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[54] **LIQUID DETERGENT COMPOSITION**
9 Claims, No Drawings

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[56] **References Cited**
UNITED STATES PATENTS

3,346,873 10/1967 Herrmann **252/152 X**

3,351,557 11/1967 Almstead et al. **252/152 X**
 3,453,144 7/1969 Morgan et al. **252/140 X**

FOREIGN PATENTS

1,447,747 6/1966 France **252/152**
 1,484,489 5/1967 France **252/152**

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ABSTRACT: Stable, liquid detergent compositions for cleaning hard surfaces containing particulate materials (e.g., abrasives), water, alkylbenzenesulfonate detergent, zwitterionic synthetic detergent and electrolyte, which preferably comprises a detergency builder.

LIQUID DETERGENT COMPOSITION

CROSS-REFERENCE TO RELATED APPLICATION

Other stable liquid detergent compositions for cleaning hard surfaces are disclosed in applicant's copending application Ser. No. 603,098, filed Dec. 20, 1966, now U.S. Pat. No. 3,520,818.

BACKGROUND OF THE INVENTION

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

There has been an increasing demand for 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 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.

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 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 $du/dr = F/\mu$ 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 $du/dr = (F-f)/\mu_a$ 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 such a particle size and density 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. No. 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 compositions separate and lose their Bingham plastic characteristics. Again, the particulate material in these 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. Pat. Nos. 3,149,078; 3,210,285; 3,281,367; Canadian Pats. Nos. 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 eight 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 applicant's U.S. Pat. No. 3,520,818. The detergent compositions of U.S. Pat. No. 3,520,818 are free of amides, but are required to contain soap. The compositions of U.S. Pat. No. 3,520,818 also differ in the kind and relative proportions of components which can be employed.

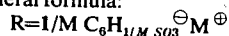
Accordingly, it is an object of this invention to provide liquid detergent compositions which exhibit Bingham plastic characteristics and which are stable for protracted periods of time. It is a further object of this invention to provide liquid detergent compositions which remain stable when subjected to both depressed and elevated storage temperatures. A still further object of this invention is to provide Bingham plastic, 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 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 detergent composition in convenient pourable form.

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

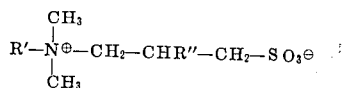
It has surprisingly been discovered, according to the present invention, that the foregoing objects are obtained with an opaque, liquid detergent composition which is substantially free of soaps, amides and hydrotropes and which has a yield value of from about 5 to about 600 dynes per square centimeter and an apparent viscosity below about 12,000 centipoises consisting essentially of, by weight of the finished composition,

1. an anionic alkylbenzenesulfonate synthetic detergent having the general formula:



wherein R is an alkyl chain containing from about nine to about 15 carbon atoms, and $\text{M}^\oplus$ is a cation selected from the group consisting of potassium, sodium, ammonium, monoethanolammonium, diethanolammonium, and triethanolammonium 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, and R'' is selected from the group consisting of a hydrogen atom and a hydroxyl group; 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 percent to about 20 percent by weight of the finished composition;

3. from 1 percent to about 60 percent 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; (The term "density" as used herein has the units of g./cc.)
4. from about 1 percent to about 10 percent of polyvalent electrolyte;
5. from about 25 percent to about 85 percent water; and
6. 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 phase is present as discrete particles, and consists mainly of organic materials such as detergent. These discrete particles are mesomorphic and

have 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.

- 5 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.

- 10 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 estimated, in dynes per square centimeter, by the following relationship:

Yield Value

- 15
$$= \frac{\text{Viscosity at 0.5 r.p.m.} - \text{viscosity at 1 r.p.m.}}{100}$$

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.

- 20 The yield value of the liquid detergent compositions of this invention ranges 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.

- 30 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

- 35 The essential individual components of the liquid detergent composition of this invention are alkylbenzenesulfonate detergent, zwitterionic synthetic detergent, insoluble particulate materials, electrolyte, 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.

- 50 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
- 55 as components of these liquid detergent compositions.

1. Alkylbenzenesulfonate Detergent

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



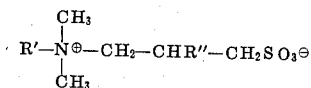
wherein R is an alkyl chain containing from about nine to about 15 carbon atoms, and $\text{M}^\oplus$ is a cation selected from the group consisting of potassium, sodium, ammonium, monoethanolammonium, diethanolammonium, and triethanolammonium cations; it is preferred that R average from 12 carbon atoms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

- 70 From about 2 percent to about 12 percent 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 percent to about 6 percent alkylbenzenesulfonate. More important than the amount of alkylbenzenesulfonate or zwitterionic detergent present in-
- 75

dividually, 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, and R'' is selected from the group consisting of a hydrogen atom and a hydroxyl group. It is preferred that R' be dodecyl or the alkyls derived from coconut fatty alcohol, and that R'' be a hydroxyl group.

The zwitterionic synthetic detergent described above is utilized in this invention in amounts of from about 2 percent to about 14 percent by weight of the finished detergent composition. It is preferred that the zwitterionic synthetic detergent be utilized in amounts of from about 2 percent to about 7 percent 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 percent to about 20 percent of the total weight of the finished composition. A preferred embodiment contains from about 5 percent to about 12 percent of these detergents. About 6 percent to about 7 percent 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 percent to about 50 percent, see below), it can be further said that between about 10 percent and about 18 percent of the supporting medium (that is, the entire composition less suspended insoluble particulate material) should be detergent, and about 10 percent to about 16 percent is preferable. About 12 percent to about 14 percent 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 percent) abrasive concentrations, the concentration of total detergent in the supporting medium becomes less important, and up to about 20 percent 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 detergents, 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. Silica is the preferred abrasive for use herein. 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

$$f = [2Dg(d-d')]/3, /$$

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 percent to about 60 percent material. It is preferred, however, that from 40 percent to about 50 percent by weight of the finished composition be insoluble, particulate material.

4. Polyvalent Electrolyte

From about 1 percent to about 10 percent of the finished composition is required to be polyvalent electrolyte. For example, from about 1 percent to about 10 percent sodium sulfate can be employed, but from about 2 percent to about 3 percent 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 percent and about 10 percent by weight of the finished composition. It is preferred that the total amount of builders be from about 1 percent to about 7 percent. 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 detergent 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 percent to about 6 percent 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 percent to about 4 percent tetrapotassium pyrophosphate should be utilized herein.

Tetraborate can be added to these detergent compositions to improve cleaning (as a detergent 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 percent to about 0.8 percent tetraborate, by weight of the finished detergent composition, can be utilized in this invention. This range corresponds to 0 percent to about 2 percent 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 trisodium ethanehydroxydiphosphonate, $\text{CH}_3\text{COH}(\text{PO}_3\text{CH}_2\text{HNa})_2$, in an amount ranging from 0 percent to about 5 percent; sodium tripolyphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$, in an amount ranging from 0 percent to about 3 percent, and trisodium orthophosphate, Na_3PO_4 , in an amount ranging from 0 percent to about 7 percent. Mixtures of these builders can also be employed.

5. Water

From about 25 percent to about 85 percent of this composition is water. It is preferred that from about 30 percent to about 50 percent 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.

6. 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.

7. 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: soluble sodium carboxymethyl cellulose, tarnish inhibitors, such as benzotriazole or ethylenethiourea, brighteners, bleaches, fluorescers, 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 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.

EXAMPLE

Twenty detergent compositions were prepared from water, abrasive, zwitterionic synthetic detergent, sodium dodecylbenzenesulfonate detergent, sodium chloride (present as an impurity in the detergent ingredients), sodium sulfate, and builder salts. Each of these twenty compositions is designated as a "Run;" of these, Runs 1, 2, 7, 8, and 13 are not examples of the invention, but are included for comparative purposes.

The abrasive, except in Runs 17 and 18, was silica (quartz, specific gravity about 2.65) of the following particle size distribution:

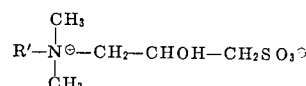
1—3 microns	0.4%
3—6 microns	4.1%
6—10 microns	11.5%
10—15 microns	16.0%
15—20 microns	16.0%
20—30 microns	24.0%
30—40 microns	17.0%
40—60 microns	11.0%
	100.0%

Run 17 contained feldspar, specific gravity about 2.65, of the following particle size distribution:

On 65 mesh (208 microns and larger)	0.022%
On 100 mesh (147 microns to 208 microns)	0.082%
On 200 mesh (74 microns to 147 microns)	2.94%
On 325 mesh (43 microns to 74 microns)	18.15%
Through 325 mesh (smaller than 43 microns)	Balance

Run 18 contained calcium carbonate (calcite), specific gravity about 2.8, and particle diameter about 25 microns.

The zwitterionic synthetic detergent had the formula



wherein R' represents alkyls derived from coconut fatty alcohol, by distillation in which the low-boiling and high-boiling fractions were excluded. The alkyl groups (so-called "middle-cut coconut") had approximately the following distribution:

C ₁₀	0.5%
C ₁₂	67.5%
C ₁₄	24.5%
C ₁₆	7.0%
C ₁₈	0.5%
	100.0%

These 20 runs had the composition given in the following table. In each case, except as noted, the run contained 50 percent abrasive and no builder; the balance necessary to give a total of 100 percent was water; and the "other" ingredients were impurities in the starting materials, unreacted starting materials, and by-products of the reactions to produce the alkylbenzenesulfonate and zwitterionic detergents, comprising alkylbenzene, alkyl sulfate, benzenesulfonate, methanol, organic chlorides e.g., sodium 1-chloro-2-hydroxypropane-3-sulfonate), alkyl dimethyl tertiary amines, quaternary-substituted ammonium compounds e.g., dimethylalkylamine quaternarized with 3-chloro-1,2-propanediol or 1,3-dichloro-2-propanol), aliphatic alcohols, olefins, epichlorohydrin polymers, paraffins, disodium 2-propanol-1,3-disulfonate, and sodium 1,3-dihydroxypropane-1-sulfonate.

TABLE

Run:	Zwitter ionic, percent	Sodium dodecyl- benzene- sulfo- nate, percent	Sodium chloride, percent	Sodium sulfate, percent	Other, percent	Total detergent—		Ratio of sodium- dodecyl- benzene sulfonate to Zwitter ionic
						In fin- ished deter- gent compo- sition, percent	In sup- porting medium, percent	
1.....	7.13	0.00	1.59	6.00	2.39	7.13	14.26	0.00:1
2.....	5.69	1.40	1.28	6.00	1.95	7.09	14.18	0.25:1
3.....	5.09	1.99	1.15	6.00	1.77	7.08	14.16	0.39:1
4.....	3.78	3.24	0.87	6.00	1.37	7.02	14.04	0.86:1
5.....	2.03	5.00	0.49	6.00	0.85	7.03	14.06	2.46:1
6.....	1.42	5.60	0.35	6.00	0.57	7.02	14.04	3.95:1
7.....	0.00	7.02	0.04	5.99	0.24	7.02	14.04	1:1
8.....	2.16	1.86	0.49	6.00	0.78	4.02	8.04	0.86:1
9.....	2.69	2.32	0.61	5.99	0.98	5.01	10.02	0.86:1
10.....	3.23	2.78	0.73	6.00	1.17	6.01	12.02	0.86:1
11.....	3.78	3.24	0.87	6.00	1.37	7.02	14.04	0.86:1
12.....	4.30	3.62	0.98	6.00	1.56	7.82	15.64	0.82:1
13.....	4.84	4.18	1.11	6.00	1.76	9.02	18.04	0.86:1
14.....	5.37	4.63	1.23	6.00	1.96	10.00	20.00	0.86:1
15.....	3.78	3.24	0.87	6.00	1.37	7.02	14.04	0.86:1
16.....	3.78	3.24	0.87	6.00	1.37	7.02	14.04	0.86:1
17.....	3.78	3.24	0.87	6.00	1.37	7.02	14.04	0.86:1
18.....	3.78	3.24	0.87	6.00	1.37	7.02	14.04	0.86:1
19.....	5.04	4.32	1.16	8.00	1.83	9.36	14.04	0.86:1
20.....	3.78	3.24	0.87	6.00	1.37	7.02	14.04	0.86:1
21.....	3.02	2.59	0.70	4.80	1.10	5.61	14.04	0.86:1

¹ Contained 3.00% tetrapotassium pyrophosphate.

² Contained 1.00% trisodium orthophosphate.

³ Contained 3.00% sodium tripolyphosphate.

⁴ Contained 33.33% silica abrasive.

⁵ Contained 60.00% silica abrasive.

Run:	pH	Percent separation— sample stored at—		Yield value—sample stored at—		Apparent viscosity— sample stored at—		100° F.
		50° F.	Room tempera- ture ¹ F.	50° F.	Room tempera- ture ¹ F.	50° F.	Room tempera- ture ¹ F.	
1.....	8.3	91	96	98 (2)	(2)	(2)	(2)	(2)
2.....	8.1	78	81	63 (2)	0	(2)	(2)	1,050
3.....	8.1	6	0	0 220	204	212 6,000	6,250	6,450
4.....	8.3	0	0	0 226	246	266 5,900	6,450	7,350
5.....	8.1	0	0	0 78	136	216 3,000	4,650	4,850
6.....	8.2	0	0	0 12	6	10 800	800	950
7.....	8.9	46	58	37 36	32	(2)	(2)	~750
8.....	8.4	16	17	11 2	0	2 350	350	400
9.....	8.3	0	0	0 12	10	16 950	1,000	1,200
10.....	8.2	0	0	0 76	60	126 2,500	2,850	3,450
11.....	8.3	0	0	0 226	246	266 5,900	6,450	7,350
12.....	8.1	0	0	0 238	264	270 5,800	7,050	7,350
13.....	7.8	5	0	0 6	(2)	(2)	550	10,000+
14.....	9.0	6	6	6 24	54	20 1,100	1,400	1,200
15.....	8.2	18	12	6 64	74	28 1,200	1,600	6,350
16.....	11.1	6	0	0 80	224	234 1,500	5,200	6,350
17.....	8.3	0	0	0 226	246	266 5,900	6,450	7,350
18.....	7.9	0	0	0 38	272	212 1,300	7,200	7,300
19.....	8.4	0	0	0 8	62	56 650	2,250	2,200
20.....	7.7	90	0	0 (2)	12	18 150	2,850	1,000
21.....	8.3	0	0	0 226	246	266 5,900	6,450	7,350
22.....	8.3	11	8	5 6	30	28 1,300	2,850	3,550

¹ Varied from day to day; mean was about 74° F.

² Separation too great, not observed.

³ Viscosity too high for meaningful reading.

Runs 1 and 2 show the effect of too small a relative amount of alkylbenzenesulfonate detergent; Run 7 shows the effect of too great a relative amount of alkylbenzenesulfonate detergent. Runs 8 and 13 illustrate the use of too little or too much total detergent, respectively: Run 8 does not contain enough total detergent to support the abrasive, even though the ratio of alkylbenzenesulfonate to zwitterionic detergents is optimum; Run 13, containing 20 percent detergent in the supporting medium and 50 percent abrasive, was too thick to form a workable composition, and was discarded. All runs except 13 were divided into three portions each, stored respectively for one week at 50° F., room temperature (about 74° F.), and 100° F. After this time, the samples were examined, and the pH, percent separation, yield value (dynes per square centimeter) and apparent viscosity (centipoises) were measured. Since the maximum separation resulted in about the bottom 40 percent of the sample bottle containing the bulk of the abrasive, this was defined as 100 percent separation. The percent separation was then calculated by measuring the height of liquid relatively free from abrasive at the top of the bottle, dividing by the total height of the sample and multiply-

ing by 166.7 percent (0.6 of sample free from abrasive × 166.7% = 100%). Thus, although the total height of the samples was not constant, a sample with a total height of 10 inches, and having the following height of liquid relatively free from abrasive, would have the following percent separation:

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Inches Relatively Free of Abrasive	Percent Separation
0.0	0.0
0.6	10.0
1.2	20.0
1.8	30.0
2.4	40.0
3.0	50.0
3.6	60.0
4.2	70.0
4.8	80.0
5.4	90.0
6.0	100.0

75 The following results were obtained.

Run	pH	Percent Separation: Sample Stored At			Yield Value: Sample Stored At			Apparent Viscosity: Sample Stored At		
		50° F	Room Temp. ¹	100° F	50° F	Room Temp. ¹	100° F	50° F	Room Temp. ¹	100° F
1	8.3	91	96	98	(²)	(²)	(²)	(²)	(²)	(²)
2	8.1	78	81	63	(²)	0	(²)	(²)	1050	1200
3	8.1	6	0	0	220	204	221	6000	6250	6450
4	8.3	0	0	0	226	246	266	5900	6450	7350
5	8.1	0	0	0	78	136	216	3000	4650	4850
6	8.2	0	0	0	12	6	10	800	800	950
7	8.9	46	58	37	36	32	(²)	(²)	(²)	≈ 750
8	8.4	16	17	11	2	0	2	350	350	400
9	8.3	0	0	0	12	10	16	950	1000	1200
10	8.2	0	0	0	76	60	126	2500	2850	3450
11	8.3	0	0	0	226	246	266	5900	6450	7350
12	8.1	0	0	0	238	264	270	5800	7050	7350
14	7.8	5	0	0	6	(²)	(²)	550	10,000 +	10,000 +
15	9.0	6	6	6	24	54	20	1100	1400	1200
16	8.2	18	12	6	64	74	28	120	1500	950
4	11.1	6	0	0	80	224	234	1500	5200	6350
17	8.3	0	0	0	226	246	266	5900	6450	7350
18	7.9	0	0	0	38	272	212	1300	7200	7300
19	8.4	0	0	0	8	52	56	650	2250	2200
20	7.7	90	0	0	(²)	12	18	150	850	1000
4	8.3	0	0	0	226	246	266	5900	6450	7350
20	8.3	11	8	5	6	30	28	1300	2850	3550

¹ Varied from day to day; mean was about 74° F.

² Separation too great; not observed.

³ Viscosity too high for meaningful reading.

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

The above runs can be considered to be five series, each of which illustrates a different point. A horizontal line separates each series. The first series contains Runs 1—7, showing the effect of varying the ratio of sodium dodecylbenzenesulfonate to zwitterionic detergent. The second series contains Runs 8, 9, 10, 4, 11, 12, and 13, showing the effect of varying the total amount of detergent. In the above tables, Run 4 is repeated in several locations for ease of comparison. In each of the series, the other variables were held as near constant as practicable, in order to clearly show the effect of varying the ratio or total detergent, respectively. All of the compositions were effective cleaning compositions; however, Runs 1, 2 and 7 (outside the ratio of detergents to be used in compositions of this invention) were poor in suspending abrasive, as was Run 8 (below the range of total detergent amount); Run 12 (at high end of total detergent amount) was very thick, and not easily manageable.

In the runs of the first two series (Runs 1—13), the amount of sodium sulfate was held constant at about 6 percent; since some sodium sulfate is present as a byproduct of sulfating dodecylbenzene, it was necessary to add up to almost 6 percent to some runs to reach this level. The more effective cleaning compositions contain less sodium sulfate (about 2 percent to about 3 percent), however, as this allows a greater proportion of detergency builders to be present without destroying the yield value and ability of the system to suspend insoluble particulate material. The addition of builders usually raises pH; any additional increase in pH is best accomplished by the addition of sodium hydroxide or potassium hydroxide.

Runs 14—16 form a third series, illustrating the use of builders. The following builders can be used, 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 percent; tetrapotassium pyrophosphate, from 0 percent to about 6 percent, from about 3 percent to about 4 percent being preferred, as it increases yield value; sodium tetraborate, from 0 percent to about 2 percent (as decahydrate); trisodium ethanehydrox-

ydiphosphonate, from 0 percent to about 5 percent; sodium tripolyphosphate from 0 percent to about 3 percent; and trisodium phosphate, from 0 percent to about 7 percent.

Runs 4, 17 and 18 constitute the fourth series which illustrates the use of various abrasives. The following can be substituted, with substantially equivalent results, for the silica, feldspar and calcium carbonate illustrated: quartz, 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.

Runs 19, 4 and 20 constitute the fifth series illustrating variations in the abrasive level. The supporting medium in each of these three runs is identical, with only the amount of abrasive varied. It can be seen that at 33.33 percent and at 60.00 percent abrasive level, some separation occurs; and although it is not excessive, except under adverse storage conditions (see, e.g., results for run 19 at 50° F.), it is therefore preferred that the total abrasive be between about 40 percent and about 50 percent.

What is claimed is:

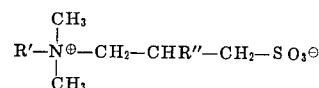
1. A stable, liquid detergent composition which is free of soaps, amides and hydrotropes and which has a yield value of from about 5 to about 600 dynes per square centimeter and an apparent viscosity below about 12,000 centipoises consisting essentially of

1. an anionic alkylbenzenesulfonate synthetic detergent having the general formula:



wherein R is an alkyl chain containing from about nine to about 15 carbon atoms, and M⁺ is a cation selected from the group consisting of potassium, sodium, ammonium, monoethanolammonium, diethanolammonium, and triethanolammonium 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; R'' is selected from the group consisting of hydrogen and hydroxyl; 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 detergent and the zwitterionic synthetic detergent ranges from about 5 percent to about 20 percent by weight of the finished composition; 3. from about 1 percent to about 60 percent, by weight of the finished composition, of 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 (g./cc.) wherein the particulate material is an abrasive 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; 4. from about 1 percent to about 10 percent by weight of the finished composition, of a polyvalent electrolyte effective to lower the solubility and thereby salt out said anionic alkylbenzenesulfonate synthetic detergent and said zwitterionic quaternary ammonio synthetic detergent from a continuous phase wherein said electrolyte is selected from the group consisting of sodium sulfate, tetrapotassium pyrophosphate, trisodium ethane hydroxydiphosphonate, sodium tripolyphosphate, trisodium orthophosphate, sodium tetraborates, and mixtures thereof;

5. from about 25 percent to about 85 percent, by weight of the finished composition, water; and

6. sufficient strong base 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.

2. The composition of claim 1 wherein the alkylbenzenesulfonate detergent is sodium n-dodecylbenzenesulfonate, and in the formula given for the zwitterionic detergent, R'' is hydroxyl.

3. The composition of claim 1 wherein the alkylbenzenesulfonate detergent comprises from about 2 percent to about 12 percent by weight of the finished detergent compositions, the zwitterionic synthetic detergent comprises from about 2 percent to about 14 percent by weight of the finished detergent

composition, and the ratio of alkylbenzenesulfonate detergent to zwitterionic detergent is from about 0.4:1 to about 2.0:1.

4. The composition of claim 1 wherein the alkylbenzenesulfonate detergent comprises from about 2 percent to about 6 percent by weight of the finished detergent composition, the zwitterionic synthetic detergent comprises from about 2 percent to about 7 percent by weight of the finished detergent composition, the ratio of alkylbenzenesulfonate detergent to zwitterionic detergent is from about 0.4:1 to about 2.0:1, and the total amount of alkylbenzenesulfonate and zwitterionic detergents is from about 5 percent to about 12 percent of the finished detergent composition.

5. The composition of claim 1 wherein the ratio of alkylbenzenesulfonate detergent to zwitterionic detergent is about 0.086:1, and the total amount of alkylbenzenesulfonate and zwitterionic detergents is from about 6 percent to about 7 percent by weight of the finished detergent composition.

6. The composition of claim 1 wherein the insoluble, particulate material comprises from about 40 percent to about 50 percent 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.

7. The composition of claim 1 wherein the electrolyte comprises a builder salt selected from the group consisting of from 0 percent to about 6 percent of potassium pyrophosphate; from 0 percent to about 2 percent of sodium tetraborate decahydrate; from 0 percent to about 5 percent of trisodium ethanehydroxydiphosphonate; from 0 percent to about 3 percent of sodium tripolyphosphate; from 0 percent to about 7 percent of trisodium orthophosphate; and mixtures of the above.

8. The composition of claim 7 wherein the electrolyte comprises from about 3 percent to about 4 percent potassium pyrophosphate.

9. The detergent composition of claim 1 wherein the pH is adjusted to from about 8 to about 11 by adding a strong base selected from the group consisting of sodium hydroxide and potassium hydroxide.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,623,990 Dated November 30, 1971

Inventor(s) Cushman Merlin Cambre

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

Column 3, line 23, " $R=1/M \text{ C}_6\text{H}_4/M \text{ SO}_3^{\ominus} \text{ M}^{\oplus}$ " should read
-- $R-\text{C}_6\text{H}_4 - \text{SO}_3^{\ominus} \text{ M}^{\oplus}$ --.

Column 4, line 11, after "exact yield values is" insert
-- quite difficult. A close approximation can be obtained by using a Brookfield viscometer. The yield value is --.

Column 6, line 42, the formula " $f = [2Dg(d-d')]/3,$ " should read -- $f = \frac{2 Dg (d-d')}{3},$ --

Column 6, line 56, after the word "percent" insert -- of the composition of this invention is insoluble particulate --.

Column 7, line 33, the formula " $\text{CH}_3\text{COH}(\text{PO}_3\text{CH}_2\text{HNa}_3)$ " should read -- $\text{CH}_3\text{COH}(\text{PO}_3)_2\text{HNa}_3$ --.

Column 9, Run 15, on the second table under the "100°F." heading the figure "6,350" should read -- 950 --.

Columns 11 and 12, Run 3, under the heading "Percent Separation: Sample Stored At 100°F" the figure "221" should read -- 212 --.

Columns 11 and 12, Run 15, under the heading "Apparent Viscosity: Sample Stored At 50°F" the figure "120;" should read -- 1200 --.

Column 14, line 28, Claim 7, after "decahydrate;" delete -- from 0 percent to about 5 percent of trisodium ethanehydroxy-diphosphate; --.

Signed and sealed this 13th day of June 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents