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3,630,922

LIQUID DETERGENT COMPOSITION
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 No Drawing. Continuation-in-part of application Ser. No. 649,018, June 26, 1967. This application June 3, 1968, Ser. No. 733,780

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4 Claims

ABSTRACT OF THE DISCLOSURE

Stable, liquid detergent compositions for cleaning surfaces, said compositions containing particulate materials (e.g., abrasives), water, arylsulfonchloramide bleaching agents, potassium iodide, alkylbenzenesulfonate detergent, zwitterionic synthetic detergent and electrolyte, which preferably comprises a detergency builder.

This application is a continuation-in-part of our co-pending application Ser. No. 649,018, filed June 26, 1967 and now abandoned.

CROSS REFERENCE TO RELATED APPLICATIONS

Other stable liquid detergent compositions for cleaning hard surfaces are disclosed in U.S. Patent 3,520,818 and the application of Cushman Merlin Cambre, entitled Liquid Detergent Composition, Ser. No. 649,019, filed June 26, 1967.

BACKGROUND OF THE INVENTION

This invention relates to liquid detergent compositions adapted for cleaning hard surfaces and containing a bleaching system. More particularly, this invention relates to liquid detergent compositions containing a stable bleaching system and having a yield value of from about 5 to about 600 dynes per square centimeter.

There has been an increasing demand for bleaching liquid detergent compositions adapted for cleaning hard surfaces. These liquid detergent compositions are provided in convenient form and are especially formulated for this particular cleaning application. To obtain optimum cleaning and consumer acceptance, these detergent compositions must be homogeneous and easily pourable. These compositions, when intended for the retail consumer market, should maintain their homogeneity and bleaching effectiveness during ordinary periods of storage and use, and should have acceptable freeze-thaw characteristics. It is highly desirable that liquid detergent compositions for cleaning hard surfaces should exhibit Bingham plastic characteristics; that is, they should exhibit a substantial yield value in order to keep particulate material from settling to the bottom of the container.

When these liquid detergent compositions are intended for industrial applications, extended product stability, as described above, is not as important as it is in the retail consumer market. In industrial applications, the compositions can be reintegrated and the particulate material redistributed before use, for example, by mixing or shaking the compositions. However, even these products should be stable for at least a 24-hour period.

It is also very important that the compositions maintain their bleaching effectiveness during storage.

(A) Yield value

The consistency of simple (or Newtonian) liquids is a function of the nature of the material, temperature, and pressure only. This consistency is known as the "fluid

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viscosity coefficient," "absolute viscosity," or merely "viscosity," and is usually measured in centipoises (1 centipoise=0.01 gram/centimeter-second). With a Newtonian liquid, any force applied to the system produces some deformation, according to the formula

$$\frac{du}{dr} = \frac{F}{\mu}$$

where du/dr =the rate of shear; F =the shear stress, or shearing force per unit area; and μ =the viscosity coefficient.

In the case of non-Newtonian liquids, on the other hand, the consistency is a function of the material, pressure, temperature, and also the shear stress applied to the system. Those non-Newtonian liquids which are classified as Bingham plastics, or real plastics, are not always deformed when a force is applied to the system. Deformation, if any, takes place according to the formula

$$\frac{du}{dr} = \frac{F-f}{\mu_a}$$

where μ_a =the apparent viscosity, or plastic viscosity, at the shear stress F ; f =a characteristic of the liquid called the yield stress, or yield value, measured in units of pressure; and du/dr and F are as defined above.

If the shear stress applied to the system is less than the yield value, the system will not be deformed at all. Hence, a Bingham plastic system is capable of supporting indefinitely insoluble particulate material which has a density greater than that of the supporting medium, so long as the material has a particle size and density such that the shear stress which each particle places on the supporting medium does not exceed the yield value.

This is to be contrasted with suspension of heavy insoluble particulate material in Newtonian liquids with high viscosities. In highly viscous Newtonian liquids, insoluble particulate material is suspended only because the rate of flow is slow. In Bingham plastics, insoluble particulate material is suspended because the stress imposed by the particles does not exceed the yield value of the liquid, and therefore, there is no flow at all. Of course, if the yield value of the supporting medium should sufficiently decrease for any reason, the particles would no longer be suspended. This could be caused, for example, by a physical or chemical change in the supporting medium. If one of the components of the supporting medium is an emulsion which settles into layers upon standing, the yield value can be lost temporarily; but in such a case, the original composition can be reconstituted by mixing. If a chemical reaction either consumes a vital component or produces a damaging one, the loss of yield value can be permanent.

(B) Previous compositions

Liquid detergent compositions containing a combination of alkali metal soaps, ethanol amides and potassium pyrophosphates are known (see U.S. Pat. 3,234,138). Although liquid detergent compositions containing alkali metal soaps, amides and phosphates exhibit useful properties, these compositions also have some disadvantageous features. For example, when particulate materials are added to these compositions and the compositions are then subjected to ordinary storage conditions, they may separate into two layers. As these liquid detergent compositions separate, they lose their ability to support particulate material and, accordingly, the particulate material settles. As another example, a portion of the amides in these compositions is hydrolyzed to soap if the compositions are subjected to high storage temperatures, e.g., 110° F. As the amide hydrolyzes, the liquid detergent characteristics. Again, the particulate material in these

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compositions separate and lose their Bingham plastic compositions is deposited on the bottom of the respective containers.

A variety of detergent compositions containing synthetic anionic detergents, soaps, or both, as well as detergency builders and abrasives, are known. See, for example, U.S. Pats. 3,149,078; 3,210,285; 3,281,367; Canadian Pats. 635,321 and 685,394. These compositions usually require the presence of amides, and frequently contain soaps.

Soaps and amides are undesirable in many situations, however. Soaps react with calcium, magnesium, and other ions present in hard water, forming undesirable scum. Soaps containing about 8 or fewer carbon atoms in their molecular structure act as solubilizing agents, and cause multiple phase systems to lose their Bingham plastic characteristics. Soaps in which the alkyl group is derived from coconut are relatively expensive, as compared to alkylbenzenesulfonate synthetic anionic detergents.

Amides are subject to hydrolysis, especially when compositions are stored at high temperatures, e.g., 110° F. Upon hydrolysis, amides yield ammonium soaps, which are subject to the disadvantages outlined above. For these and other reasons, the use of soaps and amides is to be avoided in practicing the present invention.

Other stable liquid detergent compositions for cleaning hard surfaces are disclosed in U.S. Pat. 3,520,818 and the application of Cushman M. Cambre, Ser. No. 649,019, filed June 26, 1967, for Liquid Detergent Composition. The detergent compositions of U.S. Pat. 3,520,818 are free of amides, but are required to contain soap. The compositions of U.S. Pat. 3,520,818 also differ in the kind and relative proportions of components which can be employed.

Accordingly, it is an object of this invention to provide bleaching liquid detergent compositions which exhibit Bingham plastic characteristics and which are stable for protracted periods of time. It is a further object of this invention to provide bleaching liquid detergent compositions which remain stable when subjected to both depressed and elevated storage temperatures. A still further object of this invention is to provide Bingham plastic, bleaching liquid detergent compositions in which particulate material will not settle to the bottom of the containers when the compositions are stored for protracted periods of time. Another object of this invention is to provide bleaching liquid detergent compositions which exhibit Bingham plastic characteristics and which do not contain soaps or amides. It is another object of this invention to provide a bleaching detergent composition in convenient pourable form. It is yet another object of this invention to provide a bleaching liquid detergent compositions with good bleach stability.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only since various changes and modifications within the spirit and scope of this invention will become apparent to those skilled in the art. All parts, percentages and ratios set forth herein are by weight.

SUMMARY OF THE INVENTION

Surprisingly, it has been discovered, according to the present invention, that the foregoing objects are obtained with an opaque, liquid, bleaching detergent composition which is substantially free of soaps, amides and hydrotopes and which has a yield value of from about 20 to about 600 dynes per square centimeter and an apparent viscosity below about 12,000 centipoises consisting essentially of, by weight of the finished composition.

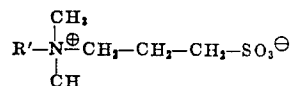
(1) An anionic alkylbenzenesulfonate synthetic detergent having the general formula:



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wherein R is an alkyl chain containing from about 9 to about 15 carbon atoms, and $M^{\oplus}$ is a cation selected from the group consisting of potassium, sodium, and ammonium cations;

(2) A zwitterionic quaternary ammonio synthetic detergent having the general formula:

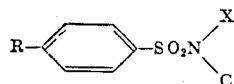


wherein R' is an alkyl chain containing from about 10 to about 18 carbon atoms; the ratio of alkylbenzenesulfonate detergent to the zwitterionic synthetic detergent ranges from about 0.4:1 to about 4:1; and the combined weight of the alkylbenzenesulfonate and zwitterionic synthetic detergents ranges from about 5% to about 20% by weight of the finished composition;

(3) From 1% to about 60% of an insoluble, particulate material having particle diameters ranging from about 1 micron to about 200 microns, and a density of from about 0.5 to about 5.0;

(4) From about 1% to about 10% of polyvalent electrolyte;

(5) From about 1% to about 5% of a bleaching agent having the formula



wherein R is a hydrogen atom or short alkyl group containing from 1 to about 3 carbon atoms and X is selected from the group consisting of sodium, potassium and chlorine atoms;

(6) From about .1% to about .5% of sodium or potassium iodide;

(7) From about 25% to about 85% water; and

(8) Sufficient strong base to adjust the pH of the composition to from about 7.5 to about 13.0; wherein said yield value is sufficient to support said insoluble particulate material.

DETAILED DESCRIPTION

At this juncture, the liquid detergent composition of this invention will be characterized, in its entirety, in order to facilitate a better understanding of the individual components and their functions in these liquid detergent compositions.

(A) Yield value

It is believed that the supporting medium of the liquid detergent composition of this invention (that is, the total composition less the insoluble particulate material) is a suspension which comprises two phases. One phase is isotropic and continuous and consists mainly of inorganic materials such as water, base, and electrolyte. The other discrete phase consists mainly of organic materials such as detergent. The discrete phase is mesomorphic and has a highly oriented physical structure. It is apparently this high degree of orientation which imparts the yield value to the system. The presence of two liquid phases is possible only in the absence of hydrotropes and other solubilizing agents. Furthermore, electrolyte is required in the system to "salt out" the organic materials from the continuous phase; i.e., to lower the solubility of the discrete (mainly organic) phase in the continuous (mainly inorganic) phase.

Because it is usually not known whether a system behaves in a truly plastic manner at low shear rates, the measurement of exact yield values is quite difficult. A close approximation can be obtained by using a Brookfield viscometer. The yield value is estimated, in dynes per square centimeter, by the following relationship:

Yield value

$$= \frac{\text{viscosity at 0.5 r.p.m.} - \text{viscosity at 1 r.p.m.}}{100}$$

This relationship represents an extrapolation of the shear curve to 0 r.p.m. since an absolute shear stress cannot be measured at 0 r.p.m.

The yield values of the liquid detergent compositions of this invention range from about 5 to about 600 dynes per square centimeter. If the yield value is too low, the insoluble, particulate material will not be suspended, because the weight of the individual particles, distributed over the area which supports the particles, will exceed the yield value. However, if the yield value is too great, the composition will become thick and unmanageable because as the yield value increases, so will the apparent viscosity.

A preferred range of yield values to support the insoluble particulate material used in the liquid detergent compositions of this invention is from about 100 to about 400 dynes per square centimeter.

(B) Individual components

The essential individual components of the liquid detergent composition of this invention are alkylbenzenesulfonate detergent, zwitterionic synthetic detergent, insoluble particulate materials, electrolyte, arylsulfoncholoramide bleaching agents, sodium or potassium iodide, and water. Optional components include detergency builders, strong base to adjust pH level, and minor ingredients which have aesthetic value or which improve the effectiveness of the composition. Strong base is not optional, however, if the pH of the detergent composition without it is below about 7.5. The pH of a composition of course varies with the identity and relative amounts of the components used in it; usually no base is necessary. The alkylbenzenesulfonate detergent, zwitterionic synthetic detergent, and, if employed the detergency builders, are the primary cleaning or detergent components of this composition.

In preferred embodiments of this invention, abrasives and detergency builders, as hereinafter defined, are added to the liquid detergent composition of this invention. All of these compositions are capable of suspending insoluble particulate materials of the hereinafter specified density and particle size and, accordingly, these particulate materials can be included as components of these liquid detergent compositions.

(1) Alkylbenzenesulfonate detergent

The alkylbenzenesulfonate detergent used in the liquid detergent compositions has the general formula:

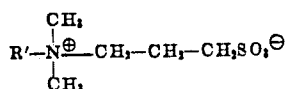


wherein R is an alkyl chain containing from about 9 to about 15 carbon atoms, and $M^{\oplus}$ is a cation selected from the group consisting of potassium, sodium, ammonium cations; it is preferred that R average about 12 carbon atoms and be a normal (straight chain) alkyl group.

From about 2% to about 12% of the above-described alkylbenzenesulfonate detergent, by weight of the finished detergent composition, is utilized in the detergent compositions of this invention. It is preferred that the finished composition contain from about 2% to about 6% alkylbenzenesulfonate. More important than the amount of alkylbenzenesulfonate or zwitterionic detergent present individually, however, is the total amount of these two detergents, and the relative amounts in which they are present, as described below.

(2) Zwitterionic synthetic detergent

The zwitterionic quaternary ammonio synthetic detergent of this invention has the following structural formula:



wherein R' is an alkyl radical containing from about 10 to about 18 carbon atoms. It is preferred that R' be

dodecyl or the alkyls derived from coconut fatty alcohol.

The zwitterionic synthetic detergent described above is utilized in this invention in amounts of from about 2% to about 14% by weight of the finished detergent composition. It is preferred that the zwitterionic synthetic detergent be utilized in amounts of from about 2% to about 7% by weight of the finished composition.

The total amount of alkylbenzenesulfonate and zwitterionic detergents and the relative amounts in which they are present, are more important than the absolute amount of either. While the absolute amount of each detergent is of little independent significance, the total amount of both detergents determines yield value and ability to dissolve grease and dirt, and if excessive, makes the detergent composition too thick and unmanageable. The relative amounts of alkylbenzenesulfonate and zwitterionic detergents sharply affect the ability of the system to support abrasive. Neither alkylbenzenesulfonate nor zwitterionic synthetic detergent, alone, will provide a stable support for insoluble particulate material; however, when they are used together as herein described, they cooperate synergistically in a surprising and unexpected way to provide a stable medium with a yield value that will support insoluble particulate material.

The combined weight of alkylbenzenesulfonate and zwitterionic detergents in the detergent compositions of this invention is from about 5% to about 20% of the total weight of the finished composition. A preferred embodiment contains from about 5% to about 12% of these detergents. About 6% to about 7% was found to be a level which produces a sufficiently high yield value, but not an unduly thick composition.

Within the preferred range of insoluble particulate material (about 40% to about 50%, see below), it can be further said that between about 10% and about 18% of the supporting medium (that is, the entire compositions less suspended insoluble particulate material) should be detergent, and about 10% to about 16% is preferable. About 12% to about 14% gives the best results. At the higher detergent concentrations, the combined detergent and abrasive make the compositions too thick to be manageable; at the lower detergent concentrations there is not enough detergent to provide sufficient yield value to support the abrasive. The upper limit on combined detergent and abrasive is a functional one, and is best expressed in terms of apparent viscosity. The detergent compositions of this invention have an apparent viscosity below about 12,000 centipoises; it is preferred that the apparent viscosity be below about 10,000. As used here and elsewhere in this specification, "apparent viscosity" means the value obtained with a Brookfield Viscometer, Model LVF, using spindle number 3 at 12 r.p.m. At lower (below 40%) abrasive concentrations, the concentration of total detergent in the supporting medium becomes less important, and up to about 20% of the total composition can be detergent.

It is important in the practice of this invention to maintain the weight ratio of alkylbenzenesulfonate to zwitterionic synthetic detergent in the range between from about 0.4:1 to about 4:1. When the alkylbenzenesulfonate to zwitterionic ratios do not fall within these limits, the detergent compositions of this invention may have unacceptably low yield values, or they may separate into two layers at room temperature, or both. It is preferred that the alkylbenzenesulfonate to zwitterionic synthetic detergent ratio be in the range of about 0.4:1 to about 2.0:1. The exact value of this ratio depends on other materials present in the system. For example, a ratio of about 0.86:1 was found particularly effective for a system containing alkylbenzenesulfonate and zwitterionic detergent, sodium sulfate and sodium chloride.

(3) Insoluble particulate material

The insoluble, particulate material which is utilized in this invention can comprise abrasives, bactericides, or

other insoluble, particulate material having a particle size diameter ranging from about 1 to about 200 microns and a density of from about 0.5 to about 5.0. It is preferred that the diameter of the particles range from about 2 microns to about 60 microns and that the density range from about 1.0 to about 2.8. The abrasives which can be utilized in this invention include, but are not limited to, quartz, pumice, pumicite, talc, silica sand, calcium carbonate, china clay, zirconium silicate, bentonite, diatomaceous earth, whiting, feldspar, and aluminum oxide. Non-siliceous abrasives and feldspar are preferred for use herein since most siliceous abrasives tend to inhibit the removal of aluminum marks. If aluminum oxide is used, the pH of the composition should not be above about 11, or the aluminum oxide will dissolve. Furthermore, if a high density abrasive (such as aluminum oxide, pumice containing aluminum oxide, or zirconium silicate) is used, particular care must be taken that the yield value is sufficiently high to support particles of the size and density used. For any particular system, the yield value required can be calculated from the density and particle size of the suspended particles, and from the density of the supporting medium. The yield value required is equal to the pressure per unit area which the weight of the particle exerts on the supporting medium, taking into account the buoyant force of the supporting medium. For a spherical particle of greater density than the supporting medium, this yield value is given by the formula

$$f = \frac{2Dg(d-d')}{3}$$

where f is the yield value in dynes per square centimeter, D is the particle diameter in centimeters; g is the gravitational constant, 980.665 centimeters per second per second; d is the density of the particle to be supported; and d' is the density of the supporting medium (both densities in grams per cubic centimeter). This theoretical yield value should be multiplied by a "safety factor" of about 1.5 or 2.0, to take into account such factors as nonspherical particles, inaccuracy in estimating yield value, and occasional agglomeration of two or more particles, in order to calculate the yield value (as observed) which is necessary to support the particular material which is to be suspended.

In the practice of this invention, from 1% to about 60% of the composition of this invention is insoluble particulate material. It is preferred, however, that from 40% to about 50% by weight of the finished composition be insoluble, particulate material.

(4) Polyvalent electrolyte

From about 1% to about 10% of the finished composition is required to be polyvalent electrolyte. For example, from 1% to about 10% sodium sulfate can be employed, but from about 2% to about 3% is preferred, as this allows higher amounts of detergency builders to be used. One or more detergency builders can be included in this electrolyte to serve as a cleaning aid and as a pH buffer. The amount of detergency builder to be included depends on the particular builder used, but in any case should be between 0% and about 10% by weight of the finished composition. It is preferred that the total amount of builders be from about 1% to about 7%. Many builders, if present in too great a quantity, will cause the system to lose its yield value and suspending capability.

Tetrapotassium pyrophosphate is preferred to other detergency builders because of its good cleaning characteristics and excellent solubility characteristics. The liquid detergent compositions built with tetrapotassium pyrophosphate also exhibit excellent stability characteristics over a wide range of temperatures.

From 0% to about 6% of tetrapotassium pyrophosphate by weight of the finished detergent composition

can be utilized in this invention. To maximize stability and optimize the cleaning characteristics of the liquid detergent compositions, about 3% to about 4% tetrapotassium pyrophosphate should be utilized herein.

Tetraborate can be added to these detergent compositions to improve cleaning (as a detergency builder), to improve low temperature stability properties, and to raise the yield value. The tetraborate can be introduced into the detergent composition in several forms, e.g., anhydrous sodium tetraborate, sodium tetraborate pentahydrate, and sodium tetraborate decahydrate. Sodium tetraborate decahydrate is preferred for use herein as it is readily available to the detergent industry. When the anhydrous or hydrated tetraborate compounds are utilized, they ionize and tetraborate ions are then present in these liquid detergent compositions. It has been found that from 0% to about 0.8% tetraborate, by weight of the finished detergent composition, can be utilized in this invention. This range corresponds to 0% to about 2% sodium tetraborate decahydrate by weight of the finished composition.

Other detergency builders which can be employed without destroying the particle suspending ability of the composition include sodium tripolyphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$, in an amount ranging from 0% to about 3%, and trisodium orthophosphate, Na_3PO_4 , in an amount ranging from 0% to about 7%. Mixtures of these builders can also be employed.

(5) The bleaching agent

The bleaching agent of this invention is an arylsulfonchloramide as described hereinbefore. Specific examples include sodium p-toluenesulfonchloramide, p-toluenesulfondichloramide, sodium benzenesulfonchloramine, and benzenesulfondichloramide. These compounds are commercially available under the names, respectively, of Chloramine T, Dichloramine T, Chloramine B, and Dichloramine B. The corresponding potassium salts are also usable.

(6) The iodide

The sodium or potassium iodide is used at very low levels, e.g., from about 0.1% to about 0.5% to enhance the bleaching effectiveness of the bleaching agent. The bleaching agent, by itself, is almost completely ineffective in the compositions of this invention. The potassium iodide is required for proper bleaching effectiveness.

It has been found, surprisingly, that the bleach system of the compositions of this invention is not stable in the presence of zwitterionic detergents containing hydroxy groups. Accordingly, it is required that the specific zwitterionic detergent claimed herein be used.

(7) Water

From about 25% to about 85% of this composition is water. It is preferred that from about 30% to about 50% by weight of the finished composition be water to optimize yield values and cleaning characteristics of the finished product. It is also preferred that soft water be utilized in this invention.

(8) Strong base

The pH of the composition is from about 7.5 to about 13, preferably from about 8 to about 11. If necessary, the pH is adjusted to this level by adding a strong base. The most desirable strong bases for use herein are sodium hydroxide and potassium hydroxide. In the preferred pH range (about 8 to about 11), the liquid detergent compositions of this invention have higher yield values and greater stability, as well as better cleaning capability. Frequently no pH adjustment is required, however, because the builder salts included raise the pH of the composition to within the desired range.

(9) Minor ingredients

Minor amounts of materials which make the composition of this invention more attractive or more effective can be added if they do not significantly alter the excellent

physical properties of this composition. The following materials are mentioned merely by way of example: tarnish inhibitors such as benzotriazole or ethylenethiourea, brighteners, fluoresters, dyes, bluing agents, perfumes, bactericides and corrosion inhibitors.

Hydrotropes such as sodium or potassium xylenesulfonate, toluenesulfonate, or benzenesulfonate, should not be present in these compositions. Even very small amounts of these hydrotropes solubilize the discrete phase into the continuous phase. The detergent composition, thus, becomes a one-phase solution and loses its Bingham plastic characteristics with concomitant settling of insoluble, particulate material, e.g., abrasive. The composition, in this condition, is aesthetically undesirable and not easily salable on the retail consumer market or the industrial market.

Also to be avoided are soaps, amides, and other materials which are presently or potentially solubilizing agents, or which combine with water hardness ions.

The following example illustrates the present invention.

The following compositions were prepared and evaluated for bleach stability and yield value.

Composition	LAS ¹	HAPS ²	APS ³	H ₂ O	Calcium carbonate abrasive	K ₄ P ₂ O ₇	Na ₂ SO ₄	Quaternary; tertiary amine	Chloramine B	KI	NaOH
1	3.0	-----	3.5	34.8	50	4	2.1	-----	2.0	.1	.5
2	3.0	-----	3.5	34.7	50	4	2.1	-----	2.0	.1	.5
3	3.0	-----	3.5	33.9	50	4	2.1	-----	2.0	.1	.5
4	3.0	8.6	-----	32.7	50	4	2.1	1.2	2.0	.1	.5

Composition	NaCl ¹	CH ₃ OH ²	Yield values		Amount of separation after 3 days 7" of sample (in.)	Percent available chlorine			
			As made	After one week		1 week		2 weeks	
						Room temperature	100° F.	Room temperature	100° F.
1-----	0.2	-----	405	270	1½	96	97	91	87
2-----	0.2	.1	450	225	1½	94	87	88	85
3-----	.8	.1	100	35	1½	91	86	87	82
4-----	.8	.02	150	100	1½	88	61	50	39

¹ Sodium alkyl (C₁₁ av.) benzenesulfonate.

² 3[N,N-dimethyl-N-alkylammonio]-3-hydroxypropane-1-sulfonate wherein the alkyl distribution is 0.5%—C₁₀, 67.5%—C₁₁, 24.5%—C₁₂, 7.0%—C₁₃, and 0.5%—C₁₄.

³ 3[N,N-dimethyl-N-dodecylammonio]-propane-1-sulfonate.

⁴ Specific gravity of about 2.8 and particle diameter of about 25 microns.

⁵ .1% methanol was added to samples 2 and 3 to show that trace amounts of methanol in HAPS were not responsible for the very great bleach loss observed. Sodium chloride was added to sample 3 to show that NaCl in HAPS was not responsible for the very great bleach loss observed.

In each case, viscosity data were measured at room temperature (about 74° F.), even though the samples may have been stored at higher or lower temperatures. The viscosities for yield values were read with a Brookfield Viscometer, Model RVT, using spindle number C2 at 1/2 and 1 r.p.m. The apparent viscosities were read with a Brookfield Viscometer, Model LVF using spindle number 3 at 12 r.p.m.

The apparent viscosities of compositions 1, 2, 3 and 4 were about 1200, about 1200, about 225 and about 400 respectively.

The pH's of compositions 1, 2, 3 and 4 were all about 11.5. The corresponding compositions with the pH's adjusted to about 10.5 are also bleach-stable compositions having similar yield values.

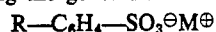
The following builders can be used in the above examples, alone or in combination, in the amounts indicated, with substantially equivalent or better results (and in particular, without destroying the yield value and ability to suspend particles), provided the level of sodium sulfate does not exceed about 3%: tetrapotassium pyrophosphate, 3.5%, as it increases yield value; sodium tetraborate, 1% (as decahydrate); sodium tripolyphosphate, 3%; and trisodium phosphate, 5%.

The following can be substituted, with substantially equivalent results, for the calcium carbonate in the above example: quartz, feldspar, silica, pumice, pumicite, talc, china, clay, zirconium silicate, bentonite, diatomaceous earth, whiting and aluminum oxide, of the same particle sizes. By "substantially equivalent" results in this and the previous paragraph, it is meant that stable suspensions with effective cleaning properties are obtained.

What is claimed is:

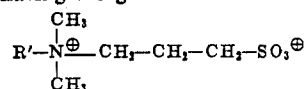
1. A stable, liquid bleaching detergent composition which is free of soaps, amides and hydrotropes and which has a yield value of from about 5 to about 600 dynes per square centimeter and an apparent viscosity below about 12,000 centipoises consisting essentially of,

(1) an anionic alkylbenzene sulfonate synthetic detergent having the general formula:



wherein R is an alkyl chain containing from about 9 to about 15 carbon atoms, and M[⊕] is a cation selected from the group consisting of potassium, sodium and ammonium cations;

(2) a zwitterionic quaternary ammonio synthetic detergent having the general formula:



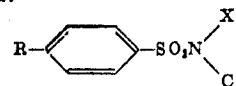
wherein R' is an alkyl chain containing from about 10 to about 18 carbon atoms; the ratio of alkylbenzenesulfonate detergent to the zwitterionic syn-

thetic detergent ranges from about 0.4:1 to about 4:1 and the combined weight of the alkylbenzenesulfonate detergent and the zwitterionic synthetic detergent ranges from about 5% to about 20% by weight of the finished composition;

(3) from about 1% to about 60%, by weight of the finished composition, of insoluble, particulate material selected from the group consisting of quartz, pumice, pumicite, talc, silica sand, calcium carbonate, china clay, zirconium silicate, bentonite, diatomaceous earth, whiting, feldspar and aluminum oxide, said insoluble particulate material having particle diameters ranging from 1 micron to about 200 microns, and a density from about 0.5 to about 5.0;

(4) from about 1% to about 10%, by weight of the finished composition, of a polyvalent electrolyte selected from the group consisting of sodium sulfate, tetrapotassium pyrophosphate, sodium tetraborate decahydrate, sodium tripolyphosphate, trisodium orthophosphate, sodium tetraborate pentahydrate, and anhydrous sodium tetraborate effective to lower the solubility and thereby salt out the anionic alkylbenzene sulfonate synthetic detergent and the zwitterionic quaternary ammonio synthetic detergent from a continuous phase;

(5) from about 1% to about 5%, by weight of the finished composition, of a bleaching agent having the formula:



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wherein R is a hydrogen atom or short alkyl group containing from 1 to about 3 carbon atoms and X is selected from the group consisting of sodium, potassium and chlorine atoms;

- (6) from about 0.1% to about 0.5%, by weight of the finished composition, of sodium or potassium iodide; 5
(7) from about 25% to about 85%, by weight of the finished composition, of water; and
(8) sufficient strong base selected from the group consisting of sodium hydroxide and potassium hydroxide 10 to adjust the pH of the composition to from about 7.5 to about 13.0;

said yield value being sufficient to support said insoluble, particulate material; said pH being adjusted to a pH of up to about 11 when said insoluble, particulate material is aluminum oxide. 15

2. The composition of claim 1 wherein the zwitterionic synthetic detergent is 3-dimethyldodecylaminopropane sulfonate.

3. The composition of claim 1 wherein the alkylbenzenesulfonate detergent is from about 2% to about 6% by weight of the finished detergent composition, the zwitterionic synthetic detergent is from about 2% to about 7% by weight of the finished detergent composition, the ratio of alkylbenzenesulfonate detergent to zwitter- 20 ionic detergent is from about 0.4:1 to about 2.0:1, and the total amount of alkylbenzenesulfonate and zwitter-

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ionic detergents if from about 5% to about 12% of the finished detergent composition.

4. The composition of claim 1 wherein the insoluble, particulate material is from about 40% to about 50% by weight of the finished detergent composition and wherein the insoluble, particulate material has particle diameters ranging from about 2 microns to about 60 microns and has a specific gravity of from 1 to about 2.8.

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