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2,994,665

HEAVY DUTY LIQUID DETERGENT COMPOSITIONS CONTAINING A PAIR OF CELLULOSIC SOIL SUSPENDING AGENTS

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No Drawing. Filed Apr. 15, 1959, Ser. No. 806,429
9 Claims. (Cl. 252-137)

The present invention relates to detergent compositions, and more particularly to concentrated heavy duty liquid detergent compositions which are uniform stable suspensions showing no separation into layers at room temperature and which are highly effective in preventing soil redeposition when used at washing concentrations.

Many detergent compositions have heretofore been prepared, but they have primarily been in a powdered form and thereby have many disadvantages enumerated below. Powdered detergent compositions are generally prepared by spray drying or drum drying, which are costly operations. When used in washing, the powdered detergent compositions must be dissolved to form dilute aqueous washing solutions. This step of dissolving or dispersing the powdered detergent compositions in the wash water is time consuming. Frequently, the powdered detergent compositions are difficultly dispersed, since they may tend to form lumps. Powdered detergent compositions, moreover, tend to vary greatly in density unless particular care is taken in their preparation. Such a variation in density makes it difficult to determine the exact amount thereof to be employed during washing. In addition, powdered detergent compositions may be difficult to dispense, since they sometimes clog the orifices of a dispenser. Also powdered detergent compositions have a tendency to cake at high humidities upon standing in their open containers. Moreover, powdered detergent compositions, being normally sold in cardboard containers, are subject to spilling and waste in the event an open container is accidentally knocked over. Furthermore, their dustiness may be bothersome, particularly to persons who suffer from dust allergies.

All of these disadvantages of powdered detergent compositions can be obviated by employing concentrated liquid detergent compositions. While light duty liquid detergent compositions have been prepared heretofore, they have proved to be suitable only for dishwashing and the cleaning of fine fabrics. Light duty liquid detergent compositions are unsatisfactory for washing heavily soiled cotton fabrics, since such compositions have inadequate soil removal characteristics. Heavy duty liquid detergent compositions, on the other hand, have excellent soil removal characteristics and are ideally suited for the washing of heavily soiled cotton fabrics and other fabrics.

A highly effective heavy duty liquid detergent composition has been fully described in U.S. Patent No. 2,859,182 issued November 4, 1958. This homogeneous heavy duty liquid detergent composition consists essentially of an aqueous solution of a potassium alkylaryl sulfonate, an alkali metal aryl sulfonate, tetrapotassium pyrophosphate or pentapotassium tripolyphosphate, and at least one alkylolamide or an ethylene oxide condensation product thereof. The composition may also have present therein alkali metal silicates, alkalies, perfumes, dyes, brighteners, and other compatible adjuvants. Complete details concerning this homogeneous heavy duty liquid detergent composition may readily be obtained by reference to said patent.

This composition could be further improved, if it were possible to incorporate therein soil suspending agents which would prevent or inhibit the redeposition of soil

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upon fabrics washed repeatedly in diluted wash solutions thereof and thereby avoid greying of the fabrics. Various cellulose derivatives have been used heretofore as soil suspending agents in powdered detergent compositions.

5 The incorporation of a cellulose derivative into a powdered detergent composition presents no particular problem, since the detergent composition is in powdered form. The incorporation of cellulosic soil suspending agents in the above described heavy duty liquid detergent compositions, however, is not a simple matter.

10 Thus, when one or a mixture of various cellulose derivatives were incorporated in the detergent composition, the cellulosic component separated out within a few hours and the composition became stratified into two or more layers, one being a clear liquid and the others being milky or cloudy. For example, separate samples of the following representative heavy duty liquid detergent formulation were prepared.

Components	Percent by Weight
Potassium Dodecylbenzene Sulfonate.....	10.0
Tetrapotassium Pyrophosphate.....	19.1
Sodium Xylene Sulfonate (Commercial).....	8.15
Lauric Diethanolamide.....	3.8
25 Lauric Isopropanolamide.....	3.2
Sodium Silicate (37%) (Na ₂ O:SiO ₂ of 1:2.5).....	7.0
Calcofluor MR.....	0.081
Tinopal RBS.....	0.048
Water+KOH to pH 12.1.....	48.171
Total Cellulose Derivatives.....	0.5
30 Total.....	100.000

In the above formulation Calcofluor MR and Tinopal RBS are optical brighteners which are respectively disodium N:N'-bis-(2,4-diphenylamino-1:3:5-triazyl [6]) 4:4'-diamino stilbene 2:2'-disulfonate and sodium-2-(stilbyl-4'')-(naphtho-1':2':4:5) - 1:2:3 - triazole-2''-sulfonate.

The 0.5% total (except where otherwise indicated) cellulose derivatives in the separate samples was made up as follows: (1) 100% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit, (2) 100% low viscosity methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule, (3) 45 100% sodium carboxymethylethylcellulose having 0.22 mole of carboxymethyl groups and 1.0 mole of ethyl groups per anhydroglucose unit, (4) 100% ethylcellulose having 1.26 moles of ethyl groups per anhydroglucose unit, (5) 100% sodium carboxymethylmethylcellulose having 0.15-0.2 mole of carboxymethyl groups per anhydroglucose unit and 14-22% of methoxyl groups per cellulose molecule (0.25% total cellulose derivatives), (6) 100% sodium carboxymethylhydroxyethylcellulose having 0.91 mole of carboxymethyl groups and 0.50 mole of hydroxyethyl groups per anhydroglucose unit, (7) 55 57.1% sodium carboxymethylhydroxyethylcellulose having 0.91 mole of carboxymethyl groups and 0.50 mole of hydroxyethyl groups per anhydroglucose unit plus 42.9% sodium carboxymethylmethylcellulose having 0.15-0.2 mole of carboxymethyl groups per anhydroglucose unit and 14-22% of methoxyl groups per cellulose molecule (0.35% total cellulose derivatives), (8) 40% sodium carboxymethylcellulose having 1.94 moles of carboxymethyl groups per anhydroglucose unit plus 60% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% of methoxyl groups per cellulose molecule, (9) 80% sodium carboxymethylhydroxyethylcellulose having 0.36 mole of carboxymethyl and 1.07 moles of hydroxyethyl groups per anhydroglucose unit plus 20% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% of meth-

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oxyl groups per cellulose molecule, (10) 57.1% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus 42.9% sodium carboxymethylmethylcellulose having 0.25 mole of carboxymethyl groups per anhydroglucose unit and 10-14% of methoxyl groups per cellulose molecule (0.35% total cellulose derivatives), (11) 60% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus 40% sodium carboxymethylethylcellulose having 0.22 mole of carboxymethyl groups and 1.0 mole of ethyl groups per anhydroglucose unit, (12) 80% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus 20% ethylcellulose having 1.26 moles of ethyl groups per anhydroglucose unit, (13) 60% sodium carboxymethylhydroxyethylcellulose having 0.91 mole of carboxymethyl groups and 0.50 mole of hydroxyethyl groups per anhydroglucose unit plus 40% of sodium carboxymethylethylcellulose having 0.68 mole of carboxymethyl groups and 0.65 mole of ethyl groups per anhydroglucose unit, (14) 100% methylhydroxypropylcellulose having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule, (15) 100% methylhydroxypropylcellulose having 28-30% methoxyl groups per cellulose molecule and 7-12% hydroxypropyl groups per cellulose molecule, and (16) 100% dihydroxypropylcellulose (6100 centipoise viscosity at 25° C. in a 2% solution in 5% aqueous sodium hydroxide) having 0.3 mole of dihydroxypropyl groups per anhydroglucose unit. In the three instances where the total cellulose derivatives were lowered below 0.5%, the amount of water in the detergent composition was raised a corresponding amount.

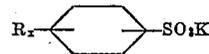
Each of these heavy duty liquid detergent compositions containing either one or a mixture of cellulose derivatives was allowed to age for one week at room temperature (70-75° F.). Within only one to twenty-four hours, however, every one of these detergent compositions became unstable and separated into two layers, one being clear and the other being a cloudy milky layer. While each of these heavy duty liquid detergent compositions contained cellulose derivatives, they were completely unsuitable because they were unstable and separated into layers, thereby presenting an unattractive appearance which would be completely unacceptable to a consumer, such as a housewife. Containers of the detergent compositions would have to be shaken prior to use in order to resuspend the separated celluloses as best as possible and insure that a dosage poured from the containers had the correct amount of celluloses therein. Moreover, the flecks of celluloses ultimately combined to form a viscous layer which was hard to resuspend even with vigorous shaking.

It was found quite surprisingly, however, that a concentrated heavy duty liquid detergent composition could be prepared containing cellulose derivatives as soil suspending agents which would be highly effective in preventing soil redeposition and greying of fabrics and which would be a stable uniform suspension showing no separation into layers at room temperature over extended periods, provided the cellulose derivative soil suspending agents were incorporated in the heavy duty liquid detergent composition in particular pairs. Accordingly, the heavy duty liquid detergent compositions of the invention which are stable uniform suspensions showing no separation into layers at room temperature and which are highly effective in preventing soil redeposition when used at washing concentrations consist essentially of an aqueous solution of from about 7% to about 10% of a potassium alkylaryl sulfonate, from about 5% to about 8% total of one or more alkali metal aryl sulfonates, from about 27% to about 10%, preferably about 20%, of tetrapotassium pyrophosphate or pentapotassium tri-

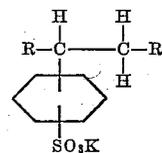
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least one alkylolamide or an ethylene oxide condensation product thereof, and a pair of cellulose derivatives as further described below.

The potassium alkylaryl sulfonates have the general formula



where R is an alkyl group, which may be saturated or unsaturated and straight or branched chain, having from 1 to 15 carbon atoms, at least one R having 8 to 15 carbon atoms, x is a number from 1 to 5, and may be an average number. Suitable potassium alkylaryl sulfonates include, for example, potassium tertiaryoctylbenzene sulfonate, potassium kerylbenzene sulfonates obtained by condensing kerosene with benzene and sulfonating the product, potassium nonylbenzene sulfonate, potassium nonyltoluene sulfonate, potassium dodecyltoluene sulfonate, potassium dodecylbenzene sulfonate, and the potassium phenyl polypropylene sulfonates, described in U. S. Patent No. 2,477,383 to Lewis, which are sulfonated phenyl alkanes in which the alkyl carbon at the benzene ring is tertiary:



where R and R' taken together with the remainder of the polypropylene radical form an alkyl group having an average molecular weight corresponding to from about 12 to about 15 carbon atoms. The potassium alkylaryl sulfonate anionic detergent is used in the composition to supply a portion of the foaming and wetting action necessary in a heavy duty liquid detergent product designed for household use.

The polyphosphate, i.e., tetrapotassium pyrophosphate or pentapotassium tripolyphosphate, is employed in the composition to supply the heavy duty detergent feature of the liquid, and impart good soil removal properties thereto. As the amount of polyphosphate is increased, the amount of potassium alkylaryl sulfonate is decreased.

Suitable alkali metal aryl sulfonate or mixtures thereof totaling from about 5% to about 8% include the following sodium or potassium aryl sulfonates; toluene sulfonate, tetralin sulfonate, ethylbenzene sulfonate, isopropylbenzene sulfonate, ortho-xylene sulfonate, metaxylene sulfonate, a mixture of 80% toluene sulfonate and 20% ethylbenzene sulfonate, a mixture of 61% ortho-xylene sulfonate and 39% isopropylbenzene sulfonate, a mixture of 15% ortho-xylene sulfonate, 70% meta-xylene sulfonate, and 15% para-xylene sulfonate, a mixture of 47% toluene sulfonate plus 53% of a mixture of 15% ortho-xylene sulfonate, 70% meta-xylene sulfonate, and 15% para-xylene sulfonate, a mixture of 22% ortho-xylene sulfonate, 53% meta-xylene sulfonate, 5% para-xylene sulfonate, 18% ethylbenzene sulfonate, and 2% toluene sulfonate, and a mixture of from about 1% to about 10% toluene sulfonate plus from about 99% to about 90% of a mixture of 22% ortho-xylene sulfonate, 53% meta-xylene sulfonate, 5% para-xylene sulfonate, 18% ethylbenzene sulfonate, and 2% toluene sulfonate. The alkali metal aryl sulfonate is employed in the heavy duty liquid detergent composition to aid in solubilizing the potassium alkylaryl sulfonate in the presence of a considerable amount of the polyphosphate and other inorganic materials. The alkali metal aryl sulfonate also solubilizes the alkylolamides which are either insoluble in water or incompatible with aqueous solutions of polyphosphates. There is no advantage in adding more of the alkali metal aryl sulfonate than is necessary for its solubilizing effect, since this material appears to contribute

nothing to the detergent and dishwashing characteristics of the heavy duty liquid detergent composition.

The alkylolamide may be either a monoalkylolamide or a dialkylolamide. Typical examples of suitable alkylolamides are lauric isopropanolamide, lauric diethanolamide, coconut monoethanolamide, capric diethanolamide, tallow diethanolamide, and the monoethanolamide of a 1:1 mixture of caprylic and capric acids. The alkylolamides act as solubilizers in conjunction with the alkali metal aryl sulfonate to prevent the separating out from solution of the potassium alkylaryl sulfonate.

Other suitable alkylolamides which may also be employed include ethylene oxide condensation products thereof, for example, the condensation product of one mole of lauric monoethanolamide with one mole of ethylene oxide and the condensation product of one mole of lauric isopropanolamide with one mole of ethylene oxide. All of the above alkylolamides may be used either singly or in suitable mixtures.

The heavy duty liquid detergent composition also contains a total of from about 0.1% to about 3%, and preferably from about 0.25% to about 1%, and more preferably from about 0.5% to about 0.7%, of a pair of soil suspending cellulose derivatives which are simple or mixed lower alkyl, hydroxyalkyl, or carboxyalkyl ethers of cellulose and form a uniform stable suspension in the aqueous solution. These pairs of cellulosic soil suspending agents include the following: (1) about 9% sodium carboxymethylhydroxyethylcellulose having 0.91 mole of carboxymethyl groups and 0.50 mole of hydroxyethyl groups per anhydroglucose unit plus about 91% sodium carboxymethylmethylcellulose having 0.15-0.2 mole of carboxymethyl groups per anhydroglucose unit and 14-22% of methoxyl groups per cellulose molecule, (2) about 8% sodium carboxymethylcellulose having 1.94 moles of carboxymethyl groups per anhydroglucose unit plus about 92% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule, (3) about 16% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus about 84% methylcellulose having 35-36% methoxyl groups per cellulose molecule, (4) about 20% sodium carboxymethylcellulose having 0.76 mole of carboxymethyl groups per anhydroglucose unit plus about 80% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule, (5) about 22% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus about 78% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule, (6) about 44% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus about 56% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule, (7) about 29% sodium carboxymethylhydroxyethylcellulose having 0.91 mole of carboxymethyl groups and 0.50 mole of hydroxyethyl groups per anhydroglucose unit plus about 71% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% of methoxyl groups per cellulose molecule, (8) about 44% sodium carboxymethylhydroxyethylcellulose having 0.36 mole of carboxymethyl groups per anhydroglucose unit plus about 56% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule, (9) about 44% sodium carboxymethylhydroxyethylcellulose having 0.73 mole of carboxymethyl groups and 0.87 mole of hydroxyethyl groups per anhydroglucose unit plus about 56% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule, (10) about 62% methylhydroxypropylcellulose (4000 centipoise viscosity in a 2% aqueous dis-

persion) having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule plus about 38% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit, (11) about 72% methylhydroxypropylcellulose (50 centipoise viscosity in a 2% aqueous dispersion) having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule plus about 28% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit, (12) about 54% methylhydroxypropylcellulose (4000 centipoise viscosity in a 2% aqueous dispersion) having 28-30% methoxyl groups per cellulose molecule and 7-12% hydroxypropyl groups per cellulose molecule plus about 46% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit, (13) about 42% methylhydroxypropylcellulose (4000 centipoise viscosity in a 2% aqueous dispersion) having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule plus about 58% dihydroxypropylcellulose having 0.3 mole of dihydroxypropyl groups per anhydroglucose unit, (14) about 64% methylhydroxypropylcellulose (50 centipoise viscosity in a 2% aqueous dispersion) having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule plus about 36% dihydroxypropylcellulose having 0.3 mole of dihydroxypropyl groups per anhydroglucose unit, and (15) from about 70% to about 90% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule plus from about 30% to about 10% dihydroxypropylcellulose having 0.3 mole of dihydroxypropyl groups per anhydroglucose unit. It will be appreciated that the sodium cation on the carboxymethyl group is equivalent to other cations, such as potassium or ammonium or organic amine cations, such as mono-, di-, or tri-ethanolamine. The substituent contents given above for the cellulose derivatives are expressed in average values.

The remaining component of the heavy duty liquid detergent composition in water which serves as a solvent for the components thereof.

If desired, the liquid detergent composition may contain minor portions of an alkali, such as potassium hydroxide, to neutralize any excess acid impurities present in the components of the composition. In addition, minor portions of compatible perfumes, dyes, optical brighteners, alkali metal silicates, and other desirable adjuvants may be added to the composition. When a water-soluble alkali metal silicate is added to the composition, the pH thereof must be adjusted to about 11.4 or above by the addition of free alkali, such as potassium hydroxide, to keep the silicate in solution. Typical alkali metal silicates include the sodium or potassium silicates having the following alkali to silica ratios: 1:3.92, 1:3.45, 1:2.4, 1:1.8, 1:2.5, and 1:2.0. An amount up to about 6% on a solids basis of the silicate may be employed.

The concentrated heavy duty liquid detergent composition of the invention may be prepared by mixing the components thereof together in the aqueous medium. Heat may be conveniently utilized during the mixing of the components to increase the rate of dissolution thereof. A preferred method for the preparation of the stable and uniform heavy duty liquid detergent composition is the addition of the pair of cellulose derivatives to hot water followed by cooling to form an aqueous solution thereof and the addition to the cellulose solution of an aqueous solution of the potassium alkylaryl sulfonate, alkali metal aryl sulfonate, alkylolamide or ethylene oxide condensation product thereof, and any optical brighteners, dyes, alkali, and alkali metal silicates. The composition is completed by the addition thereto of the tetrapotassium pyrophosphate or pentapotassium tripoly-

phosphate to give a composition having a pH of about 12.

The heavy duty liquid detergent composition of the invention will be further illustrated by the following examples.

A representative heavy duty liquid detergent composition was prepared having the following formula:

Components	Percent by weight
Potassium dodecylbenzene sulfonate	10
Tetrapotassium pyrophosphate	19.1
Sodium xylene sulfonate (commercial)	8.15
Lauric diethanolamide	3.8
Lauric isopropanolamide	3.2
Sodium silicate (37%) (Na ₂ O:SiO ₂ of 1:2.5)	7.0
Calcifluor MR	0.031
Tinopal R.B.S.	0.048
Water plus KOH to pH 12.1	48.171
Total cellulose derivatives	1.050
Total	100.000

¹ Except where otherwise indicated.

Example 1

The total cellulosics in this formulation was 0.26% and consisted of 9.5% sodium carboxymethylhydroxyethylcellulose having 0.91 mole of carboxymethyl groups and 0.50 mole of hydroxyethyl groups per anhydroglucose unit plus 90.5% sodium carboxymethylmethylcellulose having 0.15-0.2 moles of carboxymethyl groups per anhydroglucose unit and 14-22% methoxyl groups per cellulose molecule. The water in the formula was increased in an amount corresponding to the decrease in cellulose content.

Example 2

In this example the 0.5% total cellulosics of the representative formula consisted of 8% sodium carboxymethylcellulose (70 centipoise viscosity in a 2% aqueous dispersion) having 1.94 moles of carboxymethyl groups per anhydroglucose unit plus 92% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule.

Example 3

In this example the 0.5% total cellulosics of the representative formula consisted of 16% sodium carboxymethylcellulose (27 centipoise viscosity in a 2% aqueous dispersion) having 0.7 moles of carboxymethyl groups per anhydroglucose unit plus 84% methylcellulose having 35-36% methoxyl groups per cellulose molecule.

Example 4

In this example the 0.5% total cellulosics of the representative formula consisted of 20% sodium carboxymethylcellulose (3600 centipoise viscosity in a 1% aqueous dispersion) having 0.76 moles of carboxymethyl groups per anhydroglucose unit plus 80% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule.

Example 5

In this example the 0.5% total cellulosics of the representative formula consisted of 22.6% sodium carboxymethylcellulose (27 centipoise viscosity in a 2% aqueous dispersion) having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus 77.4% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule.

Example 6

In this example the total cellulosics of the representative formula was 0.32% and consisted of 43.7% sodium carboxymethylcellulose (27 centipoise viscosity in a 2% aqueous dispersion) having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus 56.3% sodium carboxymethylmethylcellulose having 0.25 mole of carboxymethyl groups per anhydroglucose unit and 10-14%

methoxyl groups per cellulose molecule. The water in the formula was increased in an amount corresponding to the decrease in cellulosic content.

Example 7

In this example the 0.5% total cellulosics consisted of 28.6% sodium carboxymethylhydroxyethylcellulose having 0.91 mole of carboxymethyl groups and 0.50 mole of hydroxyethyl groups per anhydroglucose unit plus 71.4% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule.

Example 8

In this example the 0.5% total cellulosics of the representative formula consisted of 44% sodium carboxymethylhydroxyethylcellulose having 0.36 mole of carboxymethyl groups and 1.07 moles of hydroxyethyl groups per anhydroglucose unit plus 56% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule.

Example 9

In this example the 0.5% total cellulosics in the representative formula consisted of 44% sodium carboxymethylhydroxyethylcellulose having 0.73 mole of carboxymethyl groups and 0.87 mole of hydroxyethyl groups per anhydroglucose unit plus 56% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule.

Example 10

In this example the total cellulosics in the above representative heavy duty liquid detergent formulation was increased to 0.7% with a decrease of 0.2% in the water content. The 0.7% total cellulosics consisted of 30% sodium carboxymethylcellulose (27 centipoise viscosity in a 2% aqueous dispersion) having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus 70% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule.

Example 11

In this example the 0.5% total cellulosics in the representative formula consisted of 62% methylhydroxypropylcellulose (4000 centipoise viscosity in a 2% aqueous dispersion) having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule plus 38% sodium carboxymethylcellulose (27 centipoise viscosity in a 2% aqueous dispersion) having 0.7 mole of carboxymethyl groups per anhydroglucose unit.

Example 12

In this example the 0.5% total cellulosics in the representative formula consisted of 72% methylhydroxypropylcellulose (50 centipoise viscosity in a 2% aqueous dispersion) having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule plus 28% sodium carboxymethylcellulose (27 centipoise viscosity in a 2% aqueous dispersion) having 0.7 mole of carboxymethyl groups per anhydroglucose unit.

Example 13

In this example the 0.5% total cellulosics in the representative formula consisted of 54% methylhydroxypropylcellulose (4000 centipoise viscosity in a 2% aqueous dispersion) having 28-30% methoxyl groups per cellulose molecule and 7-12% hydroxypropyl groups per cellulose molecule plus 46% sodium carboxymethylcellulose (27 centipoise viscosity in a 2% aqueous dispersion) having 0.7 mole of carboxymethyl groups per anhydroglucose unit.

Example 14

In this example the 0.5% total cellulosics in the repre-

representative formula consisted of 42% methylhydroxypropylcellulose (4000 centipoise viscosity in a 2% aqueous dispersion) having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule plus 58% dihydroxypropylcellulose (6100 centipoise viscosity at 25° C. in a 2% solution in 5% aqueous sodium hydroxide) having 0.3 mole of dihydroxypropyl groups per anhydroglucose unit.

Example 15

In this example the 0.5% total cellulose in the representative formula consisted of 64% methylhydroxypropylcellulose (50 centipoise viscosity in a 2% aqueous dispersion) having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule plus 36% dihydroxypropylcellulose (6100 centipoise viscosity at 25° C. in a 2% solution in 5% aqueous sodium hydroxide) having 0.3 mole of dihydroxypropyl groups per anhydroglucose unit.

Example 16

In this example the 0.5% total cellulose in the representative formula consisted of 70% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule plus 30% dihydroxypropylcellulose (6100 centipoise viscosity at 25° C. in a 2% solution in 5% aqueous sodium hydroxide) having 0.3 mole of dihydroxypropyl groups per anhydroglucose unit.

Example 17

In this example the 0.5% total cellulose in the representative formula consisted of 90% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule plus 10% dihydroxypropylcellulose (6100 centipoise viscosity at 25° C. in a 2% solution in 5% aqueous sodium hydroxide) having 0.3 moles of dihydroxypropyl groups per anhydroglucose unit.

At the end of one week's storage at room temperature (70-75° F.) all of the compositions in Examples 1 through 17 were still uniform stable suspensions and showed no evidence of separation into layers. Some of these compositions were stored for several months at room temperature and at the end of this period they were still uniform stable suspensions.

Repeat soil redeposition tests showed that all of these compositions were highly effective in preventing soil redeposition and greying of fabrics. There is reproduced below the data pertaining to a home laundry repeat washing test utilizing two typical heavy duty liquid detergent compositions of the invention containing pairs of cellulose derivatives and a composition without the presence of a pair of cellulose derivatives as a basis of comparison. In this test broadcloth was subjected to a large number of repeat washings in the presence of naturally soiled cloth. The reflectance values of the test cloths were read with a General Electric reflectometer, since this apparatus uses a narrow band of the visible spectrum only and accordingly the presence of optical brighteners or fluorescent whitening agents in the tested detergent formulations does not affect the measured reflectance values. The detergent compositions were as follows:

Compositions.....	A	B	C
Potassium Dodecylbenzene Sulfonate.....	10	10	10
Tetrapotassium Pyrophosphate.....	19.1	19.1	19.1
Sodium Xylene Sulfonate (Commercial).....	8.15	8.15	8.15
Lauric Diethanolamide.....	3.8	3.8	3.8
Lauric Isopropanolamide.....	3.2	3.2	3.2
Sodium Silicate (37%) (Na ₂ O:SiO ₂ of 1:2.5).....	7.0	7.0	7.0
Calcium MR.....	0.04	0.04	0.02
Timopal RBS.....	0.06	0.06	0.04
Water+KOH to pH 12.1.....	48.65	47.95	47.19
Total Cellulose Derivatives.....	0.7	1.5
Total.....	100	100	100

In compositions B and C the total cellulose derivatives consisted of 30% sodium carboxymethylcellulose (27 centipoise viscosity in a 2% aqueous dispersion) having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus 70% methylcellulose (25 centipoise viscosity in a 2% aqueous dispersion) having 27.5-32% methoxyl groups per cellulose molecule. The test results are set forth below.

Composition	Reflectance Values		
	5 Washes	10 Washes	20 Washes
A.....	84.5	80.3	78.4
B.....	84.2	81.7	80.4
C.....	85.0	83.5	81.2

The higher reflectance values for the cloth washed 10 or 20 times in the compositions of the invention (compositions B and C) compared with composition A clearly show the compositions of the invention are highly effective in preventing soil redeposition and greying of fabrics, since they show a significant improvement even at the low levels of total soil available from naturally soiled cloth.

The above examples clearly illustrate that the heavy duty liquid detergent compositions of the invention contain pairs of cellulose derivatives as soil suspending agents, and yet the compositions remain as stable uniform suspensions without separation into layers at the end of one week's storage at room temperature (70-75° F.). Moreover, the compositions are highly effective in preventing the redeposition of soil from soiled fabrics as measured by repeat soil redeposition tests. It will be appreciated that in the above examples potassium alkylaryl sulfonates, alkali metal aryl sulfonates, polyphosphates, and alkylolamides other than those specifically given in the examples may be used in lieu thereof as specified hereinabove with the same results. In addition, the optional optical brighteners, dyes, silicates, and alkalis may be readily omitted from the formulations without destroying the essential properties thereof.

It is not clearly understood at this time why individual cellulose derivatives do not form stable suspensions in the heavy duty liquid detergent composition nor why certain pairs of cellulose derivatives do form stable suspensions in the heavy duty liquid detergent composition while other pairs of cellulose derivatives are unstable in the heavy duty liquid detergent composition and cause undesirable stratification. It is apparent from photomicrographic studies, however, that the heavy duty liquid detergent compositions of the invention have the cellulosic particles present therein in a distinctive form. It was observed that in the cellulose derivative pairs of the invention, the different particles merge or react with one another in the aqueous solution to form a network or interlinking aggregation of particles of one cellulose derivative dispersed within the other, thereby forming a combination of particles which act as a single entity in producing a stable cellulosic suspension. This network of particles having one type of particle dispersed within the other naturally was absent in the case of individual cellulose derivatives and in the case of the cellulosic pairs which formed unstable suspensions.

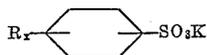
This application is a continuation-in-part of our co-pending application Serial No. 619,931, filed November 2, 1956, and now abandoned.

Various modifications and changes may be made in the compositions of this invention without departing from the spirit thereof, and accordingly it will be understood that the invention is to be limited only within the scope of the appended claims.

We claim:

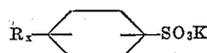
1. A concentrated heavy duty liquid detergent composition which remains uniform without separation into layers at room temperature and which is highly effective

in preventing soil redeposition when used at washing concentrations consisting essentially of an aqueous solution of (1) from about 7% to about 10% of a potassium alkylaryl sulfonate having the general formula



where R is an alkyl group containing from 1 to 15 carbon atoms, at least one R having 8 to 15 carbon atoms, and x is a number from 1 to 5; (2) from about 5% to about 8% total of alkali metal aryl sulfonate selected from the group consisting of toluene sulfonate, tetralin sulfonate, ethylbenzene sulfonate, isopropylbenzene sulfonate, ortho-xylene sulfonate, meta-xylene sulfonate, a mixture of 80% toluene sulfonate and 20% ethylbenzene sulfonate, a mixture of 61% ortho-xylene sulfonate and 39% isopropylbenzene sulfonate, a mixture of 15% ortho-xylene sulfonate, 70% meta-xylene sulfonate, and 15% para-xylene sulfonate, a mixture of 47% toluene sulfonate plus 53% of a mixture of 15% ortho-xylene sulfonate, 70% meta-xylene sulfonate, and 15% para-xylene sulfonate, a mixture of 22% ortho-xylene sulfonate, 53% meta-xylene sulfonate, 5% para-xylene sulfonate, 18% ethylbenzene sulfonate, and 2% toluene sulfonate, and a mixture of from about 1% to about 10% toluene sulfonate plus from about 99% to about 90% of a mixture of 22% ortho-xylene sulfonate, 53% meta-xylene sulfonate, 5% para-xylene sulfonate, 18% ethylbenzene sulfonate, and 2% toluene sulfonate; (3) from about 27% to about 10% of a potassium polyphosphate selected from the group consisting of tetrapotassium pyrophosphate and pentapotassium tripolyphosphate; (4) from about 4% to about 7% total of at least one compound selected from the group consisting of lauric isopropanolamide, lauric diethanolamide, coconut monoethanolamide, capric diethanolamide, tallow diethanolamide, the monoethanolamide of a 1:1 mixture of caprylic and capric acids, the condensation product of one mole of lauric monoethanolamide with one mole of ethylene oxide, and the condensation product of one mole of lauric isopropanolamide with one mole of ethylene oxide; and (5 and 6) from about 0.1% to about 3% total of a pair of soil suspending cellulose ethers selected from the group consisting of simple and mixed lower alkyl, hydroxyalkyl, and carboxyalkyl ethers of cellulose, which ethers form with one another in the aqueous solution a network of particles of one cellulose ether dispersed within the other.

2. A concentrated heavy duty liquid detergent composition which remains uniform without separation into layers at room temperature and which is highly effective in preventing soil redeposition when used at washing concentrations consisting essentially of an aqueous solution of (1) from about 7% to about 10% of a potassium alkylaryl sulfonate having the general formula



where R is an alkyl group containing from 1 to 15 carbon atoms, at least one R having 8 to 15 carbon atoms, and x is a number from 1 to 5; (2) from about 5% to about 8% total of alkali metal aryl sulfonate selected from the group consisting of toluene sulfonate, tetralin sulfonate, ethylbenzene sulfonate, isopropylbenzene sulfonate, ortho-xylene sulfonate, meta-xylene sulfonate, a mixture of 80% toluene sulfonate and 20% ethylbenzene sulfonate, a mixture of 61% ortho-xylene sulfonate and 39% isopropylbenzene sulfonate, a mixture of 15% ortho-xylene sulfonate, 70% meta-xylene sulfonate, and 15% para-xylene sulfonate, a mixture of 47% toluene sulfonate plus 53% of a mixture of 15% ortho-xylene sulfonate, 70% meta-xylene sulfonate, and 15% para-xylene sulfonate, a mixture of 22% ortho-xylene sulfonate, 53% meta-xylene sulfonate, 5% para-xylene sulfonate, 18% ethylbenzene sulfonate, and 2% toluene sulfonate, and a mixture of from about 1% to about 10% toluene sulfo-

5 nate plus from about 99% to about 90% of a mixture of 22% ortho-xylene sulfonate, 53% meta-xylene sulfonate, 5% para-xylene sulfonate, 18% ethylbenzene sulfonate, and 2% toluene sulfonate; (3) from about 27% to about 10% of a potassium polyphosphate selected from the group consisting of tetrapotassium pyrophosphate and pentapotassium tripolyphosphate; (4) from about 4% to about 7% total of at least one compound selected from the group consisting of lauric isopropanolamide, lauric diethanolamide, coconut monoethanolamide, capric diethanolamide, tallow diethanolamide, the monoethanolamide of a 1:1 mixture of caprylic and capric acids, the condensation product of one mole of lauric monoethanolamide with one mole of ethylene oxide, and the condensation product of one mole of lauric isopropanolamide with one mole of ethylene oxide; and (5 and 6) from about 0.1% to about 3% total of a pair of cellulose derivatives selected from the group consisting of about 9% sodium carboxymethylhydroxyethylcellulose having 0.91 mole of carboxymethyl groups and 0.50 mole of hydroxyethyl groups per anhydroglucose unit plus about 91% sodium carboxymethylmethylcellulose having 0.15-0.2 mole of carboxymethyl groups per anhydroglucose unit and 14-22% of methoxyl groups per cellulose molecule, about 8% sodium carboxymethylcellulose having 1.94 moles of carboxymethyl groups per anhydroglucose unit plus about 92% methylcellulose of 25 centipoise viscosity in a 2% aqueous dispersion having 27.5-32% methoxyl groups per cellulose molecule, about 16% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus about 84% methylcellulose having 35-36% methoxyl groups per cellulose molecule, about 20% sodium carboxymethylcellulose having 0.76 mole of carboxymethyl groups per anhydroglucose unit plus about 80% methylcellulose of 25 centipoise viscosity in a 2% aqueous dispersion having 27.5-32% methoxyl groups per cellulose molecule, about 22% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus about 78% methylcellulose of 25 centipoise viscosity in a 2% aqueous dispersion having 27.5-32% methoxyl groups per cellulose molecule, about 44% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus about 56% sodium carboxymethylmethylcellulose having 0.25 mole of carboxymethyl groups per anhydroglucose unit and 10-14% methoxyl groups per cellulose molecule, about 29% sodium carboxymethylhydroxyethylcellulose having 0.91 mole of carboxymethyl groups and 0.50 mole hydroxyethyl groups per anhydroglucose unit plus about 71% methylcellulose of 25 centipoise viscosity in a 2% aqueous dispersion having 27.5-32% methoxyl groups per cellulose molecule, about 44% sodium carboxymethylhydroxyethylcellulose having 0.36 mole of carboxymethyl groups and 1.07 moles of hydroxyethyl groups per anhydroglucose unit plus about 56% methylcellulose of 25 centipoise viscosity in a 2% aqueous dispersion having 27.5-32% methoxyl groups per cellulose molecule, about 44% sodium carboxymethylhydroxyethylcellulose having 0.73 mole of carboxymethyl groups and 0.87 mole of hydroxyethyl groups per anhydroglucose unit plus about 56% methylcellulose of 25 centipoise viscosity in a 2% aqueous dispersion having 27.5-32% methoxyl groups per cellulose molecule, about 62% methylhydroxypropylcellulose of 4000 centipoise viscosity in a 2% aqueous dispersion having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule plus about 38% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit, about 72% methylhydroxypropylcellulose of 50 centipoise viscosity in a 2% aqueous dispersion having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule plus about 28% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit, about

54% methylhydroxypropylcellulose of 4000 centipoise viscosity in a 2% aqueous dispersion having 28-30% methoxyl groups per cellulose molecule and 7-12% hydroxypropyl groups per cellulose molecule plus about 46% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit, about 42% methylhydroxypropylcellulose of 4000 centipoise viscosity in a 2% aqueous dispersion having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule plus about 58% dihydroxypropylcellulose having 0.3 mole of dihydroxypropyl groups per anhydroglucose unit, about 64% methylhydroxypropylcellulose of 50 centipoise viscosity in a 2% aqueous dispersion having 27-29% methoxyl groups per cellulose molecule and 5.5-7.5% hydroxypropyl groups per cellulose molecule plus about 36% dihydroxypropylcellulose having 0.3 mole of dihydroxypropyl groups per anhydroglucose unit and from about 70% to about 90% methylcellulose of 25 centipoise viscosity in a 2% aqueous dispersion having 27.5-32% methoxyl groups per cellulose molecule plus from about 30% to about 10% dihydroxypropylcellulose having 0.3 mole of dihydroxypropyl groups per anhydroglucose unit.

3. A concentrated heavy duty liquid detergent composition as set forth in claim 2 wherein the pair of cellulose derivatives totals about 0.5%.

4. A concentrated heavy duty liquid detergent composition as set forth in claim 2 wherein the pair of cellulose derivatives totals about 0.7% and consists of about 30% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus about 70% methylcellulose having a viscosity of 25 centipoises in a 2% aqueous dispersion and having 27.5-32% methoxyl groups per cellulose molecule.

5. A concentrated heavy duty liquid detergent composition as set forth in claim 3 wherein the pair of cellulose derivatives is about 22% sodium carboxymethylcellulose having 0.7 mole of carboxymethyl groups per anhydroglucose unit plus about 78% methylcellulose of 25 centipoise viscosity in a 2% aqueous dispersion having 27.5-32% methoxyl groups per cellulose molecule.

6. A concentrated heavy duty liquid detergent composition as set forth in claim 3 wherein the pair of cellulose

derivatives is about 8% sodium carboxymethylcellulose having 1.94 moles of carboxymethyl groups per anhydroglucose unit plus about 92% methylcellulose of 25 centipoise viscosity in a 2% aqueous dispersion having 27.5-32% methoxyl groups per cellulose molecule.

7. A concentrated heavy duty liquid detergent composition as set forth in claim 3 wherein the pair of cellulose derivatives is about 29% sodium carboxymethylhydroxyethylcellulose having 0.91 mole of carboxymethyl groups and 0.50 mole of hydroxyethyl groups per anhydroglucose unit plus about 71% methylcellulose of 25 centipoise viscosity in a 2% aqueous dispersion having 27.5-32% methoxyl groups per cellulose molecule.

8. A concentrated heavy duty liquid detergent composition as set forth in claim 3 wherein the pair of cellulose derivatives is about 9% sodium carboxymethylhydroxyethylcellulose having 0.91 mole of carboxymethyl groups and 0.50 mole of hydroxyethyl groups per anhydroglucose unit plus about 91% sodium carboxymethylmethylcellulose having 0.15-0.2 mole of carboxymethyl groups per anhydroglucose unit and 14-22% methoxyl groups per cellulose molecule.

9. A concentrated heavy duty liquid detergent composition as set forth in claim 3 wherein the pair of cellulose derivatives is from about 70% to about 90% methylcellulose of 25 centipoise viscosity in a 2% aqueous dispersion having 27.5-32% methoxyl groups per cellulose molecule plus from about 30% to about 10% dihydroxypropylcellulose having a viscosity of 6100 centipoises at 25° C. in a 2% solution in 5% aqueous sodium hydroxide and having 0.3 mole of dihydroxypropyl groups per anhydroglucose unit.

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