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2,941,952

DRY-CLEANING DETERGENT COMPOSITION

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No Drawing. Filed Dec. 3, 1956, Ser. No. 625,604

11 Claims. (Cl. 252-161)

The present invention relates to a dry-cleaning process and to dry-cleaning detergent compositions, and particularly to specific combination compositions characterized by high deterative efficiency when used in non-aqueous, dry-cleaning solvents. It is an object of the invention to provide a detergent composition which possesses stability against the separation of water which has been emulsified into dry-cleaning solvents, such as the hydrocarbon type exemplified by Stoddard's solvent or in halogenated solvents such as perchlorethylene. It is another object of the invention to provide concentrated compositions of the essential detergent components in a non-aqueous solvent carrier, which, upon subsequent dilution after shipping to the ultimate consumer, give a readily usable product.

It has been a difficulty of prior art detergents when dissolved in volatile, organic dry-cleaning solvents, such as perchlorethylene, naphtha, gasoline, benzene and Stoddard's solvent, that the soap-type detergents are ineffective in preventing the redeposition of soil which has been removed from soiled garments. In the conventional dry-cleaning operation, the solvents are continuously or periodically filtered in order to remove accumulated soil. However, it has often been found that the soil which is in suspension, prior to such removal, is quite readily redeposited on other garments, particularly in the cleaning of synthetic fabrics, such as viscose and acetate rayon and nylon. It is, therefore, an object of the present invention to provide a commercial detergent which is characterized in having substantial solubility in a non-aqueous solvent, while at the same time reducing the redeposition property described above.

Another difficulty which has been encountered in the use of prior art detergents in dry-cleaning operations is the separation of the water which has been added to the dry-cleaning solvent. It is common practice to add small proportions of water to the dry-cleaning solvent, which water becomes emulsified with the solvent and aids in the removal of water-soluble stains caused by soluble substances, such as candy and beverages. In connection with this practice, it has been found that difficulty is encountered in maintaining the water content of the emulsion at a sufficiently high level to be useful, while preventing phase separation from occurring. In the preparation of a detergent composition to be employed in a dry-cleaning solvent, it has been found that the common sulfonate types of synthetic detergents are unsuitable for this use because of poor solubility and/or detergency in the organic dry-cleaning fluid.

It has now been found that particularly efficacious results are obtained in dry-cleaning by the employment of certain combinations of two condensation products. The first component is (a) a hydroxy group containing organic compounds having from 8 to 18 carbon atoms condensed with from 2 to 8 moles of ethylene oxide.

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Examples of such condensation products are dodecyl phenol or tridecanol condensed with ethylene oxide. The second component (b) is a salt of a sulfuric acid ester of the aforesaid condensation product, the said sulfate, being formed by neutralization with a base to form the potassium, sodium, ammonium or amine salt. Typical amines which may be utilized for such neutralization include diethylamines, triethylamines, monopropylamines, dipropylamines, tripropylamines and butylamines, such as monobutylamines. The alkylolamines such as monoethanolamines, diethanolamines, and triethanolamines may similarly be employed.

The condensation products employed in the present invention are prepared by reacting from 2 to 8 moles of an alkylene oxide such as ethylene oxide or propylene oxide per mole of the hydroxyl compound. A particularly effective compound is obtained when using about 5.6 moles of ethylene oxide. Condensation products may also be employed in which the condensation is carried out partially with ethylene oxide and partially with propylene oxide, in either order. For example, dodecyl phenol may first be condensed with three moles of ethylene oxide, followed by 2.6 moles of propylene oxide to obtain a detergent component of particular utility.

The proportion of the condensation product relative to the alkaline salt of the sulfuric acid ester as described above is generally in the range of from 70% to 97% of the said condensation product, and 3% to 30% by weight of the alkaline salt of the type described above.

The concentration of the combination of the condensation product and the alkaline salt of the sulfuric acid ester as employed in liquid dry-cleaning compositions is preferably from 0.25% to 7.0% by weight relative to the weight of the dry-cleaning liquid, although solutions may be prepared having from 0.25% to 75% by weight of the active. When concentrates are prepared for ultimate dilution by the consumer, the concentration of the said combination of active components is preferably from 25% to 75% by weight relative to the weight of the solvent employed.

In the preparation of the said combination compositions, it has been found that a particularly effective detergent for use in a volatile, organic liquid of the dry-cleaning type may be prepared by condensing from 2 to 8 moles of an alkylene oxide, specifically ethylene oxide or propylene oxide, with a hydroxyl-containing organic compound. Such hydroxyl-containing organic compound preferably has from 8 to 18 carbon atoms, as is exemplified by dodecyl phenol. After the condensation has been formed, a partial sulfation is carried out to the extent that from 3% to 30% of the final mixture will exist as the neutralized sulfated component. Sulfation of the above condensation product is carried out by treating with a proper amount of a sulfating agent, such, for example, as sulfur trioxide, fuming sulfuric acid or chlorosulfonic acid. Neutralization of the said sulfur ester thus formed is then accomplished by treating the entire reaction mixture with the stoichiometric amount of a basic substance of the group described above. However, if it is desired to form the salt of the sulfuric acid ester as a separate preparation, this component and the condensation product may be prepared by separate reactions and the two components then mixed to obtain the dry-cleaning detergent composition. This composition is then dissolved in a dry-cleaning solvent to give a concentrate preferably having from 25% to 75% by weight of the said combination detergent together with from 25% to 75% by weight of the dry-cleaning sol-

vent. If desired, the said combination may, however, be dissolved directly in the proper amount of dry-cleaning solvent to obtain a mixture containing from 0.25% to 7.0% by weight.

Other synthetic, organic detergent components may supplement the above-described component. A preferred type of supplementary detergent component is the group of alkanolamides of fatty acids, preferably having from 10 to 20 carbon atoms. A preferred compound of this type is the diethanolamide of tall oil fatty acids. Other alkyolamides of tall oil fatty acids may be prepared such as by the use of mono- or diethanolamine, mono- or diisopropanolamine, or mono- or di-n-propanolamine. Preferred amines are monoethanolamine and diethanolamine. Other sources of fatty acids which may be used in the preparation of alkyolamides are the naturally occurring fatty acids, such as those derived from coconut oil. The said coconut oil fatty acids are within the present preferred group of fatty acids having from 10 to 20 carbon atoms in the acid radical. A desirable compound of this type in the present relationship is lauric diethanolamide derived from crude lauric acid and diethanolamine.

Another class of auxiliary detergent components are the alkylene polyamines. An example of such a compound is the reaction product of an unsaturated hydrocarbon compound, preferably having from 10 to 30 carbon atoms, condensed with a polyamine, for instance, the reaction product of kerosene with diethylenetriamine. A preferred compound of this class is that obtained by chlorinating propylene tetramer with dichlorous acid, and then reacting such product with diethylene triamine to obtain a product having the formula:



Other amines which may be employed in the preparation of such compounds are ethylene diamine, propylene diamine, dipropylene triamine, and triethylene tetramine.

The dry-cleaning solvent employed in the present invention is a volatile, organic liquid of the dry-cleaning type, such as Stoddard's solvent, naphtha, gasoline, benzene, carbon tetrachloride, trichlorethylene or perchlorethylene.

The following examples illustrate specific embodiments of the present invention:

Example 1

A dry-cleaning detergent composition was prepared by condensing 5.6 moles of ethylene oxide with one mole of dodecyl phenol. This condensation product was then partially sulfated by reaction thereof with chlorosulfonic acid. The resultant sulfuric acid ester was then neutralized by the addition of sodium hydroxide to neutrality to give about 10% by weight of the salt and 90% of the condensation product in the final mixture. This conjointly-formed mixture in the amount of 3 gallons was dissolved in 150 gallons of Stoddard's solvent, corresponding to about 2 weight percent detergent.

Water was also added in an amount corresponding to 70% relative saturation of the air directly over the dry-cleaning solvent system. By this is meant that the working solution contains 70% of the amount of water which is required completely to saturate the air over the dry-cleaning solvent containing the dry-cleaning detergent. Detergency tests were then conducted with this detergent solution in a dry-cleaning machine operating with a cycle time of 15 minutes, with a load of 25 pounds of soiled garments of various fibers and colors. Soiled test swatches were added utilizing a synthetic soil of lampblack, tallow and mineral oil (Nujol).

The machine was operated with constant recirculation of the solvents, employing constant filtration through activated carbon as the filter medium. The soiled garments were dry-cleaned, extracted and dried at 160° F. After this sequence of operation the dry-cleaned test

swatches were measured for soil removal and redeposited by determining the reflectance, and comparing the washed value with the original value. The solvent system was also analyzed to determine the water content, nonvolatiles and also the acid number as an indication of any deterioration of the detergent or pickup of soil that was not retained on the filter.

The composite results obtained in the dry-cleaning of cotton, nylon, viscose, wool and acetate rayon showed substantially complete removal of soil as determined by reflectance measurements. It was found that the water content remained subsequently constant during the dry-cleaning, and that the water was effectively maintained in emulsion form in the organic solvent without phase separation. It was also found that the non-volatile content remained constant during 24 test runs indicating the lack of any precipitation or loss of the detergent during filtration. The acid number also remained substantially constant during 24 test runs showing the stability of the detergent during prolonged use.

Example 2

The detergent composition of Example 1 was subjected to a redeposition test in comparison with a commercial dry-cleaning detergent of the soap type. This test was conducted by carrying out a dry-cleaning operation similar to that of Example 1 in a Launderometer, but with the addition of unsoiled white worsted swatches of wool which would pick up dispersed soil which had been removed from the soiled garments. The measurement of whiteness was carried out by the use of reflectometer test MIL-D-12, 150-A, QMC, 1953. It was found that the percentage retention of whiteness, as a measure of redeposition, in the use of the detergent combination of Example 1 was 87.1%, whereas the whiteness obtained utilizing the same proportion of soap type dry-cleaning detergent was only 75.9%.

Detergent compositions of the type described above were also subjected to a dispersion test conducted by storing emulsions of the dry-cleaning composition containing an amount of water as described in Example 1 above for a period of six hours after preparation with soft water and with water having 300 p.p.m. hardness. At the end of six hours the compositions were again agitated and the effectiveness of dispersion determined. In this test it was found that the detergent of Example 1 when present in 4% concentration maintained 100% of its (emulsion) volume for a six hour period, while the same concentration of the soap-type dry-cleaning detergent resulted in an emulsion which maintained only 80% of its volume. It was also found that again agitating the above mixtures after the six hours resulted in the production of a stable emulsion utilizing the detergent composition of Example 1, while the soap-type dry-cleaning detergent gave only a poor emulsion which rapidly separated after the agitation at six hours as described above.

Example 3

As an example of a dry-cleaning detergent composition utilizing individually-prepared components, a mixture was prepared as follows:

	Weight percent
Dodecyl phenol condensed with 5.6 moles of ethylene oxide	45
Decanol condensed with 30 moles of propylene oxide	45
Tridecanol condensed with 1 mole of ethylene oxide, and thereafter sulfated and neutralized with potassium hydroxide	10

The above combination was utilized as a 4.0% solution in perchlorethylene and was found to give satisfactory results in dry-cleaning.

Example 4

A dry-cleaning mixture was prepared utilizing the following active components:

	Weight percent
Dodecyl phenol condensed with 5.6 moles of ethylene oxide -----	25
Dodecyl phenol condensed with 5.6 moles of ethylene oxide, and thereafter sulfated and neutralized with sodium hydroxide -----	8
Diethanolamide of tall oil fatty acids -----	33
Alkylene polyamine obtained by reacting propylene tetramer with hypochlorous acid and then condensing with diethylene triamine -----	34

The above combination was utilized as the dry-cleaning detergent present in 4% concentration by weight in cleaner's naphtha, and was found to give satisfactory results in dry-cleaning operations.

Example 5

A dry-cleaning concentrate was prepared by dissolving 9 pounds of the condensation product of dodecyl phenol condensed with 5.6 moles of ethylene oxide, and 1 pound of the condensation product of dodecyl phenol condensed with 5.6 moles of ethylene oxide and thereafter sulfated and the resultant sulfuric acid ester dissolved in Stoddard's solvent and neutralized with sodium hydroxide. The above combination of the two components (90% condensation product and 10% salt) was slowly added to 10 pounds of Stoddard's solvent while agitating in order to provide a uniform mixture. This concentrate was found to possess excellent storage stability.

The above concentrate was diluted for use by adding thereto 100 pounds of Stoddard's solvent. This diluted working solution was found to give excellent results in dry-cleaning operations such as are described in Example 1.

What is claimed is:

1. A method of dry-cleaning fabric material which comprises contacting it with a detergent composition comprising a volatile, organic liquid of the dry-cleaning type and a mixture containing 70% to 97% by weight of a condensation product of a hydroxyl-containing organic compound having from 8 to 18 carbon atoms condensed with from 2 to 8 moles of an alkylene oxide having from 2 to 3 carbon atoms, and from 3% to 30% by weight of an alkaline sulfate of a condensation product of a hydroxyl-containing organic compound having from 8 to 18 carbon atoms condensed with from 2 to 8 moles of an alkylene oxide having from 2 to 3 carbon atoms.

2. A method of dry-cleaning fabric material which comprises contacting it with a detergent composition comprising a volatile, organic liquid of the dry-cleaning type and a mixture composed with from 70% to 97% by weight of a condensation product of dodecyl phenol with about 5.6 moles of ethylene oxide per mole of the said dodecyl phenol, and from 3% to 30% by weight of the salt of the sulfate of dodecyl phenol condensed with about 5.6 moles of ethylene oxide per mole of the said dodecyl phenol.

3. A method of dry-cleaning fabric material which comprises contacting it with a detergent composition comprising from 93% to 99.75% by weight of a volatile, organic liquid of the dry-cleaning type and from 0.25% to 7% by weight of a combination composed of from 70% to 97% by weight of a condensation product of dodecyl phenol with about 5.6 moles of ethylene oxide per mole of the said dodecyl phenol, and from 3% to 30% by weight of the sodium salt of the sulfate of dodecyl phenol condensed with about 5.6 moles of ethylene oxide per mole of the said dodecyl phenol.

4. A dry-cleaning detergent composition for fabrics which comprises from 93% to 99.75% by weight of a

volatile, organic liquid of the dry-cleaning type, and from 0.25% to 7% by weight of a combination composed of from 70% to 97% by weight of a condensation product of a hydroxyl-containing organic compound having from 8 to 18 carbon atoms condensed with from 2 to 8 moles of an alkylene oxide having from 2 to 3 carbon atoms together with from 3% to 30% by weight of an alkaline salt of the sulfate of a condensation product of a hydroxyl-containing organic compound having from 8 to 18 carbon atoms condensed with from 2 to 8 moles of an alkylene oxide having from 2 to 3 carbon atoms.

5. A dry-cleaning detergent composition for fabrics which comprises from 93% to 99.75% by weight of a volatile, organic liquid of the dry-cleaning type, and from 0.25% to 7% by weight of the combination of from 70% to 97% by weight of a condensation product of a hydroxyl-containing organic compound having from 8 to 18 carbon atoms condensed with from 2 to 8 moles of ethylene oxide, together with from 3% to 30% by weight of an alkaline salt of the sulfate of a condensation product of a hydroxyl-containing organic compound having from 8 to 18 carbon atoms condensed with from 2 to 8 moles of ethylene oxide.

6. A dry-cleaning detergent composition for fabrics which comprises from 93% to 99.75% by weight of a volatile, organic liquid of the dry-cleaning type, and from 0.25% to 7% by weight of the combination of from 70% to 97% by weight of a condensation product of dodecyl phenol with from 2 to 8 moles of ethylene oxide per mole of the said dodecyl phenol, together with from 3% to 30% by weight of the sodium salt of the sulfate of dodecyl phenol condensed with from 2 to 8 moles of ethylene oxide per mole of the said dodecyl phenol.

7. A dry-cleaning detergent composition for fabrics which comprises from 93% to 99.75% by weight of a volatile, organic liquid of the dry-cleaning type, and from 0.25% to 7% by weight of the combination of from 70% to 92% by weight of a condensation product of dodecyl phenol with about 5.6 moles of ethylene oxide per mole of the said dodecyl phenol, together with from 3% to 30% by weight of the sodium salt of the sulfate of dodecyl phenol condensed with about 5.6 moles of ethylene oxide per mole of the said dodecyl phenol.

8. The process for preparing a dry-cleaning, detergent composition for fabrics which comprises condensing from 2 to 8 moles of an alkylene oxide having from 2 to 3 carbon atoms with one mole of a hydroxyl-containing organic compound having from 8 to 18 carbon atoms, and thereafter partially sulfating the said condensation product with a sulfating agent to obtain a sulfuric acid ester, and thereafter neutralizing the said sulfuric ester with an alkali in order to form the alkaline salt of the said sulfuric acid ester, the said alkaline salt being present to the extent of from 3% to 30% by weight in the final mixture.

9. The process for preparing a dry-cleaning detergent composition for fabrics which comprises condensing from 2 to 8 moles of an alkylene oxide having from 2 to 3 carbon atoms with one mole of a hydroxyl-containing organic compound having from 8 to 18 carbon atoms, and thereafter partially sulfating the said condensation product of chlorosulfonic acid to obtain a sulfuric acid ester, and thereafter neutralizing the said sulfuric acid ester with an alkali in order to form the alkaline salt of the said sulfuric acid ester, the said alkaline salt being present to the extent of from 3% to 30% by weight in the final mixture.

10. The process for preparing a dry-cleaning detergent composition for fabrics which comprises condensing from 2 to 8 moles of ethylene oxide with dodecyl phenol, and thereafter partially sulfating the said condensation product by sulfating with a sulfating agent, and thereafter neutralizing the resultant sulfuric acid ester with sodium hydroxide in order to form the sodium salt of the said sulfuric acid ester, the said sodium salt being present to

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the extent of from 3% to 30% by weight in the final mixture.

11. The process for preparing a dry-cleaning detergent composition for fabrics which comprises condensing from 2 to 8 moles of ethylene oxide with dodecyl phenol, and thereafter partially sulfating the said condensation product by sulfating with chlorosulfonic acid, and thereafter neutralizing the resultant sulfuric acid ester with sodium hydroxide in order to form the sodium salt of the said sulfuric acid ester, the said sodium salt being present to the extent of from 3% to 30% by weight in the final mixture.

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