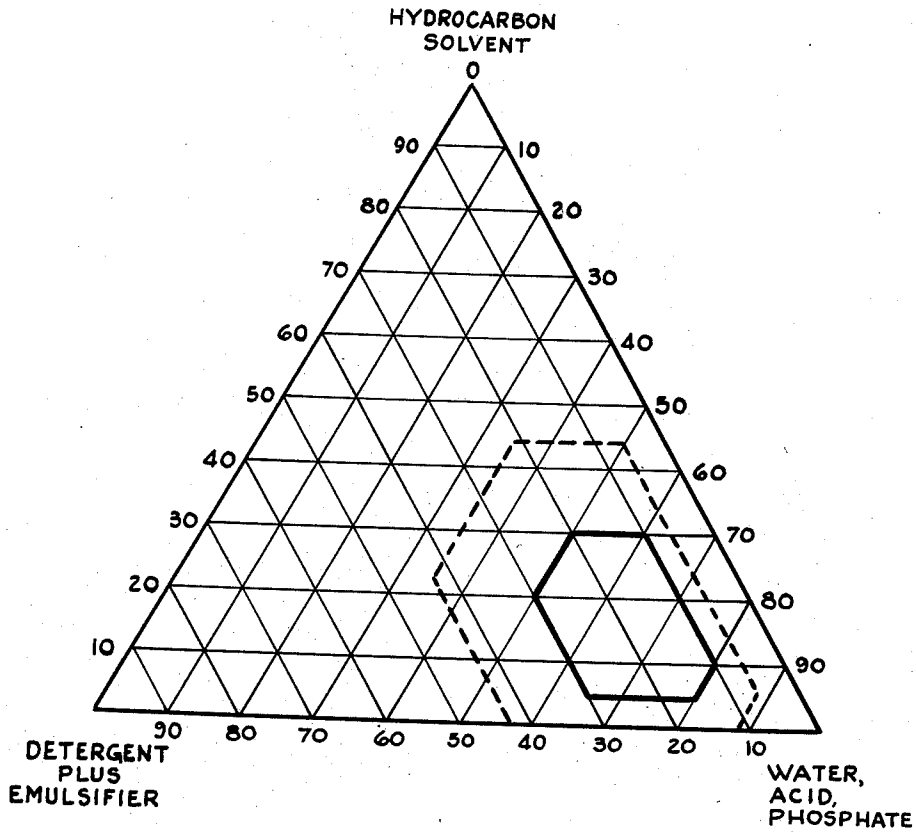
Oct. 21, 1958 C. W. SMITH 2,857,298

COMPOSITION AND METHOD FOR CLEANING AND PHOSPHATING METAL

Filed Sept. 16, 1957



INVENTOR
CHESTER W. SMITH

KOTTS & SHERIDAN
ATTORNEYS

United States Patent Office 2,857,298
Patented Oct. 21, 1958

2,857,298

COMPOSITION AND METHOD FOR CLEANING AND PHOSPHATING METAL

Chester W. Smith, Wayne County, Mich.

Application September 16, 1957, Serial No. 684,286

20 Claims. (Cl. 148—6.17)

This invention relates to the cleaning, phosphating and passivating of metal parts and is a continuation-in-part of my prior filed application Serial No. 328,795 filed December 30, 1952, now abandoned.

In many metal fabricating industries it is desirable to clean heavy grease, tar, drawing compounds, metallic oxides, and the like from metal parts and to apply a protective rust resistant phosphate coating to the parts preparatory to painting or other operations. Heretofore the cleaning and phosphating has necessitated two major operations comprising first cleansing and rinsing the parts, then the phosphating. The great demand by industry for a stable solution which would reduce the above two operations to a single process has long occupied the research facilities of the major chemical companies supplying metal phosphating and cleaning solutions. All attempts heretofore to combine the hydrocarbon solvent and the phosphating reagents satisfactorily in a single formulation have, however, resulted in an unstable solution from which the water miscible and oil soluble components would separate into two distinct layers or form a typical emulsion. Often a third layer would form containing some of the emulsifier ingredients. In consequence the cleaning actions of such formulations have been erratic and unsatisfactory.

A number of liquid preparations are available which combine a light cleaning action with a phosphating action. Such preparations commonly comprise minor proportions of a detergent or a water miscible solvent such as an alcohol or glycol. Such liquids are satisfactorily employed for phosphating metal parts which are not heavily soiled and usually depend upon application at elevated temperature and brushing or scrubbing for the removal of even light oil films. These preparations are in fact not intended primarily for cleaning, the detergent or solvent being added to assure that the acid phosphating reagents will penetrate to and wet the metal surface to be phosphated.

Attempts to provide homogeneous solutions for both cleaning and phosphating in a single operation have involved the use of major quantities of alcohols, often including minor proportions of the hydrocarbon solvent and still lesser proportions of the phosphating ingredients. Such preparations are inherently unsatisfactory because of the large quantity of alcohol solvent required in comparison to the quantity of water that can be feasily brought into stable solution with the hydrocarbon solvent. Not only does the high alcohol content constitute a serious fire hazard but the phosphoric acid concentration in the resulting proportionate low water content is usually too strong for the proper phosphating action and unduly etches the metal parts under treatment. Furthermore the solubilizing effect of the high alcohol content is readily upset by evaporation of the alcohol, rendering the solution unstable. Attempts heretofore to reduce the high alcohol content have resulted in separation of the water soluble ingredients from the hydrocarbon solvents,

particularly at the elevated temperature usually required for heavy cleaning.

An important object of the present invention is to provide a clear to opalescent, non-toxic liquid preparation of improved stability and effectiveness for simultaneously cleaning metallic parts and applying a protective rust resistant metallic phosphate coating thereto, the preparation being particularly effective at room temperatures for cleaning heavy oils, greases and tarry deposits, metallic oxides, drawing and lapping compounds, and like soils with a minimum of brushing and being adapted to be effectively applied simply by spraying the preparation on the parts to be treated, or by dipping the parts into the preparation, and thereafter rinsing the parts in a stream of clear cold water.

Another object is to provide a stable liquid preparation of the foregoing character which does not depend upon a preponderance of alcohol or other volatile solvents for its stability and which is readily miscible in cold water at ordinary faucet temperatures approximating 40° F. and is susceptible to being rinsed cleanly from the treated part in a stream of cold water.

Another object of the invention is to provide in the presence of a hydrocarbon solvent a composition with a sufficiently high proportion of water to serve as a vehicle for a relative large quantity of phosphoric acid at a relatively low concentration as compared with prior compositions where the minor proportions of water forced one to compromise between an aqueous phosphoric acid solution which had a sufficient quantity of acid for complete reaction with the metal but too high a concentration and, on the other hand, an aqueous phosphoric acid solution which had the right concentration of acid for a controlled reaction but an insufficient quantity for complete reaction.

Another object is to provide a stable preparation of the foregoing character containing a chromate rust inhibitor, whereby oxidation of the iron phosphate coating on the treated part from ferrous to ferric phosphate is facilitated to assure a more durable and satisfactory phosphate coating and whereby rusting of the treated steel parts while drying is retarded.

I have now found that the foregoing and related objects can be secured in a composition comprising essentially about 50–80 percent of an aqueous acidic phosphating solution of pH of about 2–3 and free phosphoric acid of about 0.3–0.6 percent by weight of the total preparation; about 4–30 percent of a hydrocarbon solvent for grease and oil; about 10–30 total percent of an emulsifier and an alkali metal alkyl benzene sulfonate detergent; wherein said hydrocarbon solvent has an initial boiling point of about 200°–450° F. and a final boiling point below about 700° F. and wherein the alkyl benzene sulfonate portion of said detergent has a molecular weight of about 290–420.

A major difficulty in the formulation of a solution of the character described has been the successful combination of the detergent, solvent, and emulsifier with the desired quantity of the aqueous phosphating solution. For efficient phosphating, a pH range between 2 and 3 and preferably approximately 2.5 is desired in a solu- containing not less than approximately .3% and up to .6% free phosphoric acid by weight of the total preparation. The providing of a sufficient quantity of phosphate ions for an effective phosphating capacity without exceeding the foregoing requirements requires a major proportion of water in the composition.

It is usually desirable to increase the concentration of phosphate ions above that supplied by phosphoric acid at a suitable pH. This can be done by adding a soluble phosphate such as an alkali metal phosphate. For ex-

ample about 2 parts by weight of tetra sodium pyrophosphate for each 3 parts by weight of phosphoric acid is a particularly effective proportion. Smaller quantities of phosphate reduce the efficiency of the phosphating reaction but phosphoric acid alone can carry out the phosphating reaction.

The detergents used in the composition of the invention are anionic and are of the alkali metal alkyl benzene sulfonate type. An alkyl benzene sulfonic acid of molecular weight of about 290 to 420 may be neutralized with an alkali metal hydroxide to yield detergents contemplated by the invention. Similarly, ammonium and amines can be substituted for the alkali metal and both ammonium and amines are equivalent to and are included herein under the term "alkali metal." Thus, by way of example, sodium alkyl benzene sulfonates, ammonium alkyl benzene sulfonates, and triethanolamine alkyl benzene sulfonates are suitable. The "benzene" portion of the detergent can include a number of substituents: for example; a methyl group as appears in toluene, a hydroxy group as appears in phenol, and the like.

The emulsifying agent can comprise a water soluble amine or alkali metal saponified fatty acid, such as potassium tall oil soap; the sodium and potassium salts of oleic, palmitic, or stearic acid, or the like; and will preferably amount to between approximately 2 to 5 parts by weight in Formula I. These emulsifiers are referred to herein as alkali metal soaps. Although this total quantity of emulsifier could be more than doubled without impairing the stability of the formulation, approximately 3 parts have been found satisfactory for phosphating and cleaning with the amount of hydrocarbon solvent specified.

Although I prefer an alkali metal soap as the emulsifier the invention can use any of the known emulsifiers of the art, employed individually or in combination, such as petroleum sulfonate, alkyl sulfate or sulfonate, esters of alkali metal neutralized sulfosuccinate, or such emulsifiers as represented by the following formulae wherein R represents an alkyl group and x ranges from 5 to 50:

$RCOO(CH_2CH_2O)_xH$ (fatty acid esters)

$RCON(CH_2CH_2O)_xH_2$ (fatty acid amides)

$RN(CH_2CH_2O)_xH_2$ (tertiary amines)

The preferred solvents for grease, heavy oil, tarry residues, and the like in the compositions of the invention are all water immiscible and will readily dissolve these substances at normal room temperature. Chlorinated solvents of the foregoing character can be used in a closed system but are objectionably toxic in open systems. A hydrocarbon solvent is accordingly preferred, such as kerosene or the aromatic solvents of petroleum or coal tar origin which are effective grease solvents. The initial boiling points of such solvents which can be safely and effectively handled range from about 200° F. to about 450° F. and the final boiling point is below about 700° F. For most satisfactory solvent action I prefer hydrocarbon solvents of which at least 75% boil in the 300°–350° F. range.

In preparing the present invention, the aqueous acid phosphating reagents, emulsifier, and detergent are first mixed in the approximate proportions set forth. Thereafter, unless the quantity of solvent required has been previously determined, this quantity can be determined in a trial batch by adding the solvent slowly with constant agitation of the mixture until a clear stable homogeneous solution or liquid is formed. If desired, additional solvent can be added with stirring until cloudiness is first noted.

A small quantity of a chromium ion in the formulation is important as a passivator to inhibit rusting of the treated steel parts, particularly if the parts are not dried quickly, and to accelerate oxidation of the phosphate coating from ferrous to ferric phosphate, thereby to effect a superior protective coating. Heretofore the chromium ion has not been added to a stable phosphating and cleaning solution, so that an additional operation of spraying with a rust inhibiting chromate solution has been necessary after the phosphating operation. In the present instance, although the chromium ion is not critical to the stability of the solution, the chromium ion in the proportion specified does not render the solution unstable. Accordingly the present invention permits combining the three operations of cleaning, phosphating, and passivating in a single operation.

The chromium ion may be a chromate or dichromate or may be added as the trivalent ion as in chromium chloride. The chromium compound may be added in a range of about .01% to about 0.1%. Although sodium dichromate is preferred for the source of the chromate radical in the cleaning and phosphating solution concerned herein, corresponding amounts of the chromium ion can be supplied from other sources, such as chromic acid, other alkali metal dichromates or chromates, trivalent chromium salts such as chromium chloride, and the like. The term compounds providing an ion from the class consisting of chromium and chromate includes all such sources.

I have also found that the passivating action of a chromium ion can be enhanced by a molybdenum ion. A soluble molybdenum compound can be added in a variety of forms such as molybdic oxide, sodium molybdate, and the like. The use of molybdenum in the compositions of the invention yield a heavier phosphate coating of greater corrosion resistance. The resulting coating is particularly resistant to flash rusting. The coating is also more uniform and of a beautiful blue color.

The molybdenum compound is best used in a proportion of about 0.02–0.2 percent by weight but the limits are not critical. In general best results are secured when the molybdenum compound is used in about double the proportion of the chromium compound.

Example 1

Ingredient:	Parts by weight
Phosphoric acid (anhydrous)	3
Tetra sodium pyrophosphate	2
Sodium dodecyl benzene sulfonate	13
Potassium oleate	3
Hydrocarbon	21
Sodium dichromate	0.05
Water	58

The above composition may also be defined as:

	Parts by weight
Aqueous acidic phosphate solution	63
Hydrocarbon solvent	21
Detergent plus emulsifier	16
Chromium ion	0.05

Since the above proportions add up to 100 parts by weight the numbers may also be considered as weight percent and the term "percent" as used herein is intended to mean "weight percent."

The composition of Example 1 was found to be clear, homogeneous and stable. Upon being applied to a steel surface it simultaneously removed the grease and soil from the surface, evenly phosphated the surface, and passivated the surface.

Example 2

Ingredient:	Parts by weight
Phosphoric acid	2
Triethanolamine dodecyl toluyl sulfonate	20
Sodium palmitate	5
Hydrocarbon	23
Water	50

The above composition may also be defined as:

	Parts by weight
Aqueous acidic phosphate solution	52.5
Hydrocarbon solvent	24
Detergent plus emulsifier	23.5

The above composition, when mixed, was found to be clean, homogeneous and stable. Upon being applied to steel surfaces it simultaneously removed the grease and grime therefrom and evenly phosphate the treated surface.

Example 3

Ingredient:	Parts by weight
Phosphoric acid	3
Trisodium phosphate	1
Ammonium dodecyl benzene sulfonate	8
Petroleum sulfonate	4
Hydrocarbon	14
Potassium dichromate	0.08
Molybdenum oxide	0.18
Water	70

The above composition may also be defined as:

	Parts by weight:
Aqueous acidic phosphate solution	74
Hydrocarbon solvent	14
Detergent plus emulsifier	12
Chromium ion	0.08
Molybdenum compound	0.16

The above composition, when mixed, was found to be clear, homogeneous and stable. Upon being tested on steel surfaces it simultaneously cleaned the metals, phosphated terms, and passivated them.

The above examples were repeated using a wide variety of alkali metal alkyl benzene sulfonates, emulsifiers and hydrocarbons in a wide variety of proportions in acidic aqueous phosphate solutions. Many of these were clear to opalescent, homogeneous, and stable and others were not. By plotting these compositions on a ternary diagram I found the satisfactory compositions could be clearly defined.

In this connection the accompanying drawing is a ternary diagram whose coordinates are in weight percent: hydrocarbon solvent; water plus acid and phosphate; and detergent plus emulsifier.

The solid line encloses the area of those compositions which meet the objectives of the present invention. The dotted line encloses an area of approximately clear compositions.

I claim:

1. An opalescent to clear, stable liquid compositions for simultaneously cleaning and phosphating metal surfaces consisting essentially of about 50–80 percent of an aqueous acidic phosphating solution; about 4–30 percent of a hydrocarbon solvent for grease and oil; and about 10–30 total percent of an emulsifier and an alkali metal alkyl benzene sulfonate detergent, wherein said hydrocarbon solvent has an initial boiling point of about 200°–450° F. and a final boiling point below about 700° F. and wherein the alkyl benzene sulfonate portion of said detergent has a molecular weight of about 290–420.

2. An opalescent to clear, stable liquid composition for simultaneously cleaning, phosphating and passivating metal surfaces consisting essentially of about 50–80 percent of an aqueous acidic phosphating solution; about 4–30 percent hydrocarbon solvent for grease and oil; about 0.01–0.1 percent of a compound providing an ion from the class consisting of chromium and chromate; and about 10–30 total percent of an emulsifier and an alkali metal alkyl benzene sulfonate detergent, wherein said hydrocarbon solvent has an initial boiling point of about 200°–450° F. and a final boiling point below about 700° F. and wherein the alkyl benzene sulfonate portion of said detergent has a molecular weight of about 290–420.

3. An opalescent to clear, stable liquid composition for simultaneously cleaning and phosphating metal surfaces consisting essentially of about 50–80 percent of an aqueous acidic phosphating solution; about 4–30 percent hydrocarbon solvent for grease and oil; about 2–5 percent of an emulsifier and about 5–28 percent of an alkali metal alkyl benzene sulfonate wherein said hydrocarbon solvent has an initial boiling point of about 200°–450° F. and a final boiling point below about 700° F. and wherein the alkyl benzene sulfonate portion of said detergent has a molecular weight of about 290–420.

4. The composition according to claim 1 wherein the detergent is a triethanolamine alkyl benzene sulfonate.

5. An opalescent to clear, stable liquid composition for simultaneously cleaning and phosphating metal surfaces comprising essentially about 50–80 percent of an acidic aqueous phosphate solution at pH of about 2–3; about 4–30 percent of a hydrocarbon solvent for grease and oil; and about 10–30 total percent of an emulsifier and an alkali metal alkyl benzene sulfonate detergent, wherein said hydrocarbon solvent has an initial boiling point of about 200°–450° F. and a final boiling point below about 700° F. and wherein the alkyl benzene sulfonate portion of said detergent has a molecular weight of about 290–420.

6. An opalescent to clear, stable liquid composition for simultaneously cleaning and phosphating metal surfaces comprising essentially about 50–80 percent of an acidic aqueous phosphate solution having free phosphoric acid in a proportion of about 0.3–0.6 percent by weight of the total composition; about 4–30 percent of a hydrocarbon solvent for grease and oil; and about 10–30 total percent of an emulsifier and an alkali metal alkyl benzene sulfonate detergent, wherein said hydrocarbon solvent has an initial boiling point of about 200°–450° F. and a final boiling point below about 700° F. and wherein the alkyl benzene sulfonate portion of said detergent has a molecular weight of about 290–420.

7. An opalescent to clear, stable liquid composition for simultaneously cleaning and phosphating metal surfaces comprising essentially about 50–80 percent of an acidic aqueous phosphate solution in which about 3 such percent are anhydrous phosphoric acid and about 2 such percent are an alkali metal phosphate; about 4–30 percent of a hydrocarbon solvent for grease and oil; and about 10–30 total percent of an emulsifier and an alkali metal alkyl benzene sulfonate detergent, wherein said hydrocarbon solvent has an initial boiling point of about 200°–450° F. and a final boiling point below about 700° F. and wherein the alkyl benzene sulfonate portion of said detergent has a molecular weight of about 290–420.

8. An opalescent to clear, stable liquid composition for simultaneously cleaning, phosphating, and passivating metal surfaces comprising essentially about 50–80 percent of an acidic aqueous phosphate solution at a pH of about 2–3; about 4–30 percent of a hydrocarbon solvent for grease and oil; about 0.01–0.1 percent of a compound providing an ion from the class consisting of chromium and chromate; and about 10–30 total percent of an emulsifier and an alkali metal alkyl benzene sulfonate detergent, wherein said hydrocarbon solvent has an initial boiling point of about 200°–450° F. and a final boiling point below about 700° F. and wherein the alkyl benzene sulfonate portion of said detergent has a molecular weight of about 290–420.

9. An opalescent to clear, stable liquid composition for simultaneously cleaning, phosphating, and passivating metal surfaces comprising essentially about 50–80 percent of an acidic aqueous phosphate solution having free phosphoric acid in a proportion of about 0.3–0.6 percent by weight of the total compositions; about 4–30 percent hydrocarbon solvent for grease and oil; about 0.01–0.1 percent of a compound providing an ion from the class consisting of chromium and chromate of an

ion of chromium; and about 10–30 total percent of an emulsifier and an alkali metal alkyl benzene sulfonate detergent, wherein said hydrocarbon solvent has an initial boiling point of about 200°–450° F. and a final boiling point below about 700° F. and wherein the alkyl benzene sulfonate portion of said detergent has a molecular weight of about 290–420.

10. An opalescent to clear, stable liquid composition for simultaneously cleaning, phosphating, and passivating metal surfaces comprising essentially about 50–80 percent of an acidic aqueous phosphate solution in which about 3 such percent are anhydrous phosphoric acid and about 2 such percent are an alkali metal phosphate; about 4–30 percent of a hydrocarbon solvent; about 2–5 percent of an emulsifier; about 5–28 percent of alkali metal alkyl benzene sulfonate; and about 0.05 percent of an alkali metal chromate; wherein said hydrocarbon solvent has an initial boiling point of about 200°–450° F. and a final boiling point below about 700° F. and wherein the alkyl benzene sulfonate portion of said detergent has a molecular weight of about 290–420.

11. In a method for cleaning oily deposits from a metal surface and simultaneously applying a phosphate coating to said surface, the steps of treating said surface with the composition of claim 1 and thereafter rinsing said surface with water.

12. In a method for cleaning oily deposits from a metal surface, simultaneously applying a phosphate coating to said surface and simultaneously passivating said surface, the steps of treating said surface with the composition of claim 2 and thereafter rinsing said surface with water.

13. In a method for cleaning oily deposits from a metal surface and simultaneously applying a phosphate coating to said surface, the steps of treating said surface with the composition of claim 3 and thereafter rinsing said surface with water.

14. In a method for cleaning oily deposits from a metal surface and simultaneously applying a phosphate coating to said surface, the steps of treating said surface with the composition of claim 4 and thereafter rinsing said surface with water.

15. In a method for cleaning oily deposits from a metal surface and simultaneously applying a phosphate coating to said surface, the steps of treating said surface with the composition of claim 5 and thereafter rinsing said surface with water.

16. In a method for cleaning oily deposits from a metal surface and simultaneously applying a phosphate coating to said surface, the steps of treating said surface with the composition of claim 6 and thereafter rinsing said surface with water.

17. In a method for cleaning oily deposits from a metal surface and simultaneously applying a phosphate coating to said surface, the steps of treating said surface with the composition of claim 7 and thereafter rinsing said surface with water.

18. In a method for cleaning oily deposits from a metal surface, simultaneously applying a phosphate coating to said surface, and simultaneously passivating said surface, the steps of treating said surface with the composition of claim 8 and thereafter rinsing said surface with water.

19. An opalescent to clear, stable liquid composition for simultaneously cleaning, phosphating and passivating metal surfaces consisting essentially of about 50–80 percent of an aqueous acidic phosphating solution; about 4–30 percent hydrocarbon solvent for grease and oil; about 0.01–0.1 percent of a chromium ion; about 0.02–0.2 percent of a soluble molybdenum compound; and about 10–30 total percent of an emulsifier and an alkali metal alkyl benzene sulfonate; wherein said hydrocarbon solvent has an initial boiling point below about 200°–450° F. and a final boiling point below about 700° F. and wherein the alkyl benzene sulfonate portion of said detergent has a molecular weight of about 290–420.

20. In a method for cleaning oily deposits from a metal surface, simultaneously applying a phosphate coating to said surface and simultaneously passivating said surface, the steps of treating said surface with the composition of claim 19 and thereafter rinsing said surface with water.

References Cited in the file of this patent

UNITED STATES PATENTS

2,396,776	Douty et al.	Mar. 19, 1946
2,479,423	Snyder	Aug. 16, 1949
2,585,127	Holman et al.	Feb. 12, 1952
2,744,555	Nicholson et el.	May 8, 1956