United States Patent Office 3,642,644 Patented Feb. 15, 1972

3,642,644

STABLE DRY CLEANING COMPOSITIONS

Herbert E. Grote and Wilbur G. Henry, Springfield Township, Hamilton County, Ohio, assignors to The Procter & Gamble Company, Cincinnati, Ohio

No Drawing. Filed Dec. 16, 1969, Ser. No. 885,651
Int. Cl. C11d 1/18, 3/24; D06l 1/04
U.S. Cl. 252—153 8 Claims

ABSTRACT OF THE DISCLOSURE

Concentrated dry cleaning compositions, having a pH of from about 6.5 to about 9 and consisting essentially of a dry cleaning solvent containing from about 0.25% to about 0.75% by weight of a coupling agent and from about 20% to about 60% by weight of an anionic detergent comprising the monoethanolamine salt of an essentially pure, broad cut, linear C_8 to C_{18} alkyl benzene sulfonic acid; weight ratios of detergent to coupling agent are at least about 80:1. The concentrated compositions herein exhibit satisfactory stability against phase separation and, when diluted with additional solvent and employed in conventional dry cleaning operations, achieve improved dry cleaning performance.

CROSS-REFERENCE TO RELATED COMPOSITIONS

Concentrated dry cleaning compositions, which consist essentially of a dry cleaning solvent and an anionic detergent comprising the monoethanolamine salt of an essentially pure, broad cut, linear alkyl benzene sulfonic acid, are disclosed in a concurrently filed, copending application, Ser. No. 885,652, filed Dec. 16, 1969, filed by Gordon W. Potter, Jr. and entitled "Improved Dry Cleaning Compositions"; the disclosure of said application is hereby incorporated by reference. The disclosed compositions achieve improved dry cleaning performance when employed in conventional dry cleaning operations.

The invention herein is directed to providing similar compositions in concentrated form, which concentrated compositions exhibit satisfactory stability against phase-separation as well as (after dilution with additional dry cleaning solvent) similarly improved dry cleaning performance.

BACKGROUND OF THE INVENTION

The invention herein relates generally to concentrated detergent compositions for use in the dry cleaning of fabrics.

In a conventional process of dry cleaning fabrics, the soiled fabrics are agitated in a volatile organic dry cleaning solvent which is relatively immiscible with water. Such solvents are generally effective for the removal of grease and oil stains as well as dust, dirt, lint and the like which commonly adhere to the fabrics and to the grease and oil thereon. The agitation is generally accomplished by inserting the fabrics into a perforated cylinder which is rotated in the solvent bath. The solvent is usually circulated by means of a pump through a filter which removes suspended soil particles; by means of recycling and filtering, the solvent can generally be reused many times, and after becoming badly contaminated, can be distilled and used again. After sufficient treatment, the fabrics are usually subjected to centrifugal action to remove excess solvent and then placed in a rotating cylinder or drying cabinet wherein final traces of solvent are removed by a current of warm air.

To promote the removal of water-soluble soil, such as those caused by various foods and the like, from the fabrics, the solvent generally incorporates small amounts of water and/or a fatty acid soap or an organic synthetic detergent. Detergents so employed include a variety of anionic, nonionic, and cationic compounds. Many such detergents, besides having detersive qualities, also have absorbefacient characteristics which permit water (either added to the solvent or resulting from moisture in the fabrics or in the dry cleaning system) to become finely dispersed throughout the solvent and to achieve better water-soluble soil removal. Unfortunately, however, many such detergents themselves exhibit relatively low levels of water-soluble stain removal and relatively high levels of fabric graying and often result in necessitating post-cleaning spot removal; other detergents impart relatively poor water-solubilizing properties to the dry cleaning solvent, which can lead to the presence of excess water in the solvent-detergent system and, subsequently, to irreparable damage to water-sensitive garments, e.g., woolens; still other detergents require special additives or methods of incorporation into the solvent to provide and maintain a homogenous emulsion or single-phase necessary to permit use of the dry cleaning composition with the filtration apparatus conventionally used in retail and industrial dry cleaning operations.

The detergents employed in the compositions disclosed in the above-referenced Potter application have the advantage of generally avoiding the above-noted problems and, further, provide compositions which achieve improved dry cleaning performance, i.e., improved fabric cleaning and reduced fabric graying. For economic and other reasons, it is highly desirable to market a concentrated dry cleaning composition having high amounts of these detergents.

These concentrated dry cleaning compositions, however, are susceptible to phase-separation, apparently due to the presence of water, which can lead to a multiplicity of problems which relate, for example, to the manufacture, storage, and shipment of the compositions, as well as to their dilution and subsequent use, as described hereinafter.

Therefore, a concentrated dry cleaning composition, which is stable against phase-separation and which (after dilution) is filterable and achieves improved dry cleaning performance, is highly desirable.

Accordingly, it is an object of the invention herein to provide a concentrated dry cleaning composition which is stable against phase-separation.

It is another object of the invention herein to provide a stable, concentrated dry cleaning composition which, after dilution with additional solvent, can be employed to achieve improved dry cleaning performance.

Further, it is an object of the invention herein to provide a stable, concentrated dry cleaning composition which, after dilution with additional solvent, provides a single-phase composition with improved dry cleaning performance.

BRIEF SUMMARY OF THE INVENTION

These and other objects are achieved by the invention herein which comprises a concentrated dry cleaning composition which consists essentially of a dry cleaning solvent containing from about 20% to about 60% by weight of an anionic detergent comprising the monoethanolamine salt of an essentially pure, broad cut, linear alkyl benzene sulfonic acid wherein the alkyl is a mixture of alkyls having an average chain length of from about 8 to about 18 carbon atoms, and from about 0.25% to about 0.75% by weight of a coupling agent, wherein the weight ratio of the detergent to the coupling agent is at least about 80:1, and further, wherein the composition has a pH within the range of from about 6.5 to about 9.

The concentrated dry cleaning compositions of the invention are generally stable against phase-separation even under severe conditions and, after dilution with a suitable chlorinated dry cleaning solvent, provide compositions which are filterable and which exhibit improved dry cleaning performance.

Specifically, by employing a coupling agent in the concentrated dry cleaning compositions herein, stability against phase-separation is achieved. By employing a detergent, comprising the above-described monoethanolamine salt of an essentially pure, broad cut, linear alkyl (from about C_8 to about C_{18}) benzene sulfonic acid (hereinafter also referred to herein as "MEA-LAS" for brevity), the concentrated compositions herein can be diluted with additional solvent to achieve a use level dry cleaning composition (i.e., a composition ready for direct incorporation and use in dry cleaning operations) with improved fabric cleaning, i.e. insoluble and water-soluble soil removal, and reduced fabric graying, i.e. soil redeposition.

DETAILED DESCRIPTION OF THE INVENTION

It has now been found that the presence of water in a concentrated MEA-LAS dry cleaning composition (i.e., a composition concentrated with detergent and requiring dilution with additional dry cleaning solvent prior to its incorporation and use in dry cleaning operations) can lead to phase-separation in the composition. For example, experimental observations indicate that as little as about 0.3% by weight water in such concentrated dry cleaning compositions containing about 40% by weight detergent generally causes phase-separation after a shelf-life of as little as three days.

It is believed that water present in the concentrated composition is introduced during processing or manufacturing procedures and is particularly carried over into the composition along with the detergent additive. It is further believed that the water in the concentrated composition extracts or removes the detergent from the dry cleaning solvent and otherwise prevents solubilization of the detergent in the solvent. As a consequence, the composition exhibits two phases: an aqueous phase which contains at least a substantial amount of the detergent being employed, an an organic phase consisting essentially of the dry cleaning solvent.

Problems resulting from phase-separation can be severe. For example, concentrated compositions, which have separated into aqueous and organic phases, generally exhibit unsatisfactory freeze-thaw stability and recovery to a singe-phase; thus, such phase-separated compositions can undesirably require special procedures for their storage and/or shipment.

Moreover, detergent extracted into the water present in the concentrated compositions generally does not satisfactorily redistribute or resolubilize in the solvent upon dilution of the concentrated composition; thus, sample portions of the resulting use level composition generally exhibit dissimilar or inconsistent amounts of detergent therein, thereby causing certain portions to be less effective or even unsatisfactory in dry cleaning performance.

According to the invention herein, there are provided stable, concentrated dry cleaning compositions which comprise a coupling agent, essential to achieve stability against phase-separation. The term "coupling agent," as used herein, generally refers to water-soluble organic compounds which are soluble both in the dry cleaning solvent and in water; such agents function herein to couple or link water present in the composition (including detergent solubilized therein) with the solvent to provide and maintain concentrated compositions generally stable against phase separation.

Examples of coupling agents, suitable for use in the concentrated compositions herein, are known in the art and are readily available items of commerce. Suitable coupling agents include e.g., lower ethylene glycol-monoalkyl ethers and lower monohydroxy alkanols; "lower," as used herein and in the appended claims, generally refers to those ethers and alcohols wherein the monoalkyl and alkanol contains from one to about 4 carbon atoms. Specific examples of such compounds include, e.g., the following:

ethyleneglycol-monomethyl ether;
ethyleneglycol-monoethyl ether;
ethyleneglycol-monopropyl ether;
ethyleneglycol-monobutyl ether;
methanol;
ethanol;
n-propanol;
isopropanol;
n-butanol; and
t-butanol.

Coupling agents, preferred herein for performance on freeze-thaw stability, for convenience in handling, and for economical reasons, include isopropanol and ethyleneglycol-monobutyl ether (available commercially under the trade name "Butylcellosolve").

The amount of a coupling agent employed in a concentrated dry cleaning composition herein generally ranges from about 0.25% to about 0.75% by weight of the composition. Within this range, an amount of coupling agent can be employed to couple essentially all water normally present in the concentrated compositions herein.

Because substantially all of the water present is carried over into the concentrated composition along with the detergent, the specific amount of coupling agent employed generally depends upon the amount of detergent used in the composition. For example, a concentrated composition containing about 40% by weight detergent generally contains about 0.3% by weight water; similarly, concentrated compositions containing lower or higher detergent concentrations generally contain proportionately lower or higher amounts of water, respectively.

Accordingly, the amount of coupling agent, which suffices to couple the water generally present in a concentrated composition containing a given detergent concentration in the range herein, bears a directly proportional relationship to the amount of detergent. This relationship, expressed as a weight ratio of detergent to coupling agent, is at least about 80:1. Thus, e.g., a detergent concentration of about 40% by weight necessitates the use of at least about 0.5% of a coupling agent to link or couple the 0.3% by weight water generally present in such a concentrated composition; similarly, detergent concentrations of about 20% and about 60% by weight generally require the use of at least about 0.25% and at least about 0.75% by weight coupling agent, respectively.

The concentrated compositions of the invention herein further comprise from about 20% to about 60%, preferably (for processing and handling reasons) about 40%, by weight of an anionic organic synthetic detergent which comprises the monoethanolamine salts of an essentially pure, broad cut, linear alkyl (from about C_8 to C_{18}) benzene sulfonic acid, i.e., MEA-LAS. Above about 60% by weight, the concentrated composition becomes a stiff paste which, of course, is not prone to phase-separation. With regard to the detergent additive used herein, the "alkyl," as termed herein and in the appended claims, is a mixture of alkyls having an average chain length of from about 8 to about 18 carbon atoms. For best results, the alkyls herein, preferably, have at least about 4 different carbon chain lengths, each of which contains from about 6 to about 20 carbon atoms, wherein at least about 80% by weight of the chain lengths are within the range of from about 8 to about 18 carbon atoms and wherein at least two of the chain lengths comprise at least about 20% of the alkyl. In the trade, such "mixed alkyls" are often termed "broad cuts"; thus, for example, a broad cut C_{12} or dodecyl benzene sulfonic acid (particularly preferred herein) has a mixture of alkyls having an average chain length of about 12 (specifically between 11 and 12)

carbon atoms, specifically consisting essentially of (percent is by weight):

C_9: from 0% to about 0.4%
C_{10}: from about 17% to about 19.9%
C_{11}: from about 40.6% to about 42.8%
C_{12}: from about 29.4% to about 32.7%
C_{13}: from about 6.6% to about 9.1%
C_{14}: from about 0.2% to about 0.23%

Similarly, broad cut C_8 (octyl) and C_{18} (octadecyl) benzene sulfonic acids have a mixture of alkyls having an average chain length of about 8 and 18 carbon atoms, respectively.

When the monoethanolamine salt of an alkyl benzene sulfonic acid comprising a mixture of linear alkyl carbon chain lengths (i.e., a broad cut, linear alkyl benzene sulfonic acid) is employed as a detergent additive in the concentrated dry cleaning compositions herein, use level compositions derived therefrom generally exhibit an improved level of fabric cleaning and a reduced level of fabric graying in comparison with, e.g., a "pure cut," linear alkyl benzene sulfonic acid (i.e., one in which the alkyl does not contain a mixture or distribution of various carbon chain lengths, but, instead, has only one alkyl having a definite and fixed carbon chain length).

Suitable broad cut, linear alkyls for use in compositions herein include those wherein the chain lengths average from about 8 to about 18 carbon atoms; specific examples of such compounds include, e.g., monoethanolamine salts of broad cut, linear octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl benzene sulfonic acid wherein the chain lengths average about C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, and C_{18} carbon atoms, respectively.

Methods which can be used to prepare the detergents employed in the compositions herein are generally known in the art. For example, a suitable method comprises, firstly, reacting a linear, paraffinic hydrocarbon (e.g., a petroleum distillate) containing a mixture of alkyls having a desired carbon chain length within the range of from about 8 to about 18 carbon atoms with chlorine under conventional methods to obtain the chlorinated broad cut, linear hydrocarbon which is thereafter reacted with benzene (e.g., under Friedel-Crafts reaction conditions) to obtain the broad cut, linear alkyl benzene; the latter compound can alternatively be prepared by reacting the linear, paraffinic hydrocarbon with benzene with, e.g., hydrofluoric acid. The broad cut, linear, alkyl benzene is thereafter sulfonated, preferably, with sulfur trioxide to form the broad cut, linear, alkyl benzene sulfonic acid which is thereafter neutralized, e.g., by mixing equimolar amounts of monoethanolamine and the alkyl benzene sulfonic acid to form a monoethanolamine alkyl benzene sulfonate employed as a detergent additive herein.

The broad cut, linear, alkyl benzene sulfonic acids (or their monoethanolamine salts) employed herein are essentially pure. By-products, which can result when certain methods are used to sulfonate an alkyl benzene (broad or pure cut) generally inhibit fabric cleaning and/or promote undesirable fabric graying despite the fact that such by-products, especially those occurring after the neutralization step, may themselves be otherwise suitable detergents.

By way of brief explanation, one commonly used sulfonation method comprises reacting an alkyl benzene with chlorosulfonic acid in accordance with the following unbalanced reaction:

(1) $R-\phi + ClSO_3H \longrightarrow$

$$R-\phi-SO_3H + R-\phi-SO_2Cl + R-\phi + HCl\uparrow + H_2SO_4$$

[R=broad cut C_8-C_{18} alkyl]

Unless the resulting alkyl benzene sulfonic acid is purified of the large amount of other reaction by-products, subsequent neutralization of the reaction products will yield the desired MEA-LAS detergent and other neutralization by-products which generally inhibit dry cleaning performance of the compositions herein. Thus, for example, when the products of reaction (1) are neutralized with monoethanolamine (MEA), in accordance with reaction (2), the reaction products include an MEA-LAS detergent and an MEA alkyl benzene sulfonamide plus other MEA salt by products; unless removed, the presence of the sulfonamide (itself an often used detergent) in the compositions herein generally inhibits their dry cleaning performance.

(2) $R-\phi-SO_3H$ + $R-\phi-SO_2Cl$ + $R-\phi$ + HCl + H_2SO_4 + $H_2NCH_2CH_2OH$ (MEA) $\longrightarrow$ $R-\phi-SO_3^-NH_3^+CH_2CH_2OH$ (MEA-LAS) + $R-\phi-SO_2-NHCH_2CH_2OH$ (MEA alkyl benzene sulfonamide) + MEA salt by-products

[R=broad cut C_8-C_{18} alkyl]

The presence of such by-products is generally avoided when, e.g., the above-described preferred sulfonation procedures are used; alternatively, such by-products, when formed, e.g., from the use of reaction (1) above as a method of sulfonation, can conveniently be removed after their formation by techniques known in the art, e.g., by the use of ion exchange resins. It is not desirable, for economical and practical reasons, to neutralize the alkyl benzene sulfonic acid in the presence of such by-products as are formed in reaction (1) above; however, if desired, neutralization can be so accomplished and the resulting by-products (e.g., the sulfonamide in reaction (2) above) can thereafter be removed by conventional techniques, e.g., by the use of ion exchange resins prior to formulating the MEA-LAS into a composition herein.

The compositions of the invention herein use the monoethanolamine salt of the alkyl benzene sulfonic acids. Only the monoethanolimaine (MEA) salt of the linear alkyl benzene sulfonic acids herein provides a detergent which, when incorporated into chlorinated dry cleaning solvents (preferred herein), achieves a preferred single-phase dry cleaning composition; other alkanolamine salts (e.g., dimethanolamine, diethanolamine, triisopropanolamine, and the like) of the alkyl benzene sulfonic acids employed herein provide detergents which generally are either less effective in performance or undesirably result in unfilterable two-phase dry cleaning compositions.

It has been found, however, that other alkanolamines can be employed in admixture with MEA to form salts of the broad cut, linear, alkyl benzene sulfonic acids used herein, which detergents, when utilized as substitutes for MEA-LAS, achieve effective single-phase dry cleaning compositions. Examples of such other alkanolamines which are suitable for use in admixtures with MEA, include, e.g., the mono-, di-, and tri-alkanolamines wherein the alkanol is methanol, propanol, isopropanol, and butanol the di- and tri-alganolamines wherein the alkanol is ethanol, and mixtures thereof. Specific examples of such compounds are as follows:

monomethanolamine;
dimethanolamine;
trimethanolamine;
monopropanolamine;
dipropanolamine;
tripropanolamine;
monoisopropanolamine;
diisopropanolamine;
triisopropanolamine;
monobutanolamine;
dibutanolamine; and,
tributanolamine.

Specific examples of preferred alkanolamines for use in admixtures with MEA include diethanolamine (DEA), triethanolamine (TEA), and monoisopropanolamine (IPA).

Any one or more of the foregoing other alkanolamines can be employed in admixture with MEA. When any of such other alkanolamines are employed in admixture with MEA, the amounts in which they can be admixed will vary depending upon the specific other alkanolamine or alkanolamines being used. Generally, sufficient MEA should be used in the admixtures to provide filterable use level dry cleaning compositions; i.e., finely dispersed, homogenous or, preferably, single-phase detergent additive dry cleaning compositions; for example, an admixtue of MEA with up to about 90% by weight IPA, with up to about 80% by weight DEA, or with up to about 40% by weight TEA provides detergent additive dry cleaning compositions which generally are single-phase.

Accordingly, the detergent additive of the compositions herein can further comprise an alkanolamine salt of an essentially pure, broad cut, linear alkyl benzene sulfonic acid employed herein, wherein the alkanolamine consists essentially of an admixture of from about 10% to about 99% by weight monoethanolamine and from about 1% to about 90% by weight of one or more other alkanolamines selected from the group consistsing of (A) mono-, di-, and tri-alkanolamines wherein the alkanol is methanol, propanol, isopropanol, and butanol, (B) di- and trialkanolamines wherein the alkanol is ethanol, and (C) mixtures thereof.

The concentrated dry cleaning compositions herein further comprise a dry cleaning solvent in which the detergent and coupling agent are contained. Suitable dry cleaning solvents for use in the concentrated compositions herein include those commonly referred to as chlorinated solvents and hydrocarbon solvents, as well as mixtures thereof.

Specific examples of suitable chlorinated solvents include, e.g., trichloroethylene, carbon tetrachloride, methyl chloroform, and perchlorethylene; for economical and other reasons and for handling convenience, preferred chlorinated solvents are methyl chloroform and perchlorethylene, particularly the latter.

Specific examples of suitable hydrocarbon solvents include, e.g., Stoddard's solvent, naphtha, "140°" solvent, kerosene, gasoline, mineral spirits, mineral oil, and aromatic hydrocarbons (e.g., benzene, toluene, xylene, or mixtures thereof); for economical reasons, preferred hydrocarbon solvents are the aromatic hydrocarbons, particularly mixtures of benzene, toluene, and xylene.

Generally, the concentrated compositions herein have a pH within the range of from about 6.5 to about 9; the pH's herein and in the appended claims are determined with concentrated compositions diluted to about 0.6% by weight detergent concentrations and at a 75% solvent relative humidity. Below a pH of about 6.5, the compositions tend to be too acidic and can cause corrosion and other undersirable effects; above a pH of about 9, the compositions can have an undesirable effect on fabric dyes, especially acid-set dyes.

The concentrated dry cleaning compositions herein require dilution with additional solvent in order to obtain use level compositions which improve dry cleaning performance and which, desirably, are filterable and, therefore, advantageously employed with filtration apparatus conventionally used in the industry. To be filterable, the use level composition should be a finely dispersed, homogeneous emulsion or, preferably, single-phase; to this end, the dry cleaning solvent selected for use in the concentrated compositions herein becomes important.

With regard to use level compositions derived from the concentrated compositions herein, hydrocarbon solvents are generally unsuitable for use as a major component thereof with the detergent additive employed herein and when used, generally result in compositions (use level) which undesirably are not filterable and/or are not satisfactory in dry cleaning performance. Accordingly, to be filterable, the concentrated compositions herein should be diluted with a chlorinated dry cleaning solvent, particularly perchlorethylene, regardless of the solvent employed to formulate the concentrated compositions herein. Because the required dilution necessitates the addition of large amounts of the chlorinated solvent, the use level composition resulting from a concentrated composition herein employing a hydrocarbon solvent will generally be in the form of a filterable finely dispersed, homogeneous emulsion which contains only a low amount of the hydrocarbon solvent and which, to the naked eye, generally appears as a single-phase; generally, the amount of hydrocarbon solvent present in such a use level composition will be about 20% by weight of the composition or less and about 27% by weight of total solvent or less. For example, by adding a sufficient amount of a chlorinated solvent to a concentrated composition which consists essentially of about 20% by weight MEA-LAS (C_{12}) and about 80% by weight hydrocarbon solvent, e.g., a mixture of benzene, toluene, and xylene, a filterable use level composition can be achieved which consists essentially of about 5% by weight MEA-LAS (C_{12}) and about 95% by weight solvent wherein the solvent is an admixture of the chlorinated solvent and the hydrocarbon solvent, specially about 75% by weight (of the composition) chlorinated solvent and about 20% by weight (of the composition) hydrocarbon solvent, the hydrocarbon solvent being about 27% by weight of the chlorinated solvent or about 21% by weight of total solvent; diluting the concentrated composition to lower detergent concentrations provides use level compositions having smaller amounts of the hydrocarbon solvent. Preferably, the solvent employed in the concentrated compositions herein is a chlorinated dry cleaning solvent, particularly perchlorethylene, in which event the use level compositions obtained after diluting such concentrated compositions with, e.g., additional perchlorethylene are single-phase.

The concentrated dry cleaning compositions of the invention herein should be diluted with a sufficient amount of chlorinated dry cleaning solvent to provide use level compositions consisting essentially of from about 0.06% to about 5%, preferably about 0.3%, by weight detergent and from about 95% to about 99.94%, preferably about 99.7%, by weight solvent. The use level composition, because of the coupling agent employed in the concentrated dry cleaning compositions herein, will additionally contain the coupling agent therein; however, the weight percentage of the coupling agent in the use level composition is quite small and insignificant, inasmuch as its presence in the use level composition is neither essential nor deleterious to the achievement of a filterable dry cleaning composition with improved dry cleaning performance.

A particularly preferred concentrated dry cleaning composition herein consists essentially of about 40% by weight MEA-LAS (C_{12}), about 0.5% by weight isopropanol, and about 59.5% by weight perchlorethylene, wherein the composition has a pH of about 7. This composition generally exhibits prolonged stability against phase-separation under severe conditions of temperature and excellent freeze-thaw recovery and stability; moreover, this concentrated composition can conveniently be diluted with additional perchlorethylene to provide a use level composition consisting essentially of about 0.3% by weight MEA-LAS (C_{12}) and about 99.7% by weight perchlorethylene (and, insignificantly, a minor amount of isopropanol), which use level composition is single-phase and generally achieves high levels of fabric cleaning and low levels of fabric graying.

Optionally, the concentrated compositions herein can additionally contain one or more of a variety of other fabric treating agents which are soluble in the dry cleaning solvent. Examples of such agents, which are especial-

ly desirable for inclusion herein, are, e.g., brighteners (which can be nonionic or cationic and, preferably, are of the anionic stilbene-derivative types), perfumes, antistatic agents, fabric softening agents, and germicides. Generally, the amounts of such agents (e.g., brighteners and perfumes) employed herein are quite small and range from about 0.01% to about 3% by weight of a concentrated level composition herein; larger amounts can, if desired, be used. After dilution to a use level composition, the amount of such agents generally ranges from about 0.0001% to about 0.03% by weight of the use level composition.

The following examples will serve to further illustrate the invention herein and it will be understood that said examples in no way limit the invention.

The examples herein generally illustrate, by way of comparison, the stability of the concentrated level compositions herein and the improved dry cleaning performance achieved by use level compositions derived therefrom.

Unless otherwise noted, the comparison tests performed therein, briefly, involved the following procedure:

Test swatches (4" x 4") are cut from bleached, mercerized cotton print cloth. For each test, 18 swatches are used; nine are clean or unsoiled swatches and nine are each soiled with an insoluble soil commonly referred to as rug-beater soil. Four readings of each swatch, clean and soiled, are then taken on a reflectometer to obtain its original reflectance (Ro) using an 81.4 percent reflectance backplate (Filter G) with the swatches being read in nine layers (i.e., swatches are backed by sufficient fabric, which is washed in the reference composition, to make nine layers). The swatches are thereafter placed into a relative humidity (R.H.) conditioner and conditioned for at least 36 hours over a saturated sodium acetate solution at 75% R.H. and about 75° F. Three clean and three solid swatches are then placed into each of three 500 ml. Launder-Ometer cans along with 30 stainless-steel balls and 150 ml. of a dry cleaning composition having a measured weight concentration of detergent as measured at 75% R.H. by conventional techniques. Each can, with its contents, is then placed into the Launder-Ometer and run for one hour, after which each can is removed, the swatches drained and separated by pouring the contents through a funnel, and the swatches dipped about 10 times in clean perchlorethylene. The swatches are thereafter placed on a blotter and allowed to dry, after which each swatch is again similarly read on the reflectometer to obtain its final reflectance (R_f). Cleaning performance is calculated using the average original and final reflectances for the nine soiled swatches in accordance with the equation:

(3)

$$\text{Cleaning } (C) = \frac{R_f - Ra}{R_f - Ra \text{ (reference composition)}}$$

Graying (G) is calculated using the average original and final reflectances for the nine clean swatches in accordance with Equation 3 above. Overall dry cleaning performance is then determined by dividing the cleaning performance (C) by the graying performance (G) to obtain the *C/G* ratio.

The reference composition referred to above and employed in the examples for comparative purposes, is one generally used as a standard in the industry and is a dry cleaning composition consisting essentially of about 99.4% by weight perchlorethylene as the solvent and about 0.6% of a detergent consisting essentially of sodium di-n-octyl sulfo-succinate. This composition makes an excellent standard because the detergent is a relatively pure chemical compound available in 100% pure grade; the composition has been assigned a C value of 1, a G value of 1 and a *C/G* ratio of 1.

Unless otherwise noted in the examples, all percentages and parts are by weight. Generally, a difference of 10% or better between *C/G* ratios is considered significant, in accordance with recognized grading practice in the industry. Variations in *C/G* ratios of any single composition repeatedly appearing in the following examples is generally due to the varying soil loads of the test swatches and/or to experimental error. Generally, higher *C/G* ratios reflect both better fabric cleaning and lower fabric graying.

EXAMPLE I

Thirty-five concentrated dry cleaning compositions, having a pH of about 8, were prepared consisting essentially of perchlorethylene containing about 40% of an essentially pure, broad cut MEA-LAS (C_{12}) anionic detergent additive; the compositions, each of which additionally contained about 0.3% water carried over into the compositions along with the detergent additive, were then divided in 5 groups of seven. To the first group (Group #1) was then added about 0.5% isopropanol (IPA); to the second was added about 1% IPA; to the third, about 1½% IPA; and, to the fourth group, about 2% IPA. The fifth group (Group 5) was not provided with IPA and was, therefore, used as a reference or blank.

One sample from each of the five groups was then allowed to sit undisturbed at 0°, 10°, 30°, 40°, 50°, 70°, and at room temperature (about 75°); temperatures are in degrees Fahrenheit.

In less than three days, each of the seven samples of the fifth group (i.e., the blank) were visually noted to have separated into aqueous and organic phases; moreover, those samples stored at temperatures of about 40° F. or below exhibited unsatisfactory freeze-thaw stability and did not recover.

All the samples of the remaining four groups did not exhibit phase-separation even after a testing period of about one month, indicating the effective coupling function achieved in the concentrated compositions herein.

EXAMPLE II

To further illustrate the undesirable effects of "carried over" water present in the concentrated dry cleaning compositions, three concentrated compositions consisting essentially of perchlorethylene containing, respectively, about 46%, about 42%, and about 40% essentially pure, broad cut MEA-LAS (C_{12}) were prepared and each divided into three samples. A sample of each composition was tested for stability at various conditions indicated by the following results.

The 46% detergent composition samples were cloudy at room temperature (about 75° F.) as well as at lower temperatures and did not recover or reassume a single-phase after vigorous shaking. The 42% detergent composition samples were all clear and single-phase at room temperature but did not exhibit freeze-thaw recovery to a clear, single-phase composition after overnight storage at a temperature of about 40° F. The 40% detergent composition samples were clear and single-phase at room temperature and exhibited satisfactory freeze-thaw recovery after storage at about 40° F. for three days; however, these samples subsequently (at about one week) exhibited phase-separation and were unable to recover at temperatures of about 70° F. or lower.

When, however, isopropanol or ethyleneglycol-monobutyl ether is added in a similar amount to similar concentrated composition samples (pH about 8) and similarly tested, the samples are generally stable against phase-separation and exhibit satisfactory freeze-thaw recovery even after prolonged storage.

EXAMPLE III

A concentrated composition (pH about 8) herein, consisting essentially of perchlorethylene containing about

40% essentially pure, broad cut MEA-LAS (C_{12}) and about 0.5% isopropanol, was prepared; the composition was tested for stability as described in Example I and results of the test were similar to those of IPA-containing compositions therein.

The composition was then diluted with additional perchlorethylene to obtain a single-phase use level dry cleaning composition (Composition A) having a pH about 7 and consisting essentially of about 0.3% MEA-LAS (C_{12}) and about 99.7% perchlorethylene and additionally containing a small amount of isopropanol; this composition was then tested for dry cleaning performance in accordance with the comparison test procedures described in the foregoing discussion.

Other use level compositions employed in the comparison tests were Composition B and Composition C, as follows:

Composition B (pH about 7):
- 0.3%—MEA-LAS (C_{12})
- 99.7%—Perchlorethylene

Composition C:
- 0.9%—Admixture comprising:
  - (a) C_1–C_4 amine salt of a linear C_{12} alkyl benzene—20%
  - (b) Nonionic ethoxylate of a C_8–C_9 alkyl benzene and magnesium phosphate esters thereof—40%
  - (c) Hydrocarbon solvent—40%
- 99.1%—Perchlorethylene

The results, relative to the Reference Composition, are as follows:

Composition:	*C/G* ratio
Reference Composition	1.00
A	3.87
B	3.90
C	3.39

The results indicate the stability achieved by employing a coupling agent in the concentrated compositions herein and further demonstrate that the concentrated compositions herein can be diluted with a suitable chlorinated solvent to achieve use level compositions in which the coupling agent is not essential and does not harm the improved dry cleaning performance generally obtained therewith.

EXAMPLE IV

When the procedure of Example III was repeated, substituting ethyleneglycol-monobutyl ether for the isopropanol used therein, the resulting concentrated compositions was similarly stable against phase-separation and a similar use level composition derived therefrom achieved similarly improved dry cleaning performance, specifically calculated as a *C/G* ratio of about 3.88.

EXAMPLE V

The concentrated compositions of the invention herein and use level compositions derived therefrom are advantageously suitable for the desirable incorporation of optional additives. Suitable dry cleaning compositions (pH about 7) of the invention herein, which compositions contain a perfume and a brightener, consist essentially of about:

(a) Use level composition

	Percent
MEA-LAS (C_{12})	0.3
Isopropanol	0.005
Perchlorethylene	99.6928
Perfume	0.002
Anionic brightener	0.0002
	100.000

(b) Concentrated level composition

	Percent
MEA-LAS (C_{12})	40
Isopropanol	0.5
Perchlorethylene	59.23
Perfume	0.25
Anionic brightener	0.02
	100.00

When, in any of the foregoing examples, the MEA salt of an essentially pure, broad cut, linear octyl, nonyl, decyl, undecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, or octadecyl benzene sulfonic acid is substituted for the C_{12} MEA-LAS employed therein, results similar to those therein are obtained.

Similarly, when in any of the foregoing examples, the HEA employed in the C_{12} MEA-LAS therein is substituted with an admixture of alkanolamines consisting of about 20% by weight MEA and about 80% by weight DEA or consisting of about 60% by weight MEA and about 40% by weight TEA, results similar to those reported therein are obtained.

Similarly, when in any of the foregoing examples, the perchlorethylene employed therein is substituted with methyl chloroform, results similar to those obtained therein are achieved. When the perchlorethylene employed therein is substituted with a mixture of benzene, toluene, and xylene, the resulting concentrated compositions are similarly stable and, after dilution, provide use level compositions which are finely dispersed, homogeneous emulsions and which similarly achieve improved dry cleaning performance.

Having described the invention in detail, what is now claimed is:

1. A concentrated dry cleaning composition which is stable against phase separation, said composition consisting essentially of

(A) from 20% to about 60% by weight of an anionic detergent which consists essentially of an essentially pure, broad cut, linear alkyl benzene sulfonic acid, which has been neutralized with monoethanolamine and which is substantially free of alkyl benzene sulfonamide and monoethanolamine salt by-products, and wherein said alkyl in said alkyl benzene sulfonic acid is a mixture of alkyls having an average chain length of from about 8 to about 18 carbon atoms,

(B) from about 0.25% to about 0.75% by weight of a coupling agent selected from the group consisting of ethylene glycolmonalkyl ethers wherein the monoalkyl group contains from 1 to about 4 carbon atoms, and monohydroxy alcohols containing from 1 to about 4 carbon atoms,

(C) and the balance a chlorinated dry cleaning solvent. said composition having a pH within the range of about 6.5 to about 9, and wherein the weight ratio of said detergent to said coupling agent is at least about 80:1.

2. A concentrated dry cleaning composition in accordance with claim **1**, said composition consisting essentially of about 40% by weight of component (A), wherein the alkyl is a mixture of alkyls having an average chain length of between 11 and 12 carbon atoms, about 0.5% by weight of isopropanol, about 0.25% by weight perfume, about 0.02% by weight brightener, and about 59.23% by weight perchlorethylene.

3. A concentrated dry cleaning composition in accordance with claim **1**, wherein said coupling agent is selected from the group consisting of ethyleneglycol-monobutyl ether and isopropanol.

4. A concentrated dry cleaning composition in accordance with claim **3**, wherein said composition consists essentially of said solvent containing about 40% by weight of said detergent and about 0.5% by weight of said coupling agent.

5. A concentrated dry cleaning composition in accordance with claim 4, wherein said solvent is selected from the group consisting of methyl chloroform and perchlorethylene.

6. A concentrated dry cleaning composition in accordance with claim 5, wherein said solvent is perchlorethylene.

7. A concentrated dry cleaning composition in accordance with claim 6, wherein said alkyl is a mixture of alkyls having an average chain length of about 12 carbon atoms.

8. A concentrated dry cleaning composition in accordance with claim 7, wherein said pH is about 7.

References Cited

UNITED STATES PATENTS

2,271,635	2/1942	Flett	8—142 X
3,013,973	12/1961	Bennett	252—49.5 X
3,222,286	10/1962	Barnes	252—171 X
3,310,498	3/1967	Michaels et al.	8—142 X
3,310,499	3/1967	Michaels et al.	8—142 X
3,349,038	10/1967	Michaels et al.	252—161
3,484,379	12/1969	Mankowich	252—161 X

OTHER REFERENCES

Bennett: The Chemical Formulary, vol. I. p. 79, 1933.

Gregory: Use and Applications of Chemicals and Related Materials, 1939, p. 331.

"Cellosolve" and "Carbitol" Solvents-Glycol Ethers, Union Carbide Corporation, 1962, p. 7.

LEON D. ROSDOL, Primary Examiner

H. A. PITLICK, Assistant Examiner

U.S. Cl. X.R.

8—142; 252—152, 161, 162, 170, 171

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,642,644 **Dated** February 15, 1972

Inventor(s) Herbert E. Grote and Wilbur G. Henry

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 55, delete "Ra" and insert therefor --- Ro ---.

Column 9, line 57, delete "Ra" and insert therefor --- Ro ---.

Column 12, line 19, delete "HEA" and insert therefor --- MEA ---

Column 12, line 51, delete "glycolmonalkyl" and insert therefor --- glycolmonoalkyl ---.

Signed and sealed this 4th day of July 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents