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PROCESS FOR TREATING METAL SURFACES

William J. Vullo, Tonawanda, N.Y., and Donald H. Campbell, Niagara-on-the-Lake, Ontario, Canada, assignors to Hooker Chemical Corporation, Niagara Falls, N.Y., a corporation of New York

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ABSTRACT OF THE DISCLOSURE

A non-aqueous phosphatizing composition for treating metal surfaces comprising a halogenated hydrocarbon solvent, at least 1.5% phosphoric acid by weight, and an aliphatic monohydroxy alcohol to promote solubility of the phosphoric acid in the hydrocarbon solvent. This composition is applied to the clean metal surface to be treated. Suitable solvents include trichloroethylene, perchloroethylene and methyl chloroform and preferred alcohols contain from 1 to 18 carbon atoms, such as amyl alcohol.

This application is a continuation-in-part of our copending applications Ser. Nos. 16,125 and 16,127, both filed Mar. 21, 1960, now abandoned.

This invention relates to a composition for treating metal surfaces to form a protective and/or paint base coating thereon, and more particularly relates to a substantially non-aqueous composition for treating metal surfaces to form a protective and/or paint base phosphate coating thereon.

The use of phosphate coatings to provide a protective and/or paint base coating on metal surfaces is well known. Typically, such phosphate coatings are applied by contacting the metal surface to be treated, such as a ferrous metal surface, with an aqueous acidic zinc phosphate composition or an alkali metal phosphate composition. In such processes, which are "aqueous" processes, the metal surface to be treated is first cleaned, using either an aqueous alkaline cleaning solution or an organic solvent, such as a chlorinated hydrocarbon solvent. Thereafter, the cleaned metal surface is contacted with the aqueous phosphatizing solution until the desired phosphate coating is formed on the metal surface. The thus-coated metal is then normally rinsed in water and then rinsed with a chromic acid solution and dried. Although high quality phosphate coatings are produced by this method, the process has the disadvantage of requiring a large number of expensive operating steps or stages. Additionally, because the phosphatizing compositions used are aqueous, the phosphatizing composition is not readily combined with an organic solvent cleaning process and a painting process, to provide a unified operation for the production of painted metal surfaces.

In place of the aqueous phosphatizing solution, it has been proposed to use substantially non-aqueous compositions. Thus, for example, in Belgian Patent 584,827, it is proposed to use a substantially nonaqueous phosphatizing composition containing from 0.1 to 1% phosphoric acid, from 2 to 12% of a lower aliphatic alcohol and the balance a chlorinated hydrocarbon solvent, such as trichloroethylene. Although the aforementioned difficulties encountered with the aqueous phosphatizing composition have been found to be overcome when using this non-aqueous phosphatizing bath, other problems have been encountered. Principally, it has been that when using this non-aqueous phosphatizing composition, appreciable quantities of sludge are developed in the phosphatizing bath as the metal surfaces are treated. In many instances, in a relatively short time sufficient sludge has formed in the phosphatizing bath that appreciable sludge

adheres to the metal surface which is being treated. When this happens, it is then necessary to shut down the phosphatizing bath and either remove the sludge or replace the phosphatizing solution with a new solution. This is, of course, costly, both in terms of the time and the materials which are consumed.

It is, therefore, an object of the present invention to provide a substantially non-aqueous phosphatizing composition which may be used for extended periods of time without the formation of undesirable amounts of sludge in the bath.

A further object of the present invention is to provide an improved method for the phosphate coating of metals, which method may be operated using a substantially non-aqueous phosphatizing solution without the formation of undesirable quantities of sludge in the solution.

These and other objects will become apparent to those skilled in the art from the description of the invention which follows.

Pursuant to the above objects, the present invention includes a substantially non-aqueous phosphatizing composition which comprises a halogenated lower aliphatic hydrocarbon solvent, at least 1.5% by weight of phosphoric acid and an aliphatic alcohol, in an amount sufficient to solubilize the phosphoric acid in the halogenated hydrocarbon solvent. It has been found that when using this composition to treat metal surfaces, the amount of sludge formation in the solution is appreciably reduced over that which is formed when using similar composition but containing lesser amounts of the phosphoric acid, e.g., 1% by weight phosphoric acid.

More specifically, the composition of the present invention desirably contains the following components in the amounts indicated:

Component:	Percent by weight
Halogenated hydrocarbon solvent	55 to 93.5
Aliphatic alcohol	5 to 35
Phosphoric acid	1.5 to 10

In preferred embodiments, the compositions of the present invention contain the following components in the amounts indicated:

Components:	Percent by weight
Halogenated hydrocarbon solvent	70 to 90
Aliphatic alcohol	8 to 25
Phosphoric acid	2 to 6

Various halogenated lower aliphatic hydrocarbons which are normally employed in vapor degreasing or non-aqueous phosphatizing operations may be used in the present composition. Typically, these halogenated hydrocarbons contain from about 1 to 6 carbon atoms and from about 1 to 12 halogen atoms. Exemplary of specific halogenated hydrocarbons which may be used are trichloroethylene, perchloroethylene, trichloroethanes, tetrachloroethanes, methylene chloride, ethylene chloride, ethylidene chloride, dichlorotetrafluoroethanes, trichlorotrifluoroethanes, trichlorodifluoroethanes, tetrachlorodifluoroethanes, fluorotrichloromethane, fluoropentachloroethanes, and mixtures thereof. Of these, the preferred halogenated hydrocarbons are trichloroethylene, perchloroethylene, and methyl chloroform. Accordingly, hereinafter primary reference will be made to these materials.

The halogenated hydrocarbon employed in the present composition may be either stabilized or unstabilized. When a stabilized material is desired, typical examples of stabilizers which may be suitable include olefins, as disclosed in United States Patent Nos. 1,904,450 and 2,435,312; acetylenic compounds, as disclosed in United States Patent Nos. 2,775,624 and 2,803,676; hydrocarbons, as disclosed in United States Patent Nos. 1,816,895

and 1,858,022; phenols, as disclosed in United States Patent Nos. 2,008,680 and 2,155,723; alcohols, as disclosed in United States Patent Nos. 2,775,624 and 2,887,516; esters, as disclosed in United States Patent No. 2,371,645; heterocycles containing N and O or S in ring, as disclosed in United States Patent No. 2,517,893; aldehydes, as disclosed in United States Patent No. 1,917,073; alkyl, cyanamides, as disclosed in United States Patent No 2,043,257; alkyl thioureas, as disclosed in United States Patent No. 2,041,258; alkyl amines, as disclosed in United States Patent No. 2,096,735; aryl amines, as disclosed in United States Patent No. 2,094,367; alkyl isocyanates, as disclosed in United States Patent No. 2,108,390; guanidines as disclosed in United States Patent No. 2,125,381; diols, as disclosed in United States Patent No. 2,355,319; oximes, as disclosed in United States Patent No. 2,371,647; ketones as disclosed in United States Patent No. 2,376,075; nitriles, as disclosed in United States Patent No. 2,422,556; amides, as disclosed in United States Patent No. 2,423,343; nitrates, as disclosed in United States Patent No. 2,436,772; thiophenes, as disclosed in United States Patent No. 2,440,100; pyrroles, as disclosed in United States Patent No. 2,492,048; nitroalkanes, as disclosed in United States Patent No. 2,567,621; sulfones, as disclosed in United States Patent No. 2,742,509; azines, as disclosed in United States Patent No. 2,878,297; aryl stibines, as disclosed in United States Patent No. 2,917,554; sulfoxides, as disclosed in United States Patent No. 2,919,295; and mixtures thereof.

Preferably, the phosphoric acid used in the compositions of the present invention is a highly concentrated orthophosphoric acid, such as the 85% phosphoric acid of commerce. If desired, however, more dilute or more concentrated acid solutions may be used. In this regard, it is to be appreciated that regardless of the acid concentration which is initially employed, substantially all of the water is ultimately distilled from the phosphatizing bath as the phosphatizing treatment is carried out.

Since the concentrated phosphoric acid is substantially insoluble in halogenated hydrocarbons, an aliphatic alcohol is employed, as has been indicated hereinabove, to dissolve the phosphoric acid in the halogenated hydrocarbon liquid. Any aliphatic or alicyclic monohydroxy alcohol which is capable of dissolving phosphoric acid in the halogenated solvent may be used. Typically, the alcohols employed contain from about 1 to 18 carbon atoms and include alcohols such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, tertiary butyl alcohol, n-amyl alcohol, tertiary amyl alcohol, octyl alcohol, decyl alcohol, lauryl alcohol, stearyl alcohol, cyclohexyl alcohol, and the like, including mixtures thereof. Inasmuch as the solubility of the phosphoric acid may be less in the higher alcohols than in the lower alcohols, preferably the alcohol used has less than 10 carbon atoms and more preferably from about 1 to 6 carbon atoms. Of these, the preferred alcohols for use in the compositions of the present invention are butyl alcohol and amyl alcohol, such as the normal butyl or normal amyl alcohols which are available commercially. In this regard, it is to be noted that one commercially available amyl alcohol which is particularly suitable is primary amyl alcohol which is a mixture of several isomers of amyl alcohol but contains principally normal amyl alcohol.

As has been noted hereinabove, the aliphatic alcohol is desirably present in the composition in an amount within the range of about 5 to 35% by weight of the composition. It is to be appreciated, however, that the amount of alcohol used will be that amount which is at least sufficient to solubilize the phosphoric acid in the halogenated hydrocarbon solvent, such as trichloroethylene. Additionally, it is further desirable that the resulting phosphatizing composition be substantially non-flammable and have a relatively high flash point, as compared to the alcohol. Accordingly, it is preferred to use the highest proportion of the halogenated hydrocarbon solvent in the coating

solution which is consistent with obtaining a smooth, uniform phosphate coating on the metal surface. In other words, in most instances amounts of alcohol greatly in excess of those needed to maintain the phosphoric acid in the solution will not be used. In some instances, however, particularly where the alcohol used is one having a relatively low boiling point, i.e., an alcohol which is not readily volatilized, greater amounts of the alcohol may be used while still maintaining a coating solution which is substantially non-flammable and in such instances, amounts of the alcohol in excess of the 35% desired maximum may sometimes be employed.

In the practice of the method of the present invention, the metal surface to be treated is desirably cleaned, using any suitable means, as for example by employing a halogenated hydrocarbon solvent, to remove oil and other extraneous material. The metal treated may be any metal which is capable of reacting with phosphoric acid to form the corresponding metal phospate, such as ferrous metals, aluminum, zinc, magnesium, cadmium, as well as alloys containing these metals, and the like. After cleaning, the metal surface is contacted with the phosphatizing composition as described hereinabove, contact times of up to about 30 minutes being typical, with times within the range of about 0.5 and 15 minutes being preferred. The phosphatizing solution with which the metal surface is contacted is desirably maintained at a temperature between about 0° centigrade and the boiling point of the phosphatizing solution, with temperatures between about 55° centigrade and the boiling point being preferred. Normally, the higher temperatures are employed when using the shorter contact times. It is to be appreciated that the word "contacted" and "contacting," as used in the specification and claims, in connection with treating the metal with the phosphatizing solution, are intended to include various methods for wetting the metal surface with the solution, such as by immersion, dipping, flooding, spraying, or the like.

After contact with the phosphatizing solution the thus-phosphatized metal may be again contacted with a halogenated hydrocarbon degreasing solution, as a final rinse to remove any phosphatizing solution. Normally, however, this step is not necessary since the phosphatized metal is substantially dry when it is removed from the phosphatizing bath. The thus-phosphatized metal surface, with or without rinsing, may be stored or used as is. If desired, the phosphatized metal may be subjected to further treatment, such as painting, lubricating or the like.

In some instances, it has been found that it is desirable to treat the phosphatizing compositions of the present invention with small amounts of powdered iron or other metal of the class being treated, amounts within the range of about 0.01 to about 0.1% by weight of the solution being typical. After adding the powdered metal to the solution, the resulting slurry is heated to between about 55° centigrade and the boiling point of the solution for from about 10 to 15 minutes, thereafter, the suspended solids are separated from the solution by filtering or the like. In some instances, when the present phosphatizing solutions are not thus treated with iron or other metal powder, the first articles coated with the phosphatizing solution may have phosphate coatings which are not as satisfactory as the coatings which are subsequently produced from the phosphate solution. Prior treatment of the phosphatizing solution with the iron powder as described above, results in the formation of excellent phosphate coatings on all of the metal articles treated. Thus, in many instances it may be desirable to effect a "preaging" of the phosphatizing solution in the manner described, prior to using this solution to treat the metal surfaces.

It is found that when using the phosphatizing solutions of the present invention, which contain at least 1.5% by weight of phosphoric acid, there is an appreciable reduction in the amount of sludge which is formed in the

phosphatizing solution during the phosphatizing process, as compared to the prior art compositions which contain a maximum of about 1% of phosphoric acid. Moreover, as the phosphoric acid content of the phosphatizing solution is increased to within the 2 to 6% by weight range, even greater reductions in sludge formation during the use of the solution is obtained. Additionaly, there is some evidence that the phosphate coatings, as initially produced by the solution contining at least 1.5% phosphoric acid, are less water soluble than those produced by the prior art compositions containing about 1% phosphoric acid. Moreover, the phosphate coatings of the present invention are similarly less hygroscopic than are the phosphate coatings produced by the prior art composition containing lesser amounts of phosphoric acid.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. In these examples, unless otherwise indicated, temperatures are in degrees centigrade and parts and percents are by weight. It is to be appreciated, however, that these examples are merely exemplary of the present invention and are not to be taken as a limitation thereof.

Example 1

A phosphatizing solution was formulated containing the following components in the amounts indicated:

Component:	Grams
Trichloroethylene	92.58
Primary amyl alcohol	6.00
Diisobutylene	0.40
Pentaphen	0.01
4-tertiary-butyl pyrocatecol	0.01
Orthophosphoric acid (85% aqueous solution)	1.18

Upon dehydrating the water from this solution, the resulting phosphatizing solution contained 1.0% by weight of H_3PO_4. Clean, degreased steel panels were coated by immersing the panels in this phosphatizing solution for a period of from about 45 to 60 seconds, the coating solution being maintained at a temperature of about 85° centigrade. The coating weights of the phosphate coatings obtained on the panels were within the range of about 200 to 250 milligrams per square foot. It was noted that after about 2.912 square feet of metal had been processed through the phosphatizing solution, a precipitate began to appear in the phosphatizing solution. When a total of 4.576 square feet of metal had been processed through this solution, sufficient precipitate or sludge had formed in the solution that the precipitate began coating onto the panels so that the coating of additional metal was not possible. Additionally, it was found that when a freshly coated panel was wet with water, appreciable amounts of the phosphate coating was removed from the wet surface by rubbing with a clean cloth.

Example 2

The procedure of Example 1 was repeated with the exception that the phosphatizing solution used contained the following components in the amounts indicated:

Components.	Grams
Trichloroethylene	92.04
Primary amyl alcohol	6.54
Diisobutylene	0.40
Pentaphen	0.01
4-tertiary butylpyrocatecol	0.01
Orthophosphoric acid (85% aqueous sol.)	1.76

Upon dehydration, this phosphatizing solution contained 1.5% H_3PO_4. Clean, degreased steel panels were processed through this solution as in Example 1, and it was found that a total of 7.488 square feet of metal was coated in the solution before the precipitate began coating out on the panel surface. Additionally, it was found that upon wetting the freshly coated panels with water, there was an appreciable reduction in the amount of the coating which could be removed by wiping the wet surface, as compared with that removed in Example 1.

Example 3

The procedure of Example 1 was repeated with the exception that the phosphatizing solution used contained the following components in the amounts indicated:

Components:	Grams
Trichloroethylene	91.50
Primary amyl alcohol	7.08
Diisobutylene	0.39
Pentaphene	0.01
4-tertiary butylpyrocatecol	0.01
Orthophosphoric acid (85% aqueous sol.)	2.35

Upon dehydrating this solution, the resulting phosphatizing solution had an H_3PO_4 content of 2.0% by weight. Clean, degreased steel panels were processed through this solution as in Example 1. It was found that a total of 13,212 square feet of metal was coated before the precipitate began coating onto the paneled surface. Additionally, it was found that the water solubility of the freshly coated panels was similar to that of the panels obtained in Example 2.

Example 4

The procedure of Example 1 was repeated with the exception that the phosphatizing solution used contained the following components in the amounts indicated:

Components:	Grams
Trichloroethylene	90.96
Primary alcohol	7.62
Diisobutylene	0.39
Pentaphene	0.01
4-tertiary butyl catecol	0.01
Orthophosphoric acid (85% aqueous sol.)	2.71

Upon dehydration, the H_3PO_4 content of the phosphatizing solution was 2.5% by weight. Clean, degreased steel panels were processed through this solution as in Example 1. It was found that a total of 15.92 square feet of metal was coated before the precipitate in the solution began coating onto the panel surface. Additionally, it was found that the water solubility of the freshly applied phosphate coatings was somewhat greater than that on the panels produced in Examples 2 and 3.

Example 5

The procedure of the preceding example was repeated using phosphatizing solutions which contained 3.0 and 6.0% by weight of H_3PO_4, the amyl alcohol content of these solutions being increased to 9.23 and 15.0% respectively and the trichloroethylene content being correspondingly reduced. In processing steel panels through these solutions, as in the preceding examples, corresponding increases in the square footage of the steel surfaces which were processed before the precipitate coated out onto the metal surface were obtained, as well as corresponding increase in the water solubility of the freshly applied phosphate coating.

The procedure of the preceding examples is repeated using perchloroethylene and 1,1,1, trichloroethane in place of the trichloroethylene and using normal butyl alcohol, isopropyl alcohol, and cyclohexyl alcohol, in place of the amy alcohol solvent to obtain similar results.

The phosphate coated panels produced in the preceding examples were painted and then subjected to the standard Salt Fog, Water Immersion, Knife Adhesion and Formability tests. In all cases acceptable test results were obtained.

While there have been described various embodiments of the invention, the compositions and methods described are not intended to be understood as limiting the scope of

the invention, as it is realized that changes therewithin are possible and it is intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A stable, substantially non-flammable, non-aqueous metal coating composition consisting essentially of a halogenated lower aliphatic hydrocarbon solvent containing from 2 to 6 carbon atoms, in an amount within the range of about 55 to 93.5% by weight, from about 1.5% to 10% by weight of phosphoric acid and an aliphatic monohydroxy alcohol containing from 1 to 18 carbon atoms, in an amount within the range of about 5 to 35% by weight, which amount is sufficient to solubilize the phosphoric acid in the halogenated hydrocarbon solvent.

2. The composition as claimed in claim 1 wherein the halogenated hydrocarbon solvent is present in an amount within the range of about 70 to 93% by weight, the alcohol is present in an amount within the range of about 8 to 25% by weight, and the phosphoric acid is present in an amount of about 2 to 6% by weight.

3. The composition as claimed in claim 2 wherein the alcohol contains from about 1 to 6 carbon atoms.

4. The composition as claimed in claim 3, wherein the halogenated hydrocarbon solvent is selected from the group consisting of perchloroethylene, trichloroethylene, and methyl chloroform.

5. The composition as claimed in claim 4 wherein the halogenated hydrocarbon solvent is trichloroethylene and the alcohol is amyl alcohol.

6. A method of coating metal surfaces which comprises contacting the metal surface to be coated with the composition as claimed in claim 1 and maintaining the composition in contact with the metal surface for a time sufficient to form a phosphate coating thereon.

7. The method as claimed in claim 6 wherein the phosphatizing composition with which the metal surface is contacted contains the halogenated hydrocarbon solvent in an amount within the range of about 70 to 90% by weight, the alcohol in an amount within the range of about 8 to 25% by weight and the phosphoric acid in an amount within the range of about 2 to 6% by weight.

8. The method as claimed in claim 7 wherein the alcohol in the phosphatizing composition contains from about 1 to 6 carbon atoms.

9. The method as claimed in claim 8, wherein the halogenated hydrocarbon solvent is selected from the group consisting of perchloroethylene, trichloroethylene, and methyl chloroform.

10. The method as claimed in claim 9 wherein the halogenated hydrocarbon solvent in the phosphatizing composition is trichloroethylene and the alcohol is amyl alcohol.

References Cited

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584,827	3/1960	Belgium.

RALPH S. KENDALL, *Primary Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,361,598 January 2, 1968

William J. Vullo et al.

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 66, "it has been that" should read -- it has been found that --. Column 3, line 10, "2,041,258" should read -- 2,043,258 --. Column 4, line 28, "0°" should read -- 20° --. Column 5, line 9, "contining" should read -- containing --. Column 6, line 22, "13,212" should read -- 13.212 --; line 67, "amy" should read -- amyl --.

Signed and sealed this 30th day of December 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents