

1

3,579,456

LIQUID DETERGENT COMPOSITION

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U.S. Cl. 252—137

6 Claims

ABSTRACT OF THE DISCLOSURE

Stable, liquid detergent compositions (for cleaning aluminum and rust stains from hard surfaces) containing particulate materials (e.g., abrasives), water, alkylbenzenesulfonate detergent, zwitterionic synthetic detergent and an acid electrolyte; said compositions have a pH of from about 1 to about 5.

CROSS-REFERENCE TO RELATED APPLICATION

Other stable liquid detergent compositions for cleaning hard surfaces are disclosed in applicant's copending application Ser. No. 649,019, filed June 26, 1967, and U.S. Pat. 3,520,818.

BACKGROUND OF THE INVENTION

This invention relates to liquid detergent compositions adapted for cleaning stains, e.g., aluminum or rust stains, from hard surfaces. More particularly, this invention relates to an acid 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 aluminum and rust stains from hard surfaces. These liquid detergent compositions are provided in convenient form and are especially formulated for this particulate cleaning application. To obtain optimum cleaning and consumer acceptance, these detergent compositions must be homogeneous on a macro scale and easily pourable. These compositions, when intended for the retail consumer market, should maintain their homogeneity on a macro scale during ordinary periods of storage and use, and should have acceptable freeze-thaw characteristics. It is highly desirable that low pH liquid detergent compositions for cleaning hard surfaces should exhibit real 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 this 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 $du/dr=F/u$, where du/dr =the rate of shear; F =the shear stress, or shearing force per unit area; and u =the viscosity coefficient.

In the case of non-Newtonian liquids, on the other hand, the consistency is a function of the material, pres-

2

sure, temperature, and also the shear stress applied to the system. Those non-Newtonian liquids which are classified as Bingham plastics (linear relationship between shear rate and shear stress) or real plastics (nonlinear relationship between shear rate and shear stress), are not always deformed when a force is applied to the system. Deformation, if any, takes place according to the formula

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

where u_a =the apparent viscosity, or plastic viscosity, at the shear stress F (for a real plastic system this viscosity coefficient is a variable; for Bingham plastic systems it is a constant): 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 real 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 pseudo plastic liquids with high viscosities. In highly viscous Newtonian liquids or pseudo plastic liquids, insoluble particulate material is suspended only because the rate of flow is slow. In real 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

Acid detergent compositions containing suspended abrasives are described in U.S. Pat. 3,214,380.

A variety of detergent compositions containing synthetic anionic detergents, soaps, or both, as well as detergent builders and abrasives, are known. See, for example, U.S. Pats. 3,149,078, 3,210,285, 3,234,138, 3,281,367; Canadian Pats. 635,321 and 684,394. These compositions usually require the presence of amides, and frequently contain soaps which are converted to fatty acids under extremely acid conditions. Fatty acids will not provide a yield value and will separate to form another phase.

Other stable liquid detergent compositions for cleaning hard surfaces are disclosed in applicant's copending application Ser. No. 649,019, filed June 26, 1967 and U.S. Pat. 3,520,818. The detergent compositions of U.S. Patent 3,520,818 are required to contain soap and also, differ in the kind and relative proportions of components which can be employed. The compositions of Ser. No. 649,019 are alkaline and are not sufficiently effective in removing aluminum and rust stains quickly.

Accordingly, it is an object of this invention to provide low pH liquid detergent compositions which exhibit real plastic characteristics and which are stable for protracted periods of time. It is a further object of this invention to provide low pH liquid detergent compositions which remain stable when subjected to both depressed and elevated storage temperatures. A still further object of this inven-

tion is to provide real plastic, low pH 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 low pH liquid detergent compositions which exhibit real 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.

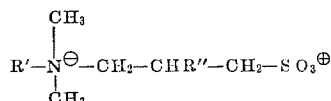
Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that the detailed description and specific example while indicating preferred embodiments of the invention, are 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 a low pH 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 consisting essentially of, by weight of the finished composition,

(1) From about 2% to about 15% of an alkylbenzenesulfonate synthetic detergent having the general formula: $R-C_6H_4-SO_3^{\ominus}M^{\oplus}$ wherein R is a straight 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) From about 1% to about 7.5% of 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 1.5:1 to about 2.5:1; and the combined weight of the alkylbenzenesulfonate and zwitterionic synthetic detergents ranges from about 3% to about 23% 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 (The term "density" as used herein has the units of g./cc.);

(4) From about 1% to about 10% of polyvalent organic acid electrolyte and sufficient to adjust the pH of the composition to from about 1 to about 5; and

(5) From about 25% to about 85% water; said yield value being 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 water and organic polyvalent acid electrolyte. The other phase is

present as discrete particles, and consists mainly of detergents. 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. 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:

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

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 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.

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.

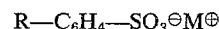
(B) INDIVIDUAL COMPONENTS

The essential individual components of the liquid detergent composition of this invention are alkylbenzenesulfonate detergent, zwitterionic synthetic detergent, insoluble particulate materials, electrolyte, and water. Optional components include minor ingredients which have aesthetic value or which improve the effectiveness of the composition. The alkylbenzenesulfonate detergent and zwitterionic synthetic detergent are the primary cleaning or detergent components of this composition.

In preferred embodiments of this invention, abrasives 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) ALKYL BENZENESULFONATE DETERGENT

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

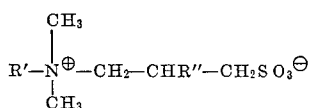


wherein R is a straight alkyl chain containing from about 9 to about 15 carbon atoms, and $M^{\oplus}$ is a cation selected from the group consisting of potassium, sodium, and ammonium cations; it is preferred that R average about 12 carbon atoms.

From about 2% to about 15% 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 4% to about 7% alkylbenzenesulfonate. As important as the amount of alkylbenzenesulfonate present individually, however, is the ratio of alkylbenzene sulfonate to zwitterionic as described below.

(2) ZWITTERIONIC SYNTHETIC DETERGENT

The zwitterionic quarternary 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 hydroxy 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 1% to about 7.5% 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 4% 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 3% to about 23% of the total weight of the finished composition. A preferred embodiment contains from about 6% to about 9% of these detergents.

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 composition 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. At lower (below 40%) abrasive concentrations, the concentration of total detergent in the supporting medium becomes less important, and up to about 23% 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 from about 1.5:1 to about 2.5:1. 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 1.8:1 to about 2.2:1. The exact value of this ratio depends on other materials present in the system.

(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, china clay, zirconium silicate, bentonite, diatomaceous earth, whiting, feldspar, and aluminum oxide. Silica is the preferred abrasive for use herein. 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 to 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 5% of the finished composition is required to be polyvalent organic acid electrolyte. Examples of electrolytes include mixtures of oxalic acid and sodium oxalate, citric acid and sodium citrate. Oxalic acid is desirable because it bleaches and citric acid is desirable because it is safe.

(5) 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.

(6) 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: brighteners, fluorsceners, 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 real 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.

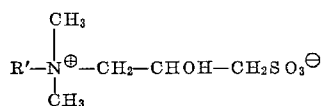
Also to be avoided are soaps, and other materials which are presently or potentially solubilizing agents, or which combine with water hardness ions.

The following example illustrates the present invention.

Example

About 31 parts of soft water were charged to a mixing vessel outfitted with an agitator and heater. The soft water was heated to about 150° F., and to it was added 1 part of oxalic acid and 1 part of sodium oxalate. After these ingredients had dissolved, 50 parts of finely ground silica sand (specific gravity about 2.65 and particle size varying from about 1 to about 60 microns) were added slowly to the solution with agitation. Ten (10) parts of an approximately 50% solution of sodium straight chain secondary alkyl (~11 carbon atoms) benzene sulfonate were then added slowly, followed by the addition of 7 parts of a 35.5% aqueous solution of a zwitterionic surfactant. The resulting suspension was mixed until a smooth product was obtained. A perfume ingredient (0.25 part) was then added. This material had an as-is pH of 1.5, and demonstrated a yield value of 275 dynes/cm.

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:

	Percent
C ₁₀ -----	0.5
C ₁₂ -----	67.5
C ₁₄ -----	24.5
C ₁₆ -----	7.0
C ₁₈ -----	0.5
	100.0

There were also some other ingredients present which 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 quaternized with 3-chloro-1,2-propanediol or 1,3-dichloro-2-propanol), aliphatic alcohols, olefins, epichlorohydrin polymers, paraffins, disodium 2-propanol-1,3-disulfonate, sodium 1,3-dihydroxypropane-1-sulfonate, sodium sulfate and sodium chloride.

When in the above example the following alkylbenzene sulfonates are substituted for the specific alkylbenzenesulfonate detergents used in the example on a mole for mole basis, substantially equivalent results are obtained in that the resulting liquid detergent compositions have approximately the same pH, yield value and performance characteristics: potassium dodecylbenzenesulfonate, ammonium nonylbenzenesulfonate, a 1:1 mixture of sodium undecyl- and tridecylbenzenesulfonate, ammonium tetradecylbenzenesulfonate, a 1:1 mixture of potassium decyl- and potassium tetradecylbenzenesulfonates and a 1:1:1:1 mixture of sodium decyl-, undecyl-, dodecyl-, tridecyl- and tetradecylbenzenesulfonates.

When in the above example the following zwitterionic quaternary ammonium synthetic detergents are substituted for the specific zwitterionic synthetic detergent in the above example on a mole for mole basis, substantially equivalent results are obtained in that the liquid detergent compositions have approximately the same pH value, approximately the same yield value and the same performance characteristics: 3-[N,N'-dimethyl-N-tallow-alkylammonio]propane-1-sulfonate; 3-[N,N'-dimethyl-N-tallow-alkylammonio]-2-hydroxypropane-1-sulfonate; 3-[N,N'-dimethyl-N-coconutalkylammonio]propane-1-sulfonate; and a 1:1 mixture of 3-[N,N'-dimethyl-N-dodecylammonio]-2-hydroxypropane-1-sulfonate and 3-[N,N'-dimethyl-N-hexadecylammonio]propane-1-sulfonate.

When in the above example citric acid is substituted for the oxalic acid on a mole to mole basis and sodium citrate is substituted for the sodium oxalate on a mole for mole basis, substantially equivalent results are obtained in that the liquid detergent composition has a pH between 1 and 5, a yield value between 5 and 600 dynes per square centimeter and the composition is an effective detergent.

When in the above example the following insoluble particulate materials having substantially the same particle size as the sand in the above example are substituted for the sand in the above example on an equal weight basis, substantially equivalent results are obtained in that the abrasives are suspended: quartz, pumice, talc, china clay, zirconium silicate, bentonite, diatomaceous earth, whiting, feldspar and aluminum oxide.

In this example, yield value data was measured at room temperature (about 74° F.), even though the samples may have been stored at higher or lower temperatures. Viscosity measurements for yield values were made with a Brookfield viscometer, Model RVT, using spindle number C2 at 1/2 and 1 r.p.m.

What is claimed is:

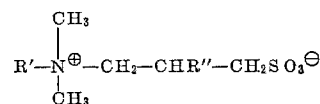
1. A stable, liquid detergent composition which is free of soaps, amides and hydrotropes and which has a yield value of from about 5 to about 600 dynes per square centimeter consisting essentially of, by weight of the finished composition,

(1) from about 2% to about 15% of an alkylbenzenesulfonate synthetic detergent having the general formula



wherein R is a straight 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) from about 1% to about 7.5% of 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 1.5:1 to about 2.5:1 and the combined weight of the alkylbenzenesulfonate detergent and the zwitterionic synthetic detergent ranges from about 3% to about 23% by weight of the finished composition;

(3) from about 1% to about 60% of water-insoluble particulate material selected from the group consisting of water insoluble abrasives and bactericides 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.);

(4) from about 1% to about 10% of a polyvalent organic acid electrolyte effective to lower the solu-

9

bility and thereby salt out said anionic alkylbenzenesulfonate synthetic detergent and said zwitterionic quaternary ammonio synthetic detergent from a continuous phase; and effective to adjust the pH of the composition to a value from about 1 to about 5; said electrolyte being selected from the group consisting of the combination of oxalic acid and sodium oxalate and the combination of citric acid and sodium citrate and

(5) from about 25% to about 85% water; said yield value being sufficient to support said water-insoluble, particulate material.

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 4% to about 7% by weight of the finished detergent composition, the zwitterionic synthetic detergent comprises from about 2% to about 4% by weight of the finished detergent composition, and the ratio of alkylbenzenesulfonate detergent to zwitterionic detergent is from about 1.8:1 to about 2.2:1.

4. The composition of claim 3 wherein the total amount of alkylbenzenesulfonate and zwitterionic detergents is from about 6% to about 9% of the finished detergent composition.

10

5. The composition of claim 1 wherein the insoluble, particulate material comprises 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.

6. The detergent composition of claim 1 wherein the insoluble, particulate material is an abrasive selected from the group consisting of quartz, pumice, pumicite, talc, silica sand, china clay, zirconium silicate, bentonite, diatomaceous earth, whiting, feldspar and aluminum oxide.

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LEON D. ROSDOL, Primary Examiner

M. HALPERN, Assistant Examiner

U.S. Cl. X.R.

252—152, 155

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,579,456

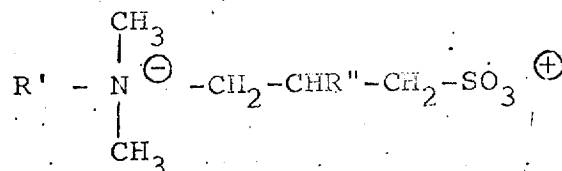
Dated May 18, 1971

Inventor(s) Cushman M. Cambre

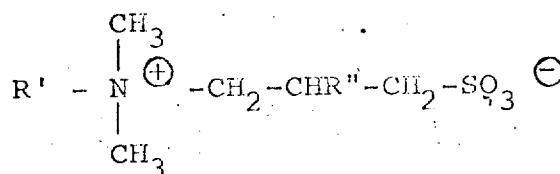
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, lines 10 and 11, "aluminium" should read "aluminum".

Column 3, line 40,

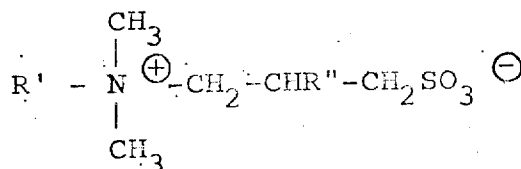


should read

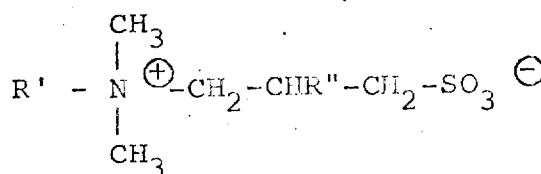


Column 8, line 28, after "pumice," insert "pumicite,".

Column 8, line 55,



should read



Signed and sealed this 14th day of September 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents