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CLEANING COMPOSITION

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This invention relates to the art of cleaning metals, and is particularly concerned with the provision of an improved cleaning composition for this purpose. It is especially useful in the cleaning of ferrous metal surfaces, although not limited thereto.

The objects of the invention will be better understood and more fully appreciated if certain of the practices now familiar to the art are briefly mentioned. For instance, it has long been the practice to clean and prepare surfaces of iron, steel, aluminum, etc. for the reception of paint or the like by the use of solutions of phosphoric acid containing one or more solvents together with compatible wetting agents, emulsifying agents, inhibitors of acid attack on the metal, etc. Among the solvents so employed may be mentioned alcohols from methanol to amyl alcohols, inclusive, ketones, such as acetones, methyl ethyl ketone, and diacetone alcohol; alcohol-ethers, such as the ethers of ethylene glycol or diethylene glycol; and many more from other classes. These are grease solvents and are both water soluble or miscible and oil soluble, and their presence in cleaning solutions tends to dissolve the oil or grease on the work to be cleaned, thereby diluting and thinning it and lowering its surface tension. This produces a tendency for the oily or greasy contaminant to draw up into droplets so that it can be more readily emulsified by mechanical action.

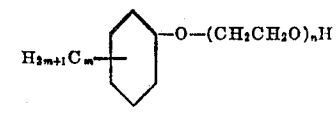
Among the "wetting agents" which have been used heretofore are sulfated oils such as "sulfonated" castor oil, cottonseed oil, etc.; sulfonated hydrocarbons, e. g., alkylated naphthalene sulfonic acids; sulfated alcohols of six or more carbon atoms, of straight or branched chain; sulfonated esters as of succinic acid, etc. These wetting agents also exhibit more or less emulsifying powers although other emulsifying agents have generally been employed in cleaning compositions of this general nature such, for example, as water soluble gums like gum arabic and gum tragacanth; gelatine or glue; molasses; soap bark extracts or purified saponins; and numerous others.

In connection with cleaners of the general nature just described it has been our experience that cleaning compositions which include solutions of phosphoric acid containing only the wetting and/or emulsifying agents are not capable of completely removing the greasy or oily matter together with the dirt from the surface of the metal, and that it is only where adequate quantities of the water miscible solvents are present that the compositions are capable of reasonably thoroughly removing the grease and the dirt. Apparently this is due to the fact that the wetting agents per se seem to cause the solution to spread over the top of the greasy surface so that even strong mechanical action is not generally able to cause the solution to penetrate the grease and to spread over the metal therebeneath without the addition of the water miscible grease solvents mentioned above.

However, the water miscible grease solvents ordinarily in use have now become of strategic importance in the war effort, and therefore are not readily available for many of the purposes for which they were formerly employed.

With the foregoing in mind the principal objects of our invention are to provide a cleaner which will remove oxide, dirt and greasy or oily substances while at the same time putting the surface of the metal in the best possible condition for the reception of an organic protective or finish coating, such as paint, varnish, lacquer, japan and the like; to provide a metal cleaner of greatly improved grease, oil and dirt removing efficiency which does not require the relatively scarce and expensive water miscible solvents above discussed; to produce a relatively much more concentrated and more highly dilutable cleaning composition than has heretofore been possible with compositions known to the art wherein large volumes of water miscible solvents are included; to provide a cleaner which is exceptionally useful in removing heavy viscous greases from metal surfaces to which end we employ water immiscible solvents emulsified with phosphoric acid solutions; to produce a cleaner which can be applied by means of a spray without the troublesome foaming which, under spraying conditions, would otherwise be associated with the presence of the emulsifying agent; to provide a cleaning composition which, because of its unusually concentrated character, can be more readily and cheaply packaged and transported; and in general to improve the efficiency, availability and all-round usefulness of a cleaner of this type.

We have discovered that remarkable cleaning action may be obtained on ordinary oily or greasy surfaces by means of an aqueous phosphoric acid solution which includes small quantities of water soluble, non-ionic emulsifying agents such as the tertiary alkylarylpolyglycols represented by the general formula:



in which formula m is at least 8, C_mH_{2m+1} is a tertiary alkyl group and n equals 10 or more, depending on the nature and weight of the substituent groups. Compounds having a polyglycol chain of such length are appreciably soluble in water and the water solubility remains appreciable to very high values of n (at least 100 or more).

An admixture of dilute phosphoric acid containing a small amount of emulsifying agent of the above type wets oily steel readily; when applied freely with a brush or rag, for example, the oil or light grease on the surface, is rapidly emulsified and removed from the surface together with any adhering dirt. Simultaneously, the acid solution thoroughly and evenly wets the surface of the metal and dissolves light oxide or rust therefrom. If the surface be now washed with water, it will be found to be completely grease free and will exhibit no "water break." The cleanliness of the surface obtained is remarkable and, in our experience, is superior to that obtainable with any previous cleaner of the phosphoric acid type, even when these previous types contain substantial amounts of oil solvent.

An example of a concentrated composition which may be used for cleaning ferrous or aluminiferous surfaces, after dilution with water, is the following:

Formula No. 1

Phosphoric acid, 75%	gallon	0.9500
Emulsifying agent	pound	0.16
Water, to make	gallon	1.000

The amount of water used in diluting the above formula depends on the amount of rust or oxide to be removed from the surface, as well as on the kind and amount of grease present.

In general, from one to eight volumes of water per volume of Formula No. 1 should be added in diluting the material for use, although we have found that for ordinary sheet steel articles, such as automobile or truck bodies, refrigerators, etc., about four volumes of water to one of Formula No. 1 is usually the most satisfactory.

The diluted material may be applied to the surface to be cleaned by brushing, spraying, flowing or by dipping the work into the solution. In most cases, removal of oil will be facilitated by gently rubbing the surface, as with a brush or rag, or by forcefully applying the solution to the metal, as by spraying.

The surface is then washed with water, and dried by any convenient means, whereupon it will be found to be very clean and ready for painting, etc.

It may be noted that very clean steel surfaces such as are produced by the action of our improved cleaners, rapidly acquire a film of oxide if allowed to stand wet with water. Rapid drying is, therefore, advisable after the cleaning operation. However, oxide formed on the surface after cleaning with our novel cleaner is "inert," i. e. it contains no rust-stimulative material and is thus innocuous under paint or the like.

For exceptionally greasy work or when the cleaning solution is to be applied to the work by forceful spraying in a recirculating system we prefer to use a material in which is emulsified a water immiscible solvent such as a petroleum naphtha according to the following example:

Formula No. 2

Phosphoric acid, 75%	gallon	0.1000
Emulsifying agent	pound	0.12
Stoddard solvent (petroleum fraction boiling between 300–400° F.)	gallon	0.6250
Water, to make	do	1.0000

The above concentrated material is violently stirred, passed through a homogenizer, or otherwise brought to a uniform emulsion by ordinary known means.

For use in a recirculating spray washing machine, it is diluted with from 3 to 19 volumes of water and forcefully sprayed upon the work to be cleaned, for about 15 to 60 seconds, more or less. The run off solution is collected and reused. After rinsing and drying the work will be found to be thoroughly cleaned.

The emulsified solvent in this material has the effect of diluting, and thus thinning out and making easier to remove any heavy grease on the surface of the work. Moreover, the strong foaming tendency of the solution is repressed by the solvent, thus preventing the solution from foaming out over the top of the spray collecting tank.

The diluted solutions of both Formulas No. 1 and No. 2 may be used either at room temperature or at elevated temperature. More rapid cleaning action is obtained, of course, at elevated temperatures which may be as high as the boiling point of the diluted phosphoric acid or of the solvent, whichever is the lower.

It must be noted, however, that it may involve some fire hazard to operate the cleaning solution above the flash point of the solvent used. This can be avoided, of course, by the use of non-inflammable solvents, as noted below.

The above examples are to be taken, qualitatively and quantitatively, as illustrative but not as limiting the scope of the invention.

For instance, the amounts of phosphoric acid and emulsifying agent of the type described may be varied within wide limits without departing from the spirit of the invention. If the work to be cleaned is very rusty, or if considerable etching of the surface is desirable, the phosphoric acid concentration is maintained high (up to 70% by volume of 75% phosphoric acid or even more, if desired, in the cleaner as diluted for use). If the work has little greasy or oily contamination the emulsifier concentration need not exceed 0.05% or even less.

On the other hand, for work which is not rusty or need not be etched, phosphoric acid concentrations as low as 0.5% by volume of 75% H_3PO_4, or even less, may be sufficient. If the work is very greasy the cleaning solution may contain as high as 2% or even more of emulsifying agent, although more than 0.5% would rarely be required.

In formulations including water-immiscible solvents like the Stoddard solvent above mentioned, a great variety of such is permissible. The only limitation on the water-immiscible solvents which may be selected is that they must be good grease solvents, and that they must not be too volatile at the temperature at which the cleaner is to be used.

As examples of water-immiscible solvents which have been found useful are: hydrocarbon solvents such as toluene, petroleum spirits of various boiling ranges, hydrogenated petroleum solvents, high-flash coal tar naphtha, decahydronaphthalene, pine oil, chlorinated hydrocarbons such as carbon tetrachloride, trichlorethylene, tetrachloroethane, etc.; and many others.

The chlorinated solvents may be used where the fire hazard attendant upon the use of inflammable solvent is serious.

The amount of water-immiscible solvent, on the one hand, in relation to the phosphoric acid and the emulsifying agent, on the other hand, may vary over a considerable range subject, of course, to the limitations imposed by the total quantity

of the latter two which may be required for the particular work in hand.

Although, in the interest of economy of storage space and reduction in transportation costs, it is both preferable and desirable to prepare our novel cleaner in the form of a concentrated admixture capable of relatively high dilution before use, it will be obvious that there is no reason why acid, emulsifying agent and/or solvent may not be separately added to the diluted material to alter their relative proportions, if necessary.

The emulsifying agents which we have found useful in the present invention dissolve in water to produce foamy solutions of low surface tension and great emulsifying power for oily matter in water. The compounds are not ionized in water and when used in cleaners of the type described are readily rinsed from metal surfaces together with the emulsified grease, suspended dirt, excess acid, reaction products of the acid and the metal, etc., leaving behind no deleterious or rust-stimulative ions. Such emulsifying agents are truly non-ionic, and we prefer to describe the useful species of agents of the class under discussion as water-soluble, non-ionic emulsifying agents of the class of polyethyleneglycols substituted in one terminal hydroxyl group with an alkyl-aryl radical.

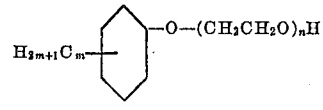
In contradistinction to the desired materials, similar compounds of low chain length such for example as alpha, alpha, gamma, gamma-tetramethylbutyl-phenoxy-ethanol are insoluble oils. They can be "solubilized" by introducing polar groups such as HSO_3 or HSO_4 into their molecules, but such polar groups make the resulting compounds ionic in nature, i. e. they yield charged ions when dissolved in water. Such ionic compounds are not suitable for this invention. Although they will wet and emulsify well, they may leave behind, on work cleaned with a solution containing them, traces of rust-stimulative anions. We thus wish to limit ourselves to compounds of the class described which are non-ionic and are appreciably water soluble, per se.

A wide variety of suitable materials is available to the chemist. They may be prepared, in general, by treating the halides or halohydrins of the polyethylene-glycols with fatty acids, alcohols or phenols in the presence of alkali metal hydroxide or carbonates.

To our cleaning preparations as described hereinabove may be added, if desired, any compatible proportion of water miscible solvent, inhibitor, thickening agent, oil, etc., without departing from the spirit of the invention. Such additions are not ordinarily necessary, but may have usefulness for special applications.

We claim:

1. A solution for cleaning metal preparatory to painting including water, phosphoric acid, and tertiary alkylarylpolyglycol represented by the formula:



in which m is at least 8, C_mH_{2m+1} is a tertiary alkyl group and n equals at least 10.

2. The composition of claim 1 which also includes emulsified substantially water-insoluble grease solvent.

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