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DRY CLEANING DETERGENT COMPOSITION

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Int. Cl. C11d 1/37; D06l 1/02

ABSTRACT OF THE DISCLOSURE

An improved dry cleaning composition and method of using the same comprising an emulsion of water in a volatile dry cleaning solvent with a small amount of a dry cleaning assistant which is a detergent component. The detergent component (*a*) is generally classified as a neutralized alpha-sulfo fatty ester or amide which is usable per se in the dry cleaning composition or may be combined with certain minor proportions of (*x*) sulfated alkyl chalcophenol polyalkoxide condensates and/or with (*y*) neutralized sulfated alkoxylated fatty alcohols in addition with conventional additives such as lubricants, anti-static agents, etc.

This invention relates to improvements in dry cleaning, and more particularly, to improved compositions and methods for the dry cleaning of textile fabrics, and related fibrous materials.

It is well known that certain materials, particularly textile fabrics and similar fibrous materials, cannot usually be cleaned by means of ordinary soap and water for the reason that they tend to shrink, fade, and/or otherwise develop undesirable characteristics when they are wetted substantially with water. It is also known that the dry cleaning process has been developed for the purpose of cleaning such materials. In the dry cleaning process, a suitable volatile organic solvent such as Stoddard's solvent, trichlorethylene, perchlorethylene, naphtha or the like known volatile organic solvents are used and these solvents are applied to the textile fabric or other material to be dry cleaned by a process hereinafter referred to generically as "rinsing," but which generally involves recirculation or flowing of a stream of the solvent through a retainer or basket containing the material to be dry cleaned for a sufficient period of time to effect the desired cleaning thereof. Such solvents are effective in removing from the fabrics or other materials many grease or similar organic stains as well as dust and dirt which would ordinarily adhere to such grease stains. It is also known that it is preferable to disperse small amounts of water in the dry cleaning fluid or solvent, and this water is believed to carry out an additional function of assisting in the cleansing and removal of water-soluble stains such as those caused by sugary liquids, etc.

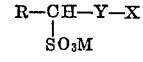
Although it is known that it is usually preferable to incorporate a small amount of water (ordinarily in emulsified form in the solvent) into the dry cleaning composition, the problems of controlling this amount of water so that it may suitably carry out its own function and will not simultaneously effect undesirable results have been complicated in recent times by the use of conventional coin operated dry cleaning units by the public generally. Although the commercial dry cleaner is quite skilled in his art and ordinarily operates with various process controls so that he may maintain a desired water or moisture concentration in his dry cleaning fluid, the present dry cleaning compositions still leave much to be desired in versatility of use even by the skilled commercial operator. On the other hand, the members of the public using coin operated dry cleaning devices make little or no effort to control the moisture content in the dry cleaning

fluid, the relative proportions of fabric to be cleaned in quantity of dry cleaning fluid, the relative proportions of dirt to be removed and quantity of dry cleaning fluid, or even the rinsing or cleansing time in the device. This indiscriminate use of dry cleaning fluids in publicly available coin operated dry cleaning units has resulted in a number of disappointments in the dry cleaning results obtained and has made necessary the development of much more versatile dry cleaning compositions than those heretofore available.

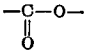
The instant invention provides a much more versatile dry cleaning composition, primarily by virtue of the selection of the detergent or "dry cleaning assistant" that is added thereto in small "detersive" quantities. Such use of certain detergents is known and is suggested in such prior art disclosures as Flett U.S. Patent No. 2,326,772 and others. The instant invention involves the use of novel dry cleaning compositions containing certain selected detergents which have been found to impart unusual versatility, detersive or cleansing effect, moisture tolerance, and the like desirable properties.

It is therefore an important object of the instant invention to provide an improved dry cleaning composition and method.

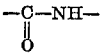
It is a further object of the instant invention to provide an improved dry cleaning composition comprising an emulsion of water in a volatile organic dry cleaning solvent and, as a dry cleaning assistant in a small detersive amount, a detergent component comprising (*a*) detergent having the formula:



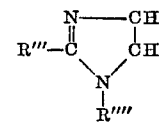
wherein Y is selected from the class consisting of



and



R is a C_4 to C_{20} fatty acid residue; X is selected from the group consisting of C_1 to C_{22} hydrocarbon, glyceryl, C_1–C_6 alkyl ether of glycerol, $(C_2$—C_4 alkoxy$)_nR'$ wherein *n* is an integer from 1 to 50 and R' is selected from the group consisting of H and C_1–C_6 alkyl groups; and M is selected from the group consisting of alkali metals, alkaline earth metals, ammonium, (C_2–C_4 alkylol) ammonium, (C_2–C_4 alkoxy)$_n$(C_2–C_4 alkylol) ammonium wherein *n* is an integer from 1 to 50, poly(C_2–C_4 alkylene) amines, and primary, secondary, tertiary and quaternary alkyl ammonium wherein the alkyl groups contain a total of two to twenty carbon atoms, C_{10} to C_{20} aliphatic (C_2–C_4 alkylol) amines, C_{10} to C_{20} alkyl-NH—$(CH_2)_m$ amines wherein *m* is an integer from 1 to 4 and imidazolines having the formula:



wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H; the minimum total number of carbon atoms in any C to C chain in X plus any C to C chain in M, plus the carbon chain in R being twelve; and it is also an object of the instant invention to provide an improved dry cleaning method using the foregoing composition with or without certain small detersive quantities of other detergents which will be described in detail herein.

The dry cleaning fluid or solvent composition which

forms the main bulk of the dry cleaning composition of the invention is conventional and well known. The solvent used may comprise a halogenated hydrocarbon or hydrocarbons using a C_1–C_6 alkane or alkene base that is halogenated with from a single halogen atom to the number of halogen atoms necessary to completely replace all of the hydrogens. Although any halogen may be employed for this purpose, including chlorine, fluorine, bromine and iodine, it is well known that the most conventional halogenatd hydrocarbons used for dry cleaning are chlorinated hydrocarbons. Even carbon tetrachloride (which is not ordinarily used now because of toxicity) may be used in the practice of the instant invention, but more commonly used halogenated hydrocarbons such as perchlorethylene, trichlorethylene, and the like are preferred. The halogenated hydrocarbons commercially available as the "Freon" solvent may also be used, but preferably the "Freon" solvent used is one having a boiling point at least as high as about room temperature. The material "Freon 113" has been suggested for dry cleaning purposes and this material may be used as the solvent in the practice of the instant invention. Other normally liquid materials, including the hydrocarbons may be used also as part or all of the dry cleaning solvent. The hydrocarbons used are preferably relatively volatile materials but liquid at room temperature, and these would have at least 5 carbon atoms in the molecule and may have as many as 16 to 20 carbon atoms in the molecule. Such materials may be aromatic, aliphatic, paraffinic, olefinic or even terpenic hydrocarbons. Preferably petroleum spirits (having C_6–C_7 paraffinic composition) and/or mineral spirits of the "Stoddard Solvent" type can be used.

The dry cleaning solvent may also contain a number of known additives. For example it may contain up to 10% of such known additives as ketones (acetone, methyl ethyl ketone, diethyl ketone, etc.), ethers (methyl ethyl ether, diethyl ether, etc.), alcohols (isopropyl alcohol, isobutyl alcohol, etc.), Cellosolves (glycol methyl ether, glycol ethyl ether, etc.), glycols (e.g. ethylene glycol, propylene glycol, etc.) and/or dialkyl sulfoxides (e.g. dimethyl sulfoxide, diethyl sulfoxide, etc.).

Another additive which may be incorporated in the dry cleaning solvent is formamide, which may be included in proportions up to 10%.

Other conventional additives which may be incorporated include conventional lubricants, such as paraffin waxes and/or paraffin oils. Anti-static agents such as polyglycols, fatty acid amides, etc. may also be incorporated.

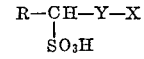
In essence, the dry cleaning solvent per se and any of the conventional additives currently employed may be used in the practice of the instant invention, and this particular component per se is old and well known and will be described generally hereinafter as a volatile organic dry cleaning solvent. As is well known, this solvent component is substantially immiscible with water.

The water in the conventional dry cleaning solvent is present in very small amounts and is generally understood to be in emulsified or dispersed form in the organic solvent.

Preferably, commercial dry cleaners have in the past tried to maintain their water or moisture content in the dry cleaning fluid in the neighborhood of about 0.25%. The instant invention contemplates the use of a moisture content this low, but it also permits the use of substantially higher moisture contents without harmful side effects. The amount of moisture present in the dry cleaning solvent is preferably an amount at least sufficient to carry out the desired cleansing effect on typical water-soluble soil, which may range from an amount as low as 0.1%, but is preferably a minimum of about 0.25%. In the practice of the instant invention, however, by selective use of the instant detergent materials, it is possible to tolerate much higher moisture contents in the solvent of as much as perhaps 5%. Preferably, moisture contents in the range of 1% to 2% are contemplated for use in the practice of the instant invention and the detergents disclosed herein for use in the practice of the instant invention may be selected so as to obtain the most effective detersive effect with water or moisture contents in this range. The reason for the comparatively high range of moisture content is, as already mentioned, that exact control of the moisture content and maintenance of the same at a minimum effective amount is not commercially feasible in connection with the typical coin operated dry cleaning units available to the public. In fact, the members of the public unskilled in the dry cleaning art will often attempt to dry clean moist clothing in these units and thereby add small but very appreciable amounts of water to the dry cleaning composition.

It will also be appreciated that the detergents disclosed herein may be used in dry cleaning compositions that are substantially "dry" in the sense that they contain little or no moisture. In such instances, the instant detergent has been found to effect extremely good cleansing or detersive efficiency.

Another essential ingredient used in the practice of the instant invention will be referred to herein as ingredient (*a*), which is a deteregnt having the formula:



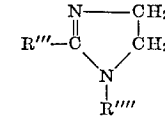
wherein Y is selected from the class consisting of

and

R is a C_4 to C_{20} fatty acid residue; X is selected from the group consisting of C_1 to C_{22} hydrocarbon, glyceryl, C_1–C_6 alkyl ether of glycerol, $(C_2$–C_4 alkoxy$)_nR'$ wherein *n* is an integer from 1 to 50 and R' is selected from the group consisting of H and C_1–C_6 alkyl groups; and M is selected from the group consisting of alkali metals, alkaline earth metals, ammonium, (C_2–C_4 alkylol) ammonium,

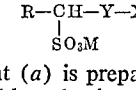
$$(C_2\text{–}C_4 \text{ alkoxy})_n(C_2\text{–}C_4 \text{ alkylol})$$

ammonium wherein *n* is an integer from 1 to 50, poly(C_2–C_4 alkylene) amines, and, primary, secondary, tertiary and quaternary alkyl ammonium wherein the alkyl groups contain a total of two to twenty carbon atoms, C_{10} to C_{20} aliphatic (C_2–C_0 alkylol) amines, C_{10} to C_{20} alkyl-NH—$(CH_2)_m$ amines wherein *m* is an integer from 1 to 4 and imidazolines having the formula



wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H; the minimum total number of carbon atoms in any C to C chain in X plus any C to C chain in M, plus the carbon chain in R being twelve.

Ingredient (*a*) is a neuaralized alpha-sulfo fatty ester or amide having the formula:

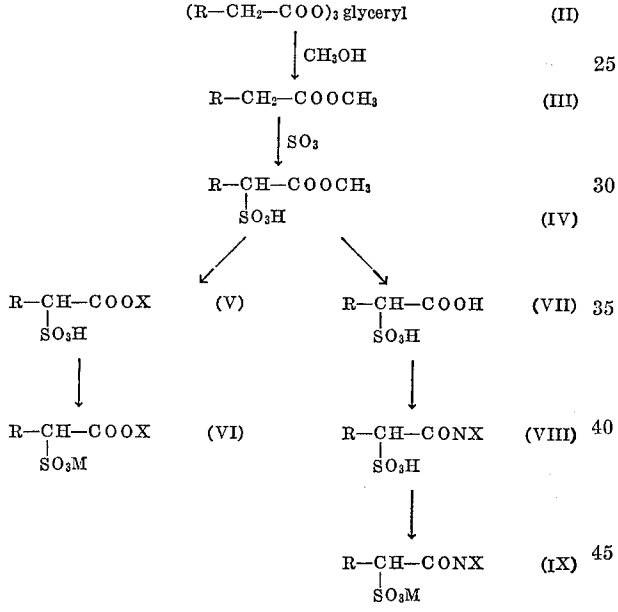


In general, ingredient (*a*) is prepared by the alpha-sulfonation of a fatty acid base having the general formula:

$$R\text{—}CH_2\text{—}COOH \qquad (I)$$

wherein R is a C_4–C_{20} fatty acid residue. The fatty acid "base" material (I) is preferably an ester at the time it is sulfonated, although it can be alpha-sulfonated as the acid per se (I). The radical R in the acid (I) is a typical C_4–C_{20} fatty acid residue, i.e. it is a fatty acid residue containing from 4 to 20 carbon atoms, so that the fatty acid base (I)

is that of a C_6–C_{22} fatty acid. Such fatty acids include hexanoic (caproic), heptanoic (enanthylic), octanoic (caprylic), nonanoic (pelargonic), decanoic (capric), undecanoic (hendecanoic), dodecanoic (lauric), tridecanoic; tetradecanoic (myristic), pentadecanoic, hexadecanoic (palmitic), heptadecanoic (margaric), octadecanoic (stearic), nonadecanoic, eicosanic (arachidic), heneicosanic; and docosanic (behenic) acids. The acids preferred in this use are palmitic and stearic, which makes the radical R preferably a C_{14}–C_{16} radical (i.e. tetradecyl to hexadecyl radical). The sulfo group replaces one of the hydrogens on the alpha carbon in the fatty acid base material (I) just described and this alpha-sulfonation may be carried out by sulfonating the fatty acid per se (in a suitable solvent) or a salt of the fatty acid (also in a suitable solvent) with a conventional sulfonating agent such as oleum, chlorsulfonic acid or sulfur trioxide (SO_3). Preferably, however, the alpha-sulfonation is carried out in the practice of the instant invention by the sulfonation of a suitable ester of the fatty acid, such as the methyl ester; and the general scheme for preparing the compounds of the instant invention is set forth hereinafter:



It will be seen from the foregoing that one may start with a suitable natural oil or fat that is a triglyceride of one of the foregoing fatty acids, which fatty acids are preferably saturated by an initial hydrogenation procedure, and then by transesterification replace the glyceryl group by a methyl group so as to obtain the methyl fatty acid ester (III). This is next sulfonated with SO_3 to obtain the alpha-sulfonic acid of the methyl ester (IV). This general procedure is preferred for use in the practice of the instant invention, for the reason that the methyl ester (III) is easily produced with economic advantage of producing the by-product glycerol; and the sulfonation of the methyl ester (III) with SO_3 is carried out without the necessity for any additional solvents or other complications so as to obtain the alpha-sulfonic acid (IV).

Next in the preparation of the ester compounds of the type employed in the practice of the instant invention, one may carry out additional transesterification, if desired, to replace the methyl group with another ester group X, which will be defined in further detail hereinafter, and neutralize the alpha-sulfo group with M, which will also be defined hereinafter. In contrast, if it is desired to prepare an amide for use in the practice of the instant invention, the initial alpha-sulfonated methyl ester (IV) is preferably converted to an alpha-sulfo fatty acid (VII), which in turn is converted to the amide (VIII) and neutralized to obtain the amide (IX) used in the practice of the invention.

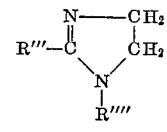
The neutralization of the alpha-sulfonic acid group is a conventional procedure for neutralizing sulfonic groups in detergent materials, which involves merely reaction with a suitably alkaline material to obtain the —SO_3M group, wherein M is an alkali metal (sodium and potassium being preferred, but lithium, etc, also being usable), ammonium, or alkaline earth (or any suitable neutralizing metallic ion from Group II of the Periodic Table, which includes magnesium, calcium, zinc, strontium, barium, etc.). In addition, the alpha-sulfonic acid group may be neutralized with a C_2–C_4 alkylol amine, so as to obtain the corresponding C_2–C_4 alkylol ammonium radical, wherein there may be one to three ethanol, propanol and/or butanol radicals attached to the ammonium N. Such radicals include monoethanol, diethanol, triethanol, monopropanol, dipropanol, etc., monobutanol, etc., ammonium radicals. In addition, the foregoing alkylol ammonium compounds may be reacted with C_2–C_4 alkylene oxides to obtain alkoxylated compounds, wherein the radical M will be a $(C_2$–C_4 alkoxy$)_n C_2$–C_4 alkylol ammonium group, wherein n is an integer from 1 to about 50. This group is prepared by conventional alkoxylation of the corresponding alkylol ammonium group, and it is possible to modify the hydrophobic-hydrophilic characteristics of the molecule by such ethoxylation procedure, although in the practice of the instant invention it is generally preferable to carry out such alkoxylation with approximately from 1 to about 50 mols of the alkylene oxide per mol of the alpha-sulfo compound. The alkylene oxide thus used is preferably ethylene oxide, although propylene or butylene oxide may be used in the practice of the instant invention; or mixtures thereof may be used.

It will also be appreciated that the radical M may be a primary, secondary, tertiary or quaternary alkyl ammonium radical, wherein the alkyl groups contain a total of 2 to 20 carbon atoms. Such alkyl radicals may range from ethyl, isopropyl, isobutyl, etc. up to C_{20} alkyl groups. The alkyl ammonium radical may be quaternary methyl ammonium, tertiary methyl ammonium, etc., but preferably this radical M used in the practice of the instant invention is a primary alkyl ammonium group such as isopropyl ammonium or isooctyl ammonium radical.

In addition the radical M may be derived from poly-(C_2–C_4 alkylene) amines, such as ethylene diamine, diethylene triamine, triethylene tetramine, etc., propylene diamine, butylene diamine, etc. In general, the polyamines contain ethylene, propylene or butylene carbon-to-carbon chains between amine groups, in a single diamine, or in repeating units in a polyalkylene polyamine compound.

The radical M may also be a C_{10}–C_{20} aliphatic (C_2–C_4 alkylol) amine, wherein the aliphatic group is an alkyl or alkenyl group derived from a typical fatty acid. A commercially available amine of this type which has been found to be particularly useful in the practice of the instant invention is oleyl diethanol amine.

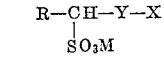
The radical M may also be derived from polyamines such as the commercially available "Duomeen" compounds. The polyamines of this type are C_{10}–C_{20} alkyl-NH—$(CH_2)_m$ amines wherein m is an integer from 1 to 4. A typical amine of this class is stearyl propylene diamine (i.e. C_{18}—$NHCH_2CH_2CH_2NH_2$). The radical M may also be derived from the imidazolines having the formula:



wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H. In the compounds of the invention the imidazoline used preferably has a C_{15}–C_{17} fatty alkyl group for the radical R''', and hydrogen or an ethanol group for the radical R''''. The imidazolines are

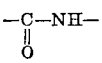
well known per se and these compounds are commercially available.

The ingredient (*a*) has, as previously indicated, the general formula:



wherein Y is selected from the class consisting of

and



The compound is thus an alpha-sulfo fatty acid ester or amide. The radical X may be a C_1–C_{22} group in that it may be methyl (which is preferred for use in the practice of the instant invention and which is also preferred for use in transesterification to obtain compound (III) from the starting material (II) hereinafter referred to). The radical X may also be ethyl, propyl, isopropyl, butyl, sec.-butyl, isobutyl, amyl, isoamyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, cosanyl, docosanyl, etc. and in each case the preferred procedure involves transesterification with the methyl compound using the corresponding ethyl, propyl, butyl, etc. alcohol to obtain the desired radical in the position X.

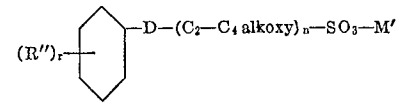
The radical X may also be a glyceryl or glceryl ether radical. Again, the methyl radical in the X position can be replaced by the glyceryl or glyceryl ether group (i.e. $-CH_2CH(OH)CH_2OH$ or $-CH_2CH(OH)CH_2O(C_1$–C_6 alkyl) groups), wherein the C_1–C_6 alkyl group just mentioned may be any of the typical alkyl groups such as methyl, ethyl, propyl, etc. up to hexyl. This may be done in, for example, the compound (V) merely by transesterification, or in the compound (IX) either by replacement of an alkyl group or replacement of a hydrogen on the amide group (by conventional synthesis).

In addition, the group X may be selected from (C_2–C_4 alkoxy)$_n$—H groups wherein *n* is an integer from 1 to 50. It will be appreciated that the methyl ester (III) may be converted to a corresponding ethylene glycol ester of the general Formula V merely by a propylene or butylene glycol ester (V). Any such C_2–C_4 alkylene glycol ester may then be used as such in the practice of the invention or it may be alkoxylated with from 1 to 50 mols of ethylene oxide, propylene oxide and/or butylene oxide. Again, the alkoxylation process is conventional per se. Such a compound might thus be referred to as the sodium alpha-sulfo ethylene glycol stearate ester, ethoxylated with 6 mols of ethylene oxide. In addition, the ethoxylated compound may be etherified with a C_1 to C_6 alkyl group, such as the methyl through hexyl group hereinbefore described.

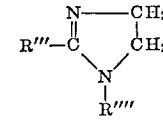
In the practice of the instant invention it has been found that there is a certain relationship concerning the total number of carbon atoms in various chains in the molecule of ingredient (*a*). For example, it has been found that the preferable minimum total number of carbon atoms in any carbon-to-carbon chain in X plus any carbon-to-carbon chain in M, plus the carbon chain in R should be twelve. In other words, in the computation of this total number of carbon atoms, if the radical X is an ethanol group that has been ethoxylated with 20 mols of ethylene oxide, the total number of carbon atoms in any carbon-to-carbon chain in the radical X is only two. If this radical had been reacted with propylene oxide, then the total number of carbon atoms in any chain would be only three. If, for example, the M radical were isopropyl ammonium, this radical would contain a total of three carbon atoms in the chain, so that in the last mentioned situation the total number of carbon atoms in such chains in the radicals X and M would be only six. This would require a minimum of six more carbon atoms in the alkyl group R, to make a total of twelve.

Although ingredient (*a*) may be used alone in the practice of the instant invention, as the detersive dry cleaning assistant, it is often advantageously used in combination with certain other detergents. Another detergent useful in the practice of the instant invention in this respect is herein referred to as ingredient or detergent (*x*).

Ingredient (*x*) is a detergent having the formula:



wherein R'' is a C_6–C_{12} alkyl group, *r* is an integer from one to two, *n* is an integer from one to fifty, D is selected from the group consisting of O and S; and M' is selected from amine bases consisting of C_{10} to C_{20} aliphatic mono-, di-, tri- and quaternary amines, C_{10} to C_{20} aliphatic (C_2–C_4 alkylol) amines, C_{10} to C_{20} alkyl-NH—$(CH_2)_m$ amines wherein *m* is an integer from 1 to 4 and imidazolines having the formula:

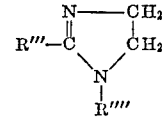


wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H.

Ingredient (*x*) is a sulfated alkyl chalcophenol polyalkoxide condensate wherein there are one to two C_6–C_{12} alkyl groups attached to the benzene nucleus. Such alkyl groups may be hexyl, heptyl, octyl, nonyl, decyl, or dodecyl, and preferably the groups are octyl or nonyl, as in octyl phenol, nonyl thiophenol, octyl thiophenol, nonyl phenol and dinonyl phenol. These basic phenol materials are used as starting materials for the preparation of detergent (*x*). The phenol "base" just referred to its alkoxylated with from 1 to 50 mols of an appropriate C_2–C_4 alkylene oxide. In general, the total number of alkylene oxide units in the molecule is less if ethylene oxide is used alone (usually in a range of from 1 to 20 mols), but if propylene oxide is used alone or in combination with ethylene oxide, as many as 15 mols total alkoxide units may be employed. The resulting alkoxylated material is then sulfated by conventional sulfation, and then neutralized by certain selected amines or amine "bases" to give the radical M'. The radical M' may be derived from C_{10}–C_{20} aliphatic mono-, di-, tri- and quaternary amines. The radical M' may also be derived from C_{10}–C_{20} aliphatic (C_2–C_4 alkylol) amines which are also available commercially. Typical amines which may be useful in the practice of the instant invention are oleyl diethanol amine, oleyl amine, lauryl amine, palmityl amine, stearyl amine, etc. Preferably the aliphatic radical in these amines is an alkyl or an alkenyl radical from a typical fatty acid source.

Another amine which may be used to obtain the radical M' is a typical commercially available C_{10}–C_{20} alkyl dialkylene amine. In the alkylene group there is preferably 1to 4 ethylene groups. A typical commercially available compound (i.e. "Duomeen") is stearyl propylene diamine.

Still another amine which may be used to obtain the radical M' in ingredient (*x*) is an imidazoline having the formula:



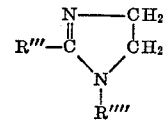
wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H. Such imidazolines are well known compounds and are commercially available. Preferably the radical R''' in the imidazoline is a C_{15}–C_{17} alkyl group

(or alkenol group, if an oleyl compound is used as the starting material); and preferably the radical R'''' is H, ethanol or the stearyl group.

Still another detergent which may be used in the practice of the instant invention to advantage is referred to herein as detergent (*y*). Ingredient (*y*) is a detergent having the formula:

$$A—O—(C_2–C_4 \text{ alkoxy})_m—SO_3—M''$$

wherein A—O— is the residue of a fatty alcohol: A—OH wherein A has from six to twenty-two carbon atoms, *m* is an integer from 1 to 50 and M'' is selected from the group consisting of alkali metals, alkaline earth metals, ammonium, (C_2–C_4 alkylol) ammonium, (C_2–C_4 alkoxy)$_n$(C_2–C_4 alkylol) ammonium wherein *n* is an integer from 1 to 50, poly(C_2–C_4 alkylene) amines, primary, secondary, tertiary and quaternary alkyl ammonium wherein the alkyl groups contain a total of one to twenty carbon atoms, C_{10} to C_{20} aliphatic (C_2–C_4 alkylol) amines, C_{10} to C_{20} alkyl-NH—$(CH_2)_m$ amines wherein *m* is an integer from 1 to 4 and imidazolines having the formula:



wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H.

Ingredient (*y*) is derived essentially from the fatty alcohol A—OH wherein the radical A has from 6 to 22 carbon atoms. Such fatty alcohols are available commercially as hexanol, heptanol, octanol, nonanol, decanol, dodecanol (lauryl), tetradecanol, octadecanol (stearyl and, also, oleyl alcohols), cosanol, and docosanol. In the preparation of ingredient (*y*), the fatty alcohol is first alkoxylated with from 1 to 50 mols of a C_2–C_4 alkylene oxide, such as ethylene oxide, propylene oxide or butylene oxide. The alkoxylated compound is then sulfated, also in conventional manner; and finally the sulfated compound is neutralized to obtain the radical M''.

The radical M'' may be an alkali metal (sodium and potassium being preferred, but lithium, etc. also being usable), ammonium, or alkaline earth (or other suitable neutralizing metallic ion from Group II of the Periodic Table, which includes magnesium, calcium, zinc, strontium, barium, etc.). In addition, the sulfated alkoxylated alcohol may be neutralized with a mono-, di- or tri- (C_2–C_4 alkylol) amine. Such amines include monoethanol amine, diisopropanol amine, butanol amine, triethanol amine, etc.

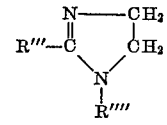
Also, the aforementioned alkylol amines may be alkoxylated before or after neutralization to form the radical M''. These radicals are alkoxylated with from 1 to 50 mols of a suitable C_2–C_4 alkylene oxide such as ethylene oxide, propylene oxide or butylene oxide. The alkoxylation procedure is conventional.

Still other amines which may be used to form the radical M'' are the polyamines, and particularly, the polyalkylene polyamines. Ethylene diamine, propylene diamine and butylene diamine may be used, but also diethylene triamine, triethylene tetramine, etc. may be used. Preferably the polyalkylene amine used does not have more than about 4 alkylene groups therein.

In the practice of the instant invention, the alkyl amines have been found to be particularly useful in the formation of the radical M''. Such amines as isopropyl amine and isooctyl amine have been found to be particularly useful, but primary, secondary, tertiary and quaternary alkyl amines may be used, including quaternary methyl amine, trimethyl amine, diethyl amine, lauryl amine, stearyl amine, oleyl amine, and similar means wherein the alkyl group or groups contain a total of 1 to 20 carbon atoms.

Other amines which may be used to form the radical M'' include the C_{10}–C_{20} aliphatic (C_2–C_4 alkylol) amines, such as oleyl diethanolamine, and the alkyl substituted alkylene diamines, i.e., the C_{10}–C_{20} alkyl-imino-alkylene-amines (e.g. "Duomeen") wherein the alkylene group has from 1 to 4 methylene groups. A typical compound of this group is stearyl propylene diamine.

Still another amine which may be used to form the radical M'' is an imidazoline. In particular, the amines of this type which may be used in the practice of the instant invention are imidazolines having the formula:



wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H. These imidazolines are well known and commercially available. The radical R''' is preferably a C_{15}–C_{17} alkyl or alkenol group, and the radical R'''' is preferably hydrogen, ethanol, or a stearyl group.

In the practice of the instant invention the total amount of detergent used may range from a minimum effective amount of about 0.25% to a maximum effective amount of about 5%, based on the weight of the total composition. The terms "percent" and "parts" as used herein refer to percent and parts by weight, unless otherwise designated. Preferably, the total amount of detergent used in the practice of the instant invention is within the range of 1% to 2%.

As previously indicated, the detergent component may consist entirely of ingredient (*a*), or it may consist of combinations of ingredient (*a*) with ingredient (*x*) and/or (*y*). In fact, ingredients (*a*), (*x*) and (*y*) may be used in equal proportions, but preferably the amount of (*a*) used is greater than the amount of (*x*) and it is also preferably greater than the amount of (*y*) used in the practice of this invention. If all three ingredients are used, the ratio by weight of (*a*) to (*x*) plus (*y*) may range from about 36:66 to 100:1. If only (*a*) and (*x*) are used in combination, the weight ratio is preferably within the range of 51:49 to 100:1; and if (*a*) and (*y*) are used in combination, the weight ratio is preferably within the range of 51:49 to 100:1.

It will be understood that modifications and variations may be effected without departing from the spirit and scope of the novel concepts of the present invention.

Examples of the instant invention include dry cleaning compositions formed of perchlorethylene containing 0.1% by weight of water (emulsified therein) and 1% by weight of each of the following detergent formulations:

(*a*) Sodium salt of ethylol myristamide alpha-sulfonic acid.

(*a*) Sodium salt of methylmyristate alpha-sulfonic acid.

(*a*) Calcium basic salt of isobutylpalmitate alpha- sulfonic acid.

(*a*) Ammonium salt of methylstearate alpha-sulfonic acid.

(*a*) Ethylolammonium salt of methylmyristate alpha-sulfonic acid.

(*a*) Ethylolammonium salt of methyl laurate alpha-sulfonic acid ethoxylated with 3 mols of ethylene oxide.

(*a*) Trimethylammonium salt of methyl myristate alpha-sulfonic acid.

(*a*) Tetradecyl propylenediamine (basic) salt of methyl-myristate alpha-sulfonic acid.

(*a*) Ethylenediamine (neutralized) salt of methyl-myristate alpha-sulfonic acid.

(*a*) Palmityl imidazoline salt of methylmyristate alpha-sulfonic acid.

(A) 75% (*a*) sodium salt of ethylol myristatamide alpha-sulfonic acid and 25% of (*x*) sulfated nonylphenol (ethoxylated with 3 mols of ethylene oxide) neutralized with lauryl amine.

(B) 80% of (*a*) sodium salt of methylmyristate alpha-sulfonic acid, 10% of (*x*) sulfated dinonylphenol (ethoxylated with 10 mols of ethylene oxide) neutralized with octadecyl propylenediamine and 10% of (*y*) sulfated glycol tetradecyl ether neutralized with sodium.

(C) 75% of (*a*) calcium basic salt of isobutylpalmitate alpha-sulfonic acid and 25% of (*y*) sulfated lauryl alcohol (ethoxylated with 6 mols of ethylene oxide) neutralized with ethanolamine.

(D) 80% of (*a*) ammonium salt of methylstearate alpha-sulfonic acid, 10% of (*x*) sulfated nonylthiophenol (ethoxylated with 6 mols of 50–50 ethylene oxide and propylene oxide) neutralized with stearoyl imidazoline, and 10% of (*y*) alkoxylated lauryl alcohol (6 mols 50:59 ethylene and propylene oxide) basic calcium sulfate.

(E) 80% of (*a*) ethylolammonium salt of methylmyristate alpha-sulfonic acid, 10% of (*x*) sulfated nonylphenol (ethoxylated with 6 mols of ethylene oxide) neutralized with trimethylamine, and 10% of (*y*) ethoxylated palmityl alcohol (10 mols of ethylene oxide) sulfate neutralized with octadecyl propylenediamine.

(*a*) Octylamine salt of methylmyristate alpha-sulfonic acid.

The preparation of component (*a*) is done by neutralization as follows:

(I) One gram mol of methylmyristate alpha-sulfonic acid (in a paste-form with an equal weight of water) is mixed with one gram mol of ethylenediamine, and the reaction proceeds readily with stirring and gentle warming (to about 50° C.) to obtain the basic salt of ethylenediamine and methylmyristate alpha-sulfonic acid.

(II) A procedure is carried out that is the same as that described in the previous paragraph (I) except that the polyamine used is diethylene triamine, propylene diamine, butylene diamine, penta-ethylene hexamine, stearyl propylene diamine, hexadecyl propylene diamine, tetradecyl ethylene diamine, stearoyl imidazoline, myristoyl ethanol imidazoline, palmitoyl propanol imidazoline and, in each case, the corresponding basic salt is obtained.

(III) A procedure is carried out that is the same as the previous paragraph (II) except that the ester-acid used is ethyl palmitate alpha-sulfonic acid, isopropyl stearate alpha-sulfonic acid, sec.-butyl myristate alpha-sulfonic acid, iso-amyl laurate alpha-sulfonic acid and n-hexyl decanoate alpha-sulfonic acid; and, in each case, the corresponding basic salt is obtained. But if 2 gram mols of each of such ester-acids is used to react with the aforesaid polyamines in the same procedure, the resulting salts are substantially neutralized (although actually still quite alkaline reacting) salts in the case of ethylene diamine, propylene diamine, butylene diamine, hexadecyl propylene diamine, stearyl propylene diamine, and the like diamines. With polyamines containing more than two amino groups, however, the resulting reaction product is still a basic salt. Reaction of one mol of the ester-acid for each amino group in a polyamine results in the neutralized salt (e.g., 3 mols of methyl myristate alpha-sulfonic acid and one mol of diethylene triamine).

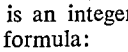
(IV) The basic and neutralized salts of polyvalent metals are prepared in substantially the same manner. Thus, one gram mol of methylmyristate alpha-sulfonic acid (in paste form with an equal weight of water) is mixed with one gram mol of calcium hydroxide and the reaction proceeds readily with stirring and gentle warming (to about 50° C.) to obtain the basic calcium salt of methylmyristate alpha-sulfonic acid. Using the same procedure with twice as much of the methylmyristate alpha-sulfonic acid, one obtains a neutralized salt. Using barium hydroxide, one obtains the basic barium salt and the neutralized barium salt, respectively, using the two procedures just set forth. Likewise, the basic and neutralized salts of other polyvalent metals such as magnesium, zinc, strontium, copper (cupric), tin (stannous), aluminum, manganese, cobalt, nickel, etc. are obtained in each case using either the base of the metal or a soluble salt thereof such as the chloride which permits the formation of the relatively less soluble sulfonic acid of the particular metal. These salts of metals other than the alkali metals and the alkaline earth metals are functional emulsifiers (and may thus be used in dry cleaning compositions or the like), but they are more useful in other fields, for such purposes as paint dryers, lubricating oil additives, etc.

In addition, it is believed that the amine salts of certain alpha-sulfonic acids used in the practice of the instant invention are per se new and these various amine salts have been found to be particularly useful as emulsifiers in the present use as well as in other uses. Such novel compounds may be defined as the basic or neutralized salt of an alpha-sulfonic acid having the formula:

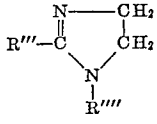
wherein Y is selected from the class consisting of

and

R is a C_4 to C_{20} fatty acid residue; X is selected from the group consisting of C_1 to C_{22} hydrocarbon, glyceryl, C_1–C_6 alkyl ether of glycerol, $(C_2$–C_4 alkoxy$)_nR'$ wherein *n* is an integer from 1 to 50 and R' is selected from the group consisting of H and C_1–C_6 alkyl groups; and an amine containing a plurality of N atoms selected from the group consisting of poly-(C_2–C_4 alkylene-amines, C_{10} to C_{20} aliphatic (C_2–C_4 alkylol) amines, C_{10} to C_{20} alkyl



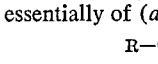
amines wherein *m* is an integer from 1 to 4 and imidazolines having the formula:



wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H; the minimum total number of carbon atoms in any C to C chain in X plus any C to C chain in M, plus the carbon chain in R being twelve.

We claim as our invention:

1. A dry cleaning composition consisting essentially of a mixture of water emulsified in a volatile organic dry cleaning solvent, said mixture being in amounts sufficient for dry cleaning operations and, as a dry cleaning assistant in a small detersive amount ranging from about 0.25% to about 5% by weight a detergent component consisting essentially of (*a*) detergent having the formula:

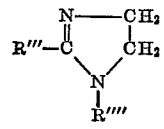


wherein Y is selected from the class consisting of

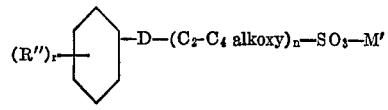
and

R is a C_4 to C_{20} fatty acid residue; X is selected from the group consisting of C_1 to C_{22} hydrocarbon, glyceryl, C_1–C_6 alkyl ether of gylcerol, $(C_2$–C_4 alkoxy$)_nR'$ wherein *n* is an integer from 1 to 50 and R' is selected from the group consisting of H and C_1–C_6 alkyl groups; and M is selected from the group consisting of alkali metals, alkaline earth metals, ammonium, (C_2–C_4 alkylol) ammonium, (C_2–C_4 alkoxy$)_n$(C_2–C_4 alkylol) ammonium wherein n is an integer from 1 to 50, poly(C_2–C_4 alkylene) amines, and primary, secondary, tertiary and

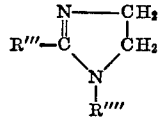
quaternary alkyl ammonium wherein the alkyl groups contain a total of two to twenty carbon atoms, C_{10} to C_{20} aliphatic (C_2–C_4 alkylol) amines, C_{10} to C_{20} alkyl-NH—$(CH_2)_m$ amines wherein M is an integer from 1 to 4 and imidazolines having the formula:



wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H; the minimum total number of carbon atoms in any C to C chain in X plus any C to C chain in M, plus the carbon chain in R being twelve, (*x*) detergent having the formula:



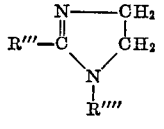
wherein R'' is a C_6 to C_{12} alkyl group, *r* is an integer from 1 to 2, *n* is an integer from 1 to 50, D is selected from the group consisting of O and S; and M' is selected from the amine bases consisting of C_{10} to C_{20} aliphatic mono-, di-, tri-, and quaternary amines, C_{10} to C_{20} aliphatic (C_2–C_4 alkylol) amines, C_{10} to C_{20} alkyl-NH—$(CH_2)_m$ amines wherein *m* is an integer from 1 to 4 and imidazolines having the formula:



wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H, and (*y*) detergent having the formula:

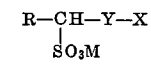
$$A—O—(C_2–C_4\ alkoxy)_m—SO_3—M''$$

wherein A—O— is the residue of a fatty alcohol: A—OH wherein A has from six to twenty-two carbon atoms, *m* is an integer from 1 to 50 and M'' is selected from the group consisting of alkali metals, alkaline earth metals, ammonium, (C_2–C_4 alkylol) ammonium, (C_2–C_4 alkoxy)$_n$(C_2–C_4 alkylol) ammonium wherein *n* is an integer from 1 to 50, poly(C_2–C_4 alkylene) amines, primary, secondary, tertiary and quaternary alkyl ammonium wherein the alkyl groups contain a total of one to twenty carbon atoms, C_{10} to C_{20} aliphatic (C_2–C_4 alkylol) amines, C_{10} to C_{20} alkyl-NH—$(CH_2)_m$ amines wherein *m* is an integer from 1 to 4 and imidazolines having the formula:

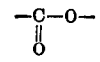


wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H, the weight ratio of (*x*) to (*y*) ranging from 20:1 to 1:20, and the weight ratio of (*a*) to (*x*) plus (*y*) ranging from 34:66 to 100:1, and the amount of (*a*) being greater than the amount of (*x*) alone and greater than the amount of (*y*) alone.

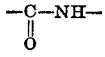
2. A method of dry cleaning textile fabrics which comprises rinsing the fabric in a dry cleaning composition consisting essentially of a mixture of water emulsified in a volatile organic dry cleaning solvent, said mixture being in amounts sufficient for dry cleaning operations and, as a dry cleaning assistant in a small detersive amount, a detergent component consisting essentially of (*a*) detergent having the formula:



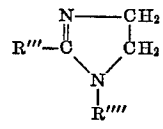
wherein Y is selected from the class consisting of



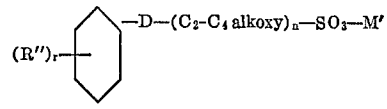
and



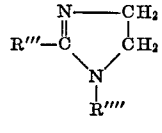
R is a C_4 to C_{20} fatty acid residue; X is selected from the group consisting of C_1 to C_{22} hydrocarbon, glyceryl, C_1–C alkyl ether of glycerol, (C_2–C_4 alkoxy)$_n$R' wherein *n* is an integer from 1 to 50 and R' is selected from the group consisting of H and C_1–C_6 alkyl groups; and M is selected from the group consisting of alkali metals, alkaline earth metals, ammonium, (C_2–C_4 alkylol) ammonium, (C_2–C_4 alkoxy)$_n$(C_2–C_4 alkylol) ammonium wherein *n* is an integer from 1 to 50, poly(C_2–C_4 alkylene) amines, and primary, secondary, tertiary and quaternary alkyl ammonium wherein the alkyl groups contain a total of two to twenty carbon atoms, C_{10} to C_{20} aliphatic (C_2–C_4 alkylol) amines, C_{10} to C_{20} alkyl-NH—$(CH_2)_m$ amines wherein *m* is an integer from 1 to 4 and imidazolines having the formula:



wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H; the minimum total number of carbon atoms in any C to C chain in X plus any C to C chain in M, plus the carbon chain in R being twelve, (*x*) detergent having the formula:



wherein R'' is a C_6 to C_{12} alkyl group, *r* is an integer from 1 to 2, *n* is an integer from 1 to 50, D is selected from the group consisting of O and S; and M' is selected from the amine bases consisting of C_{10} to C_{20} aliphatic mono-, di-, tri-, and quaternary amines, C_{10} to C_{20} aliphatic (C_2–C_4 alkylol) amines, C_{10} to C_{20} alkyl-NH—$(CH_2)_m$ amines wherein *m* is an integer from 1 to 4 and imidazolines having the formula:

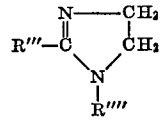


wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H, and (*y*) detergent having the formula:

$$A—O—(C_2–C_4\ alkoxy)_m—SO_3—M''$$

wherein A—O— is the residue of a fatty alcohol: A—OH wherein A has from six to twenty-two carbon atoms, *m* is an integer from 1 to 50 and M'' is selected from the group consisting of alkali metals, alkaline earth metals, ammonium, (C_2–C_4 alkylol) ammonium, (C_2–C_4 alkoxy)$_n$(C_1–C_4 alkylol) ammonium wherein *n* is an integer from 1 to 50, poly(C_2–C_4 alkylene) amines, primary, sec-

ondary, tertiary and quaternary alkyl ammonium wherein the alkyl groups contain a total of one to twenty carbon atoms, C_{10} to C_{20} aliphatic (C_2–C_4 alkylol) amines, C_{10} to C_{20} alkyl-NH—$(CH_2)_m$ amines wherein *m* is an integer from 1 to 4 and imidazolines having the formula:



wherein R''' is a C_4 to C_{24} fatty acid residue and R'''' is selected from the group consisting of C_4 to C_{24} alkyl, C_2 to C_4 alkylol and H, the weight ratio of (*x*) to (*y*) ranging from 20:1 to 1:20, and the weight ratio of (*a*) to (*x*) plus (*y*) ranging from 34:66 to 100:1, and the amount of (*a*) being greater than the amount of (*x*) alone and greater than the amount of (*y*) alone.

References Cited

UNITED STATES PATENTS

2,236,528	4/1941	Epstein	260—401
2,941,952	6/1960	Lewis et al.	252—161
3,128,294	4/1964	Stirton et al.	252—161 X

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U.S. Cl. X.R.

252—152, 171, 161; 8—142