolac resin is as follows.

A reaction vessel is charged with 1 mol of phenol per 0.8 mol formalin. Approximately 0.2 to 0.3 percent by weight sulfuric acid, based on the weight of phenol, is added following dilution to about 1 N with water. Following the exothermic reaction on the addition of the catalyst, the reaction mixture is heated at reflux for about 2 hours. The reaction mixture is then neutralized with a lime-in-water slurry, dehydrated under reduced pressure, and discharged from the reaction vessel at elevated temperatures. Following a period of cooling, the resin is recovered and ground to the proper particle size.

Preparation of the novolac-containing phosphatizing solution is conveniently effected by dissolving a suitable amount of the resin in commercially available non-aqueous phosphatizing solutions. Generally, it has been found that non-aqueous phosphatizing solutions containing from about 3 to about 10 percent by weight of novolac resin are particularly suited for use in the present process.

The non-aqueous phosphatizing solutions to which the novolac resins are added generally contain a chlorinated hydrocarbon solvent, phosphoric acid, and a solubilizing agent for the phosphoric acid. Additionally, the phosphatizing composition may contain materials which are effective in inhibiting or controlling the amount of the phosphate coating produced, so as to obtain a hard, thin, substantially uniform phosphate coating, and materials which are effective in stabilizing the solution against oxidation and thermal degradation.

More specifically, any chlorinated hydrocarbon normally used as a degreasing solvent may be employed in the phosphatizing compositions used the in present process. Examples of such chlorinated hydrocarbons include trichloroethylene, perchloroethylene, tetrachloroethanes, methylene chloride, ethylene dichloride, ethylidene chloride, dichloro-tetra-fluoroethanes, trichlorotrifluoroethanes, trichlorodifluoroethanes, tetrachlorofluorethanes, fluorotrichloroethanes, fluorotetrachloroethanes, methyl trichloroethylene, 1,2-dichloropropane, carbon tetrachloride and mixtures thereof. The chlorinated hydrocarbons used may be unstabilized or, if desired, may contain one or more of the various known stabilizers which are effective in preventing or inhibiting the decomposition of the chlorinated hydrocarbon.

Of the chlorinated hydrocarbons hereinabove enumerated, the preferred chlorinated hydrocarbon is trichloroethylene.

In addition to chlorinated hydrocarbon solvents such as those hereinbefore set forth, such organic solvents as aliphatic ketones may be used in formulating the phosphatizing compositions to which the novolac resin is to be added. Exemplary of the ketones which may be used are acetone, methyl ethyl ketone, and the like. Preferably, the primary solvent used in the present process is trichloroethylene.

The phosphoric acid of the phosphatizing composition is preferably high strength phosphoric acid. The weight concentration of the phosphoric acid in the phosphatizing composition can be between about 0.1 and about 2.0 percent, and preferably between about 0.2 and about 1.5 percent by weight of the phosphatizing solution.

Co-solvents are generally used in such compositions to aid in solubilizing the phosphoric acid. Suitable co-solvents include the 3 aliphatic alicyclic alcohols. Exemplary of suitable alcohols are those alcohols containing between one and about eighteen carbon atoms such as methyl alcohol; secondary butyl alcohol; amyl alcohol; cyclohexyl alcohol; octyl alcohol; decyl alcohol; steary alcohol; mixtures of such alcohols, and the like. Also suitable for such use are organic compounds as 2-choroethanol, alkyl acetates such as ethyl acetate, amyl acetate and the like, amides such as N,N-dimethyl formamide and dimethyl acetamide, dioxane, monoethers of polyalkylene oxide glycols, and dialkyl sulfoxides. Generally, the co-solvent will be present in the composition in amounts within the range of about 1 to about 25 percent by weight of the total composition.

In addition to the above, the phosphatizing compositions may also contain various materials which act as stabilizers. Exemplary of such materials are resorcinol, hydroquinone, pyrocatechol, mono-, di and trialkylated pyrocatechols, alkylated resorcinols, alkylated hydroquinones, alkylated thioureas, diisobutylene, alkyl phenols, pentaphen, calcium hydroxide and the like.

Generally, the stabilizers are employed in the compositions in amounts of less than about 5 percent by weight. For example, a suitable stabilized composition is one which contains about 0.01 percent by weight 4 tertiary butylpyrocatechol, and 0.4 percent by weight diisobutylene.

The non-aqueous novolac resin-containing treating solution, as stated, is generally formulated in such manner as to provide a solution containing from about 3 to about 10 percent by weight of the novolac resin. Preferably, those solutions containing from about 3 to about 7 percent by weight of novolac resin are employed. However, the use of more highly concentrated or dilute solutions is not thereby precluded.

The novolac resin-containing phosphatizing solution may be applied to the metal article to be treated by spraying or by dipping the article in to the solution to deposit resin in an amount of from about 4 to about 400 milligrams per square foot of surface area. The deposition process is usually effected within a period of from about 15 to about 90 seconds at a temperature of about 80°C, when using trichloroethylene as the solvent. After the article is sufficiently treated with the resin-containing phosphatizing solution, the article is removed from the treating solution and the solvent removed by any suitable means.

Following the removal of the solvent, the treated article is then heated at a temperature in excess of about 190°C, generally from about 190° to about 270°C, and preferably at about 205°C, in the presence of an oxygen-containing atmosphere for a period of from about 15 seconds to 5 minutes, if desired. The time required to complete the heat treatment is, of course, dependent upon the make of the resin-containing phosphatizing solution, the temperature employed and the nature of the article being treated. Generally, at a temperature of about 270°C, a finished treatment is provided in less than about 60 seconds.

The treated metal article is corrosion-resistant, exceptionally receptive to the application of paints, varnishes, lacquers and other final finish coating compositions. Thus, metal articles treated according to the process of the present invention may receive organic finishes having as end uses such as automobile finishes, exterior trim, appliance coatings, metal furniture, coatings for venetian blinds, coatings for interior lighting fixtures and the like.

Metal surfaces which may be treated according to the process of the present invention include ferrous metals, aluminum, galvanized metals, alloys and the like.

Prior to application of the novel treating compositions of the present invention, as in accepted phosphatizing practice, the surface of the metal article to be treated is usually cleansed by physical and/or chemical means such as immersion in or spraying with an aqueous caustic cleanser, mechanical abrading or polishing, vapor degreasing or the like. For the purpose of the present invention it is preferred to cleanse the metal article to be treated by immersing the article for a period of about 60 seconds in a commercial aqueous caustic metal cleanser at a temperature of from about 30° to about 80°C. Following the cleansing of the metal article, the article is generally rinsed with hot water to prevent contamination of the resin-containing phosphatizing solution, and dried. It is understood that, where a cleansing step is utilized, any suitable cleansing method known in the art may be employed.

The application of the non-aqueous novolac resin-containing phosphatizing solution to the metal article to be treated may be accomplished by any suitable means. Because the solutions are generally applied at a temperature on the order of from about 75° to about 125°C, immersion techniques are well-adapted for providing the treating materials to the metal article to be treated, The manner of immersion, however, is not important in that quiescent baths can be used or, alternately, continuous baths may be advantageously employed.

The temperature of the novolac resin-containing conversion treating composition is preferably maintained at a temperature of from about 75° to about 125°C during application to the metal article, and the treated metal article is subsequently heated at a temperature of from about 190° to about 270°C for a period of from about 15 to about 180 seconds in the presence of an oxygen-containing atmosphere.

The following examples serve to illustrate the present invention but are not to be construed as limiting it hereto.

In the following examples, following the novolac resin-phosphatizing solution treatment of the metal articles, each metal article was painted with enamel and then subjected to 5 percent salt spray and physical tests. The salt spray test is the American Society for Testing and Materials (ASTM) test B117-61 with painted panel scribed as given in ASTM test D-165461. This test employs a five percent sodium chloride fog or spray. The ratings given depend on the creepage from the scratch, given in one-sixteenths of an inch. Ratings given at spt (S) indicate no creepage except in a small area. In the salt spray test, unless otherwise indicated, the exposure time was 120 hours. In the physical test, adhesion was determined by knife blade and results are reported on the scale of 0 to 10, where 10 is excellent, 8 is good, 6 is fair, 4 is poor, 2 is very poor and 0 is complete loss of adhesion.

EXAMPLE 1

A polished steel panel is cleansed for 60 seconds in a commercial aqueous hot caustic metal cleanser,

rinsed with hot water and flashed in an air circulating oven at 160°C. The dried panel is then immersed for 30 seconds in the following conversion treating composition 87°C, following which the panel is heated at 270°C for a period of 90 seconds in an air circulating oven.

Orthonovolac resin (MW 1000) wgt. %	5
Phosphoric acid	1
Stabilizers	0.42
Trichloroethylene	93.58
	100.00

A conversion coating-type deposition containing less than 110 milligrams of resin per square foot of surface area is formed on the panel. The treated panel, when topcoated with commercial melamine alkyd enamel, exhibits a knife blade adhesion rating of 9, an undercutting of one-sixteenth of an inch and a paint retention of 93 percent.

EXAMPLE 2

The procedure of Example 1 is observed with the exception that the treated panel is heated for 120 seconds. The treated panel, when topcoated, exhibits an undercutting of less than one-sixteenth inch and a paint retention of 96 percent.

EXAMPLE 3

The procedure of Example 1 is observed with the exception that the panel is immersed in the resin-containing phosphatizing solution for a period of 60 seconds. Similar results obtain as in Example 1.

EXAMPLE 4

The procedure of Example 1 is observed with the exception that the panel is immersed for 60 seconds and heat-treated for 120 seconds. The treated panel, when topcoated, exhibits a knife blade adhesion rating of 9, an undercutting of less than one-sixteenth inch and a paint retention of 95 percent.

EXAMPLE 5

The procedure of Example 1 is observed with the exception that the panel is immersed in the resin containing phosphatizing solution for 90 seconds. Similar excellent results are obtained as in Example 1.

EXAMPLE 6

The procedure of Example 1 is observed with the exception that the panel is immersed in the resin-containing phosphatizing solution for 120 seconds and heated for 60 seconds. The treated panel, when topcoated, has a knife blade adhesion rating of 9, an undercutting of less than one-sixteenth an inch, and a paint retention of 96 percent.

EXAMPLE 7

The procedure of Example 1 is observed with the exception that the resin-containing phosphatizing solution contains 0.2 percent by weight calcium hydroxide, based on the resin content of the solution. The panel is immersed for a period of 30 seconds and heat-treated for 120 seconds. Similar excellent results obtain as in Example 1.

EXAMPLE 8

The procedure of Example 7 is observed with the exception that the immersion time is 60 seconds. Similar excellent results obtain as in Example 1.

EXAMPLE 9

The procedure of Example 1 is observed with the exception that the resin content is 3 percent by weight and the heat-treatment is continued for 120 seconds. Similar excellent results obtain as in Example 1.

EXAMPLE 10

The procedure of Example 9 is observed with the exception that the immersion time is 120 seconds. Similar excellent results obtain as in Example 1.

EXAMPLE 11

The procedure of Example 9 is observed with the exception that the immersion time is 90 seconds and the heating is effected for 60 seconds. Similar excellent results obtain as in Example 1.

EXAMPLES 12–13

The procedure of Example 11 is observed with the exception that the heating time is 90 and 120 seconds. Similar excellent results obtain as in Example 1.

EXAMPLES 14–17

The procedure of Example 11 is observed with the exception that the immersion time is 120 seconds and the heating times are 30, 60, 90 and 120 seconds. Similar excellent results obtain as in Example 1.

EXAMPLES 18–25

The procedure of Example 1 is observed with the exception that the resin content is 7 percent by weight, the immersion times are 30, 60, 90, and 120 seconds. Similar excellent results obtain as in Example 1.

EXAMPLE 26

A polished steel panel is cleansed for 60 seconds in a commercial aqueous hot caustic cleanser, rinsed with hot water and flashed in an air circulating oven at 160°C. The dry, clean panel is then immersed in the following conversion coating composition at 87°C, removed and heated at 205°C for 150 seconds in an air circulating oven.

Random novolac resin (MW 1000) wgt. %	5
Phosphoric acid	1
Stabilizers	0.42
Trichloroethylene	93.58
	100.00

A conversion coating-type deposition containing less than about 110 milligrams of resin per square foot of surface area is formed on the panel. The panel when topcoated with commercial melamine alkyd enamel, exhibits properties similar to those of Example 1.

EXAMPLE 27

The procedure of Example 1 is observed with the exception that acetone is employed as the solvent in the phosphatizing solution. Similar excellent results obtain as in Example 1.

EXAMPLE 28

The procedure of Example 26 is observed with the exception that acetone is employed as the solvent in the phosphatizing solution. Similar excellent results obtain as in Example 1.

EXAMPLE 29

The procedure of Example 26 is observed with the exception that acetone/carbon tetrachloride 50:50 is employed as the solvent in the phosphatizing solution. Similar excellent results obtain as in Example 1.

Similar results as are exhibited in Examples 1–29 are obtained when the molecular weight of the resin is varied from about 300 to up to about 5000 and the heating step is varied from 190°C to 270°C.

What is claimed is:

1. A process for treating surfaces of zinc, aluminum, ferrous metal and alloys of these to render them corrosion-resistant, paint-receptive and paint-retentive which comprises

a. applying to said surface a non-aqueous phosphatizing composition which consists essentially of 0.1 to 2.0 percent by weight phosphoric acid, 3 to 10 percent by weight of a novolac phenol-formaldehyde resin having a molecular weight of from about 300 to 5000 and a non-aqueous solvent for said phosphoric acid and said resin, said phosphatizing composition being applied in an amount sufficient to provide on said surface a resin coating weight of from about 4 to 400 milligrams per square foot and

b. thereafter, heating the thus-treated surface at a temperature of at least about 190°C in the presence of an oxygen-containing atmosphere for a period of from about 15 seconds to 5 minutes.

2. A process as defined by claim **1** wherein the novolac resin is an ortho-novolac resin.

3. A process as defined by claim **2** wherein the resin has a molecular weight of about 1000.

4. A process as defined by claim **1** wherein the novolac resin is a random novolac resin.

5. A process as defined by claim **4** wherein the resin has a molecular weight of about 1000.

6. A process as defined by claim **1** wherein trichloroethylene is employed as the solvent in the non-aqueous phosphatizing solution.

7. A process a defined by claim **1** wherein a 50:50 carbon tetrachloride:acetone solution is employed as the solvent in the non-aqueous phosphatizing solution.

8. A process as defined by claim **1** wherein the surface is treated with the non-aqueous phosphatizing solution for a period of at least 60 seconds and heated at a temperature of about 205°C for a period of at least 60 seconds.

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